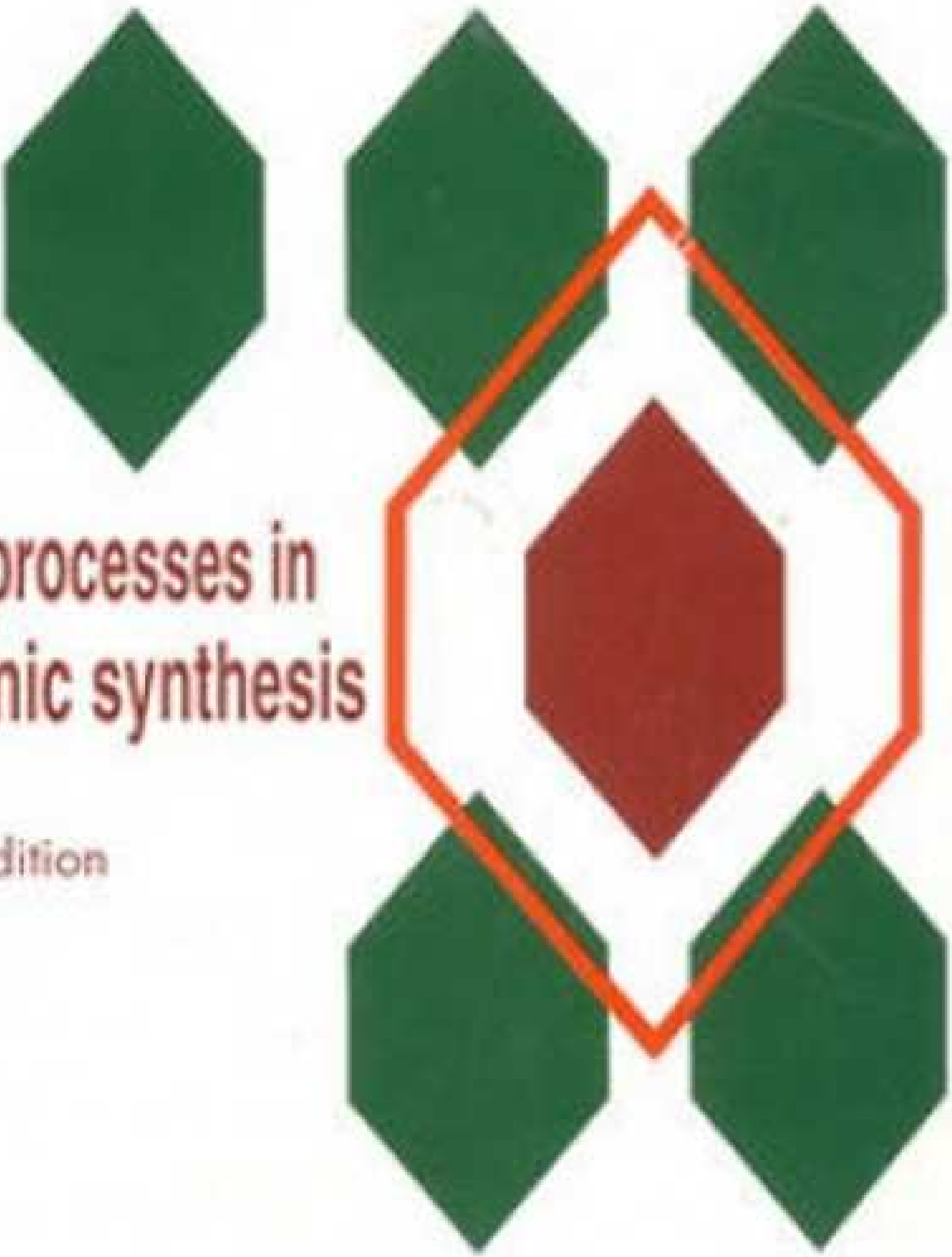

unit processes in organic synthesis

fifth edition

P. H. GROGGINS

TATA McGRAW-HILL
EDITION

Unit Processes in Organic Synthesis

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PREFACE

A quarter of a century has elapsed since the first edition of "Unit Processes in Organic Synthesis" went to press. During that span of years the domestic synthetic organic chemical industry has grown enormously. The production of petrochemicals, plastics, protective coatings, surfactants, chlorinated solvents, and elastomers—all involving organic synthesis—has multiplied many times. New technics have been developed, and chemical engineers have contributed much to make production processes more efficient.

If adoption as a teaching tool and use as a plant reference work may serve as criteria, "Unit Processes in Organic Synthesis" has apparently served a useful purpose. Acceptance of the work has been world-wide, and it is with gratification that the authors note that the book has been or is currently being translated into five foreign languages. Apparently this reflects the need for such a textbook in a growing technological economy.

In the preface to the first edition, the editor distinguished between the now well-established terms *unit processes* and *unit operations* and showed how they are intimately related in the chemical engineering aspects of organic synthesis. The prime objective of the present volume continues to be the presentation of the industrial technic used in converting organic raw materials into usable products by various processes. Accordingly, the underlying principles and factors for each unit process are organized in a systematic manner with most of the emphasis on fundamental scientific and technological principles. Detailed discussion of manufacturing processes is included only to the extent required for the elucidation of these basic principles. Thus it is expected that the present volume will continue to serve as a "semiworks course" to facilitate the student's transition from the university classroom to an industrial environment.

In keeping with the modern trend toward the so-called chemical engineering sciences, the authors have stressed fundamental advances in theory as well as in industrial practice. Thus, thermodynamics and kinetics have received increased emphasis. These subjects are inextricably associated with all chemical reactions and, therefore, are particularly important in the study and practice of unit processes. In this fifth edition, three new introductory chapters are devoted to these subjects.

PREFACE

To ensure that the present text reflects the most recent advances in the technology of unit processes, many new coauthors have been invited to contribute to its pages. These new collaborators represent an accurate cross section of the American chemical industry. Their contributions to the technical literature in their specialized fields are evidence of their competence. Their cooperation in the preparation of the present edition should assure a technologically sound text.

The editor is deeply obligated to managements of many chemical organizations for making possible employee participation in the preparation of this volume. It is accordingly hoped that their combined contributions will make possible a better training of chemical engineers and chemists for the plants of our expanding chemical industry.

P. H. Groggins

CONTENTS

CHAPTER 1

APPLICATIONS OF THERMODYNAMICS IN UNIT PROCESSES

BY THOMAS E. CORRIGAN AND KENNETH A. KOBE

"Unit Processes in Organic Synthesis" deals with the major chemical transformations which are of importance to the chemical industry. One of the most important tools that can be used to predict the behavior of these chemical reactions is chemical thermodynamics. Whether certain chemical reactions can take place, to what extent chemical conversions can occur, the effect of temperature and pressure on the behavior of a chemical reaction, the composition of reactor effluents if equilibrium is reached, the driving force of each of several competing reactions taking place, and the amount of heat released are some of the aspects of chemical processes which can be determined from thermodynamic calculations alone. Thermodynamics cannot, however, tell anything about the speed of the reaction, the effect of the shape of the reactor used, or the relative speeds of competing reactions. If these questions are to be answered, it will be by the use of experimental kinetic data.

Not only is a knowledge of thermodynamics necessary to an understanding of unit processes, but also it is a prerequisite to the application of kinetics. A knowledge of both thermodynamics and kinetics is fundamental to a complete understanding of the unit organic processes. The process engineer finds that before the kinetics of a chemical reaction can be utilized its thermodynamics must be known. Before becoming concerned with how fast a reaction will go, one must know if it can go at all and, if so, how far. For a more thorough discussion of the principles reviewed here, the reader is referred to some of the standard texts on chemical engineering thermodynamics.[1]

Energy Relations—First Law. The subject of thermodynamics deals almost exclusively with energy relationships. Many problems such as the

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[1] DODGE, "Chemical Engineering Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1944; HOUGEN, WATSON, and RAGATZ, "Chemical Process Principles," parts I and II, John Wiley & Sons, Inc., New York, 1954 and 1947; SMITH, "Introduction to Chemical Engineering Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1949.

equilibrium conversion in an adiabatic reactor or the heat requirements and quantity of catalyst needed in a catalytic reactor depend upon energy balances for their solution. Energy balances are based upon the first law of thermodynamics, which states that energy cannot be created or destroyed during a process, although it may change from one form to another. The total energy of a system entering a process plus any addition during the process must equal the total energy of the system leaving the process.

Classification of Energy. The forms of energy can be classified into two groups: (1) the first is related to the system and (2) the second is associated with the process. The former includes energy possessed by material of the system; the latter includes energy produced or transferred by the processing.

Group I	Group II
Properties of a system:	Properties of a process:
Internal energy	Heat
Flow or pressure energy	Work
Kinetic energy	
Potential energy	
Surface energy	
Magnetic energy	

Internal energy (U) is that which a substance possesses because of the motion and configuration of its molecules, atoms, and subatomic particles. The flow or pressure energy PV is the product of pressure and volume. It may be regarded as the energy a substance possesses by virtue of the space it occupies. Kinetic energy is the energy a substance possesses because of its motion and is $mu^2/2$, where m and u are the mass and velocity of the substance, respectively. Specific kinetic energy is $u^2/2g_c$, where g_c is the gravitational constant, with $1/g_c$ being the mass of a unit weight. The energy which a material possesses because of its position in relation to some datum plane is called the potential energy. Two forms of energy, that due to surface tension and that due to magnetic effects, are usually negligible in magnitude compared with the other forms and are not used in the energy balance. The forms of energy which depend upon the process are heat q and work w. Heat is a term applied to that form of energy which flows as the result of a temperature gradient. Work applies to the expenditure of energy by mechanical processes.

Energy Balance over a Flow System. The first law of thermodynamics when applied to two points in a flow system may be expressed by the following equation:

$$U_1 + P_1V_1 + Z_1 + \frac{u_1^2}{2g_c} + q - w = U_2 + P_2V_2 + Z_2 + \frac{u_2^2}{2g_c}$$

The term q refers to the heat absorbed by the system; w refers to the work done by the system on the surroundings. In the over-all energy balance for chemical processes, the changes in kinetic and potential energy are frequently negligible compared with internal energy and may be disregarded. The equations for a flow system then become the same as those for a nonflow (or batch) system. For those cases in which the system performs no work upon its surroundings, the equation reduces to

$$U_1 + P_1V_1 + q = U_2 + P_2V_2$$

or

$$q = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

or

$$q = H_2 - H_1 = \Delta H$$

where H (enthalpy) is defined by the equation

$$H = U + PV$$

Standard States. To fix exactly the properties of a component in a system, a standard state must be defined which specifies the temperature, pressure, and physical state of the component. The standard temperature is 25°C (298.15°K); standard pressure is 1 atm (or unit fugacity $f^\circ = 1.0$ atm). The physical state must be specified, for the energy of water depends on whether it exists as a liquid or a gas; or the energy of carbon depends on whether it exists as β-graphite or diamond.

Heat of Reaction. The change in enthalpy of a system when a reaction occurs at constant pressure is usually called the heat of reaction, though more properly it is the enthalpy change on reaction. The system may have to give off or absorb heat (q) in order to maintain a constant temperature in the system.

Exothermic	System loses heat	$\Delta H = -$
Endothermic	System gains heat	$\Delta H = +$

When reactants and products are in their standard states, the enthalpy change is the *standard heat of reaction.* If the reaction is a combustion reaction, the enthalpy change is the *standard heat of combustion* ΔH_c. If the reactants are the elements in their standard state, the product is a compound in its standard state, the enthalpy change is the *standard heat of formation* ΔH_f.

For the general reaction $aA + bB \rightarrow cC + dD$, the standard heat of reaction ΔH_{rx} can be calculated from either standard heat-of-formation or heat-of-combustion data.

From heat-of-formation data:

$$\begin{aligned}\Delta H_{rx} &= \Sigma(\Delta H_f)_{\text{products}} - \Sigma(\Delta H_f)_{\text{reactants}} \\ &= c(\Delta H_f)_C + d(\Delta H_f)_D - a(\Delta H_f)_A - b(\Delta H_f)_B\end{aligned}$$

Values for the heat of formations per mole can be found in the references for thermodynamic data listed at the end of this chapter.

From heat-of-combustion data:

$$\begin{aligned}\Delta H_{rx} &= \Sigma(-\Delta H_c)_{\text{products}} - \Sigma(-\Delta H_c)_{\text{reactants}} \\ &= c(-\Delta H_c)_C + d(-\Delta H_c)_D - a(-\Delta H_c)_A - b(-\Delta H_c)_B\end{aligned}$$

It is important that the physical state of all components be the same in all values for heats of formation or combustion. In a combustion reaction, the water formed may be either liquid (the usual standard state) or gas.

$$\begin{array}{lr} C_2H_6(g) + 3.5O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) & -\Delta H_c = 372.82 \text{ kcal/g mole} \\ C_2H_6(g) + 3.5O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) & -\Delta H_c = \underline{341.26} \\ \text{Latent heat of vaporization of 3 moles } H_2O & = 31.56 \\ H_2O(l) \rightarrow H_2O(g) \quad & \Delta H_{rx} = 10.52 \end{array}$$

The heat of combustion when the water formed is in the liquid state is known as the *gross* heat of combustion; when the water formed remains as a gas, it is the *net* heat of combustion.

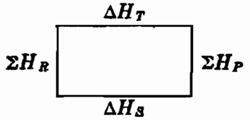
The heat of reaction may also be calculated by combining equations for which the heats of reaction are already known. To calculate the heat of reaction for any reaction requires merely adding algebraically the equations for reactions having known values of ΔH so that their sum gives the reaction desired. This enables the heat of reaction to be calculated for a reaction that will not go quantitatively in a calorimeter. In the following case if the heats of reaction of the first two chemical equations are known, the heat of reaction of the third is the difference between the first two:

$$\begin{array}{c} C(\beta) + O_2 \rightarrow CO_2(g) \\ \underline{CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)} \\ C(\beta) + \frac{1}{2}O_2(g) \rightarrow CO(g) \end{array}$$

The usual form in which reaction-heat data are available in the literature is a tabulation of either the heat of formation or the heat of combustion of the individual compounds in their standard states. For inorganic compounds the heat of formation is usually tabulated, while for organic compounds the data given are heats of combustion. Sources of data are listed at the end of this chapter.

Although both temperature and pressure are specified in designating the standard state for the reaction, the change of heat of reaction with small changes in pressure is generally small and often may be neglected. For ideal gases, the heat of reaction is not affected by pressure. For liquids and solids, there is some slight effect, but it is so small that it may be ignored in most cases. The cases in which the effect of pressure upon heat of reaction may be significant are those involving reactions of nonideal gases at high pressures.

Effect of Temperature upon Heat of Reaction. The effect of temperature upon heat of reaction may be quite extensive and cannot be ignored in most cases. This is especially true in the case of reactions occurring at high temperatures. The heat of reaction at any temperature may be calculated from the following expression:



$$\Delta H_T = \Delta H_S + \Sigma H_P - \Sigma H_R$$

where ΔH_T = heat of reaction at temperature T
ΔH_S = standard heat of reaction at T_S
ΣH_P = sum of enthalpies of all products between T_S and T
ΣH_R = sum of enthalpies of all reactants between T_S and T

ΣH_P and ΣH_R may be evaluated by the most convenient method. This may be done by looking up values for individual enthalpies in tables, calculating them from mean heat capacities, or by integrating heat-capacity equations.

$$\Delta H_T = \Delta H_S + \Delta Cp_m (T - T_S)$$

$$\Delta H_T = \Delta H_S + \int_{T_S}^{T} \Delta Cp \, dT$$

ΔCp_m = difference between mean heat capacities of all products and all reactants
ΔCp = difference between heat capacities of all products and all reactants

$$\Delta Cp = c(Cp)_C + d(Cp)_D - a(Cp)_A - b(Cp)_B$$

Entropy Change of a Reaction. Let us now consider what makes the reaction proceed. The subject of thermodynamics contributes information on why it is possible for a process to take place and how far it may proceed as well as on the total energy relations involved when the reaction occurs. Thermodynamics is concerned not alone with the total energy relations in a given system but also with the degree to which this energy can be utilized to cause a given process to occur.

Thermodynamic energy terms such as enthalpy and internal energy are a measure of the total energy in a system but make no reference to the degree to which that energy is available. There are also terms which are a measure of the degree to which the energy present in a system will make the process go. These terms are the free energy G and the entropy S.

The latter term, entropy, is defined mathematically by the differential equation relating it (the entropy) to the heat transferred in a reversible process:

$$dS = \frac{dq_r}{T}$$

A reversible process is regarded as one in which the driving force causing the process is at all times only infinitesimally greater than that resisting the process. It is at all times, therefore, at equilibrium. The reversible process is also an ideal or imaginary one from the point of view that all sources of energy dissipation are eliminated.

Free-energy Term. Entropy, defined in this manner and when multiplied by the absolute temperature, gives a quantity TS which is a measure of that portion of the energy which is unavailable. The term TS subtracted from the enthalpy leaves a quantity which is that portion of the enthalpy in a flow process, or constant-pressure batch process, which is available for useful work. The latter term is called the free energy and is defined as: $G = H - TS$.

The free energy may be regarded as a property of a system which is a direct measure of that portion of the total energy which will cause the reaction to proceed. The total energy that a system possesses may be represented as shown in Fig. 1-1. The total energy H, can be divided into internal energy U, and flow or external energy PV, or it can be divided into energy available for useful work G, and unavailable energy TS.

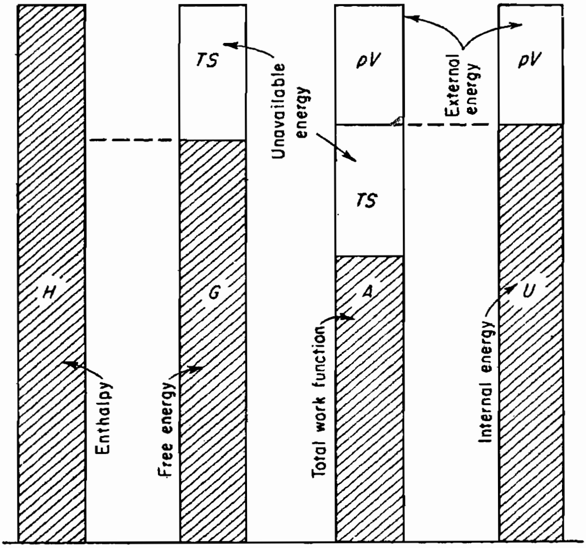


FIG. 1-1. Relations of energy terms H, G, A, and U.

A similar function is the work function A, defined as: $A = U - TS$.

Basic Energy Relations. The following equations summarize the basic relationships of thermodynamics:

$$\begin{aligned} dU &= dq - dw & \Delta U &= q - w \\ dS &= dq_r/T & \Delta S &= \int_1^2 dq_r/T \\ H &= U + PV & \Delta H &= \Delta U + \Delta(PV) \\ A &= U - TS & \Delta A &= \Delta U - \Delta(TS) \\ G &= H - TS & \Delta G &= \Delta H - \Delta(TS) \end{aligned}$$

Usually an enthalpy change is a constant-pressure process, changes in work function are for a constant-temperature process, and changes in free energy are for a process occurring at constant pressure and temperature; so these equations are usually written

$$\begin{aligned} \Delta H &= \Delta U + P\Delta V \\ \Delta A &= \Delta U - T\Delta S \\ \Delta G &= \Delta H - T\Delta S \end{aligned}$$

Chemical Equilibrium. Two important things that a chemical engineer wishes to know about a chemical reaction are:

Can it go?

How long will it take?

The first question is one of thermodynamics; the second is one of kinetics. The prediction of chemical reaction equilibria is one of the most useful aspects of thermodynamics. It is possible to calculate the equilibrium conversion of a given reaction from data taken on other reactions or from thermal data on the individual substances involved.

Free Energy As a Criterion of Equilibrium. The decrease in free energy of a system during any isothermal, isobaric process is a measure of the net reversible work (w_f) that the system can do upon its surroundings.

$$w_f = -\Delta G$$

Equilibrium conditions are those in which the forces resisting the process are just balanced by those which cause it. Therefore, any small change that would take place would have to be a reversible one if no dissipative actions are involved. Since a reversible process is one which takes place always at equilibrium conditions, the criteria of reversibility must include the criteria for equilibrium conditions at constant pressure and temperature.

Since for a reversible process at constant pressure and constant temperature

$$-dG = w_f$$

and since

$$w_f = 0$$

when only the work of expansion is involved, then if the process is at equilibrium for a differential change which it might undergo,

$$dG = 0$$

As most chemical reactions of industrial importance are restricted to constant pressure and are not harnessed to produce useful work, the free energy is useful in calculating the composition of the equilibrium mixture.

Equilibrium Constant for Ideal Gases. When a chemical reaction takes place at constant temperature and pressure, the free energy of the system continues to decrease as long as the reaction proceeds spontaneously. When the free energy has reached the lowest value possible for the system at that temperature and pressure, the reaction has come to equilibrium. Any further reaction in the same direction would have to be accompanied by an increase in free energy. Therefore, it could not occur unless some extra force (such as, for instance, electromotive) were applied to the system. In most reactions there is no extra force applied, and the reaction stops at the point where the free energy reaches the minimum value. The composition of the mixture of reactants and products is the *equilibrium composition*. It is this composition that chemical engineers are interested in calculating for the purpose of estimating the maximum possible yield of a process.

Development of the Equilibrium Equation. The actual value of the free energy at this point has little practical significance. However, we shall see that through use of the free-energy relationships it is possible to calculate the equilibrium composition.

Let us consider the application of these principles to a specific chemical reaction. The water gas shift reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

is one of universal interest to engineers. A chemical reaction may be generalized as follows:

$$aA + bB \rightleftharpoons cC + dD$$

The standard free-energy change for this system may be calculated from the standard free energies of formation (ΔG_f°) of the individual components:

$$\Delta G^\circ = \Sigma(\Delta G_f^\circ)_{\text{products}} - \Sigma(\Delta G_f^\circ)_{\text{reactants}}$$

All chemical thermodynamic texts[1] derive the relationships between the standard free-energy change and the equilibrium constant K, which is

$$-\Delta G^\circ = RT \ln K$$

The equilibrium constant for the generalized reaction may be written in terms of partial pressure p if the components are behaving as ideal gases; or thermodynamic functions as activity a or fugacity f may be used for nonideal systems.

$$K = \frac{p_C^c\, p_D^d}{p_A^a\, p_B^b} \qquad \text{for ideal gases}$$

---

[1] See footnote 1, p. 1.

Equilibrium Composition of Nonideal Gases. In order to provide equations which would be useful for all substances, Lewis and Randall[1] defined a term, *fugacity*. This is an arbitrarily defined term that may be substituted for pressure in the preceding equation and which will make it applicable for all substances. The mathematical definition of fugacity f is

$$dG = RT\, d \ln f$$

Since the numerical value of the fugacity of a substance is often difficult to calculate, the ratio of the fugacity at one state to that at some other arbitrarily defined state is often used. The second such condition is called the *standard* state. The ratio is called the *activity* and is defined thus:

$$a = \frac{f}{f^\circ}$$

where f° refers to the fugacity of the substance at the standard state. Although any arbitrary standard state may be chosen, custom has limited this choice. In the study of chemical equilibria involving gas reactions, the standard state is chosen as that in which the fugacity of the pure gas is equal to unity. This for most gases means the pure gas at 1 atm pressure. The standard-state temperature must be the same as that of the system for which we are calculating the equilibrium composition. (This must not be confused with the standard thermochemical temperature of 25°C = 298.15°K.)

Calculation of the Fugacity of Gases. In the application of the chemical equilibrium equation to nonideal gases, it is the fugacities and not the partial pressures that are important. Therefore, we must have a means of relating the fugacity to the partial pressure in order to use the equation. Fugacity is really another term which is a measure of the deviation of a gas from ideality. Since this is the case, there must be a relationship between fugacity and the compressibility factor

$$z = \frac{PV}{RT}$$

which is another measure of this deviation.

The Law of Corresponding States. When a gas is nonideal, PV does not equal RT. However, the quantity RT can be multiplied by a correction factor so that for 1 mole of gas

$$PV = zRT$$

This correction factor (the compressibility factor) varies with both temperature and pressure for each gas. If there were no relation between the factors for different gases, it would be necessary to have charts or tables showing z as a function of temperature and pressure for each individual

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[1] LEWIS and RANDALL, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923.

gas. This would make the use of the compressibility factor impractical.

However, it has been found by experiment that when gases are at the same reduced temperature ($T_r = T/T_c$) and reduced pressure ($P_r = P/P_c$) their compressibility factors are approximately the same. The degree to which a gas deviates from ideal behavior, therefore, depends upon its reduced temperature and pressure. At equal reduced conditions the deviation is the same for all gases. This rule is an empirical one which has been found to hold with a fair degree of accuracy for most gases. It is called the law of *corresponding states.*

The principal value of the law of corresponding states is that it makes possible the construction of charts or tables which give the value of the compressibility factor for any gas as a function of reduced temperature and pressure. The data are usually presented in chart form, with z plotted against P_r and with T_r as the parameter.[1] Such a chart is shown in Fig. 1-2.

The law of corresponding states may also be used in the construction of charts or tables which give the deviation of enthalpy, entropy, or heat capacity from that of the ideal gas as a function of reduced temperature and pressure.

One of the most important uses of this law is the development of a mathematical relationship between the fugacity f of a nonideal gas and its compressibility factor z. From this relationship, charts have been made[2] which permit the calculation of the fugacity of those nonideal gases which obey the law of corresponding states. A chart of this type is shown in Fig. 1-3. The ordinate is the ratio of fugacity to pressure (f/P) and is called the *fugacity coefficient* (ν). This is plotted against reduced pressure, with reduced temperature as a parameter. The fugacity-coefficient chart may also be used to calculate the fugacity of individual components of gaseous mixtures and also to calculate the fugacity of a pure liquid at its vapor pressure.

Equilibrium Constant for Nonideal Gases. When the equilibrium constant is applied to nonideal gas mixtures, the fugacities are used instead of partial pressures. Thus, the equilibrium equation for the reaction

$$aA + bB \rightleftharpoons cC + dD$$

becomes

$$K = \frac{f_C^c f_D^d}{f_A^a f_B^b}$$

but since

$$f_A = \nu_A p_A$$

where

$$\nu_A = \frac{f_A}{P_A}$$

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[1] Nelson and Obert, *Chem. Eng.*, 61 (7), 203–208 (1954).

[2] Hougen and Watson, "Chemical Process Principles," part II, p. 622, John Wiley & Sons, Inc., New York, 1947.

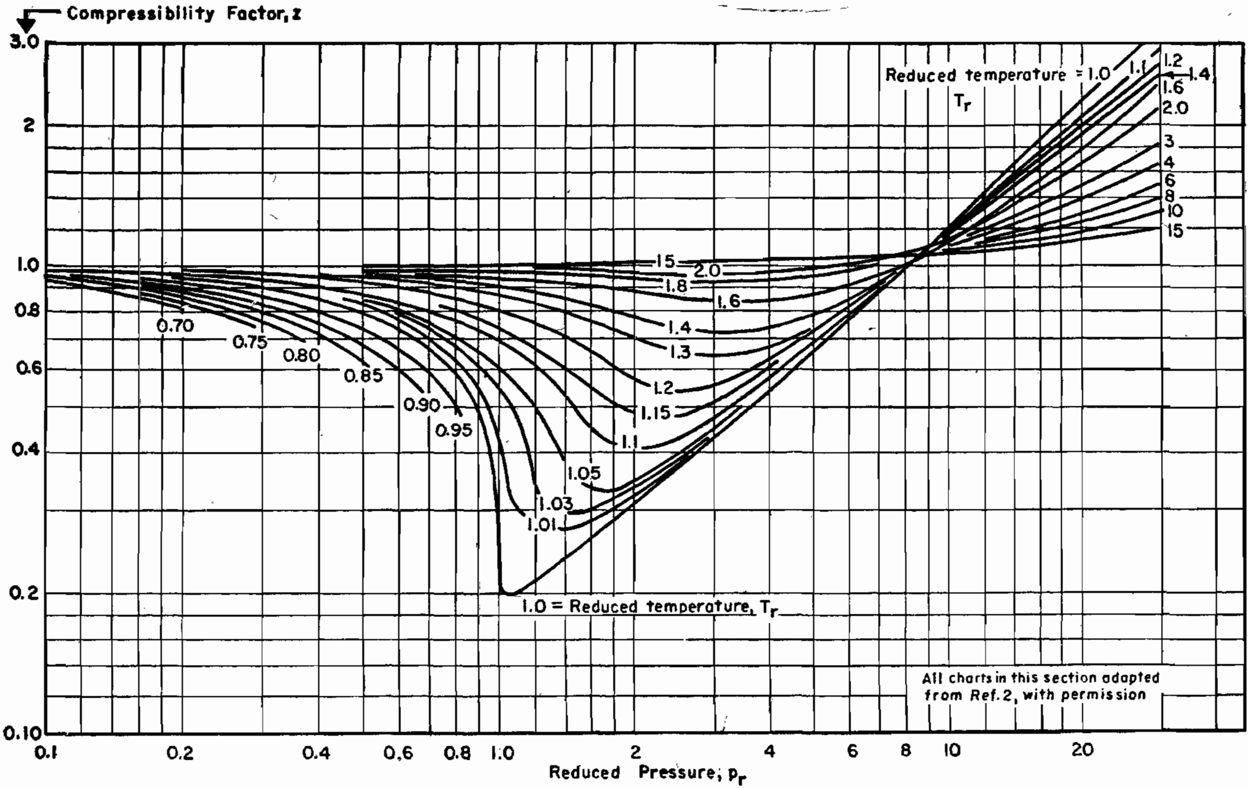

FIG. 1-2. Compressibility factor plotted against reduced pressure with reduced temperature parameters.

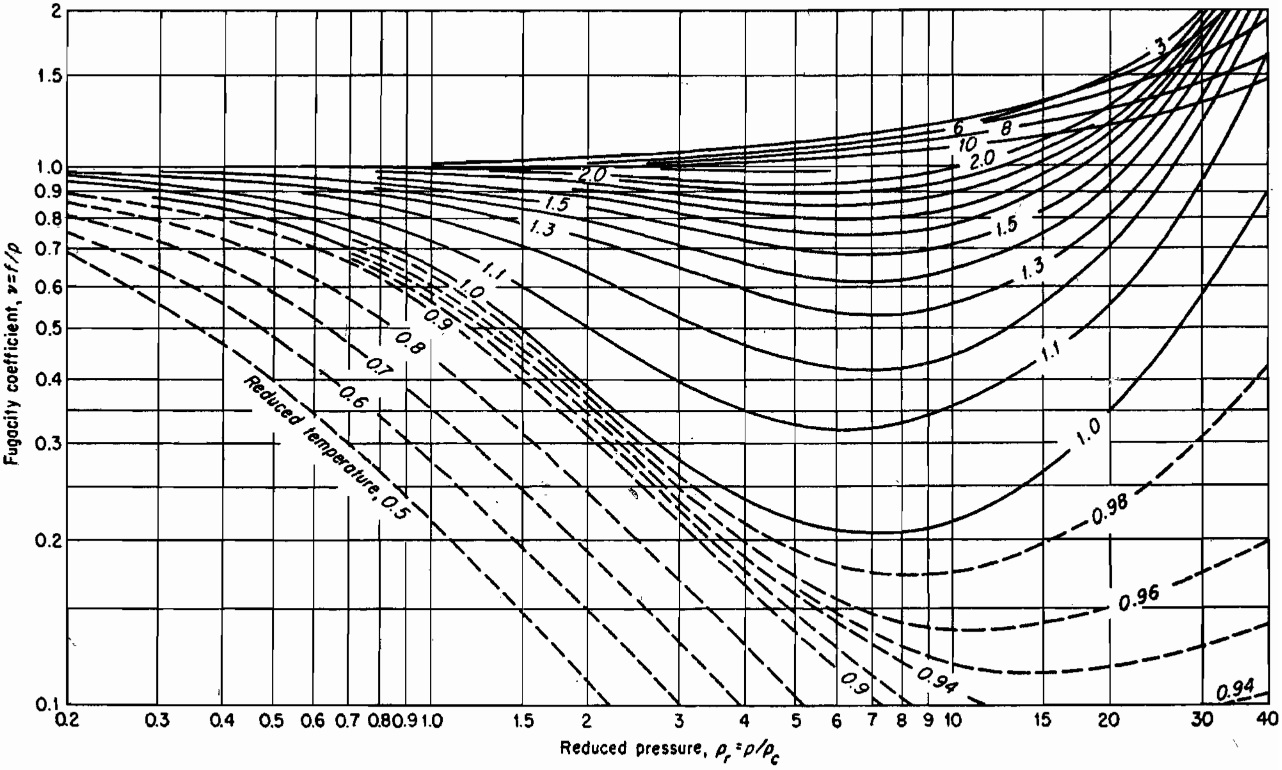

FIG. 1-3. Generalized fugacity coefficient ~~vs. reduced~~ pressure.

this may be written

$$K = \frac{\nu_C^c p_C^c \nu_D^d p_D^d}{\nu_A^a p_A^a \nu_B^b p_B^b}$$

or

$$K = \frac{\nu_C^c \nu_D^d p_C^c p_D^d}{\nu_A^a \nu_B^b p_A^a p_B^b} = K\nu \quad \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

where

$$K\nu = \frac{\nu_C^c \nu_D^d}{\nu_A^a \nu_B^b} \qquad \text{by definition}$$

Here $K\nu$ is a direct measure of the effect of nonideality of the gases upon the equilibrium composition.

Calculation of the Equilibrium Constant. The equilibrium constant, K, for a chemical reaction can be calculated from the standard free-energy functions or from changes in enthalpy and entropy for the process. Data will be found in the references listed at the end of this chapter. Since,

$$-\Delta G_T^\circ = RT \ln K$$

and

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$$

for a process occurring at constant temperature and pressure, data must be available for the temperature at which the reaction takes place. If values of ΔG_T° are not available, calculate them from enthalpy and entropy data. ΔH_T° was calculated on p. 5. ΔS_T° can be calculated in a similar manner:

$$\Delta S_T^\circ = \Delta S_S^\circ + \int_{T_S}^{T} \frac{\Delta C_p{}^\circ}{T} dT$$

$$\Delta S_S^\circ = \Sigma(S^\circ)_{\text{products}} - \Sigma(S^\circ)_{\text{reactants}}$$

The standard entropy change of the reaction is calculated from the values of the absolute entropy of the products and reactants at the standard temperature $T_S = 25°\text{C}$.

The calculation of absolute entropy of many substances is possible because the substances follow the third law of thermodynamics. This states that the absolute entropy of a pure substance in the crystalline state is zero at the temperature of absolute zero. Thus, if the latent heats λ of all the phase changes are known and if the heat capacity is known, the absolute entropy of the pure substance may be calculated by the following equation:

$$S^\circ = \Sigma \int \frac{C_p^\circ}{T} dT + \Sigma \frac{\lambda}{T}$$

Entropies calculated in this manner were compared with absolute entropies computed backward from measurable equilibrium constants and were found to check quite closely.

If the standard free energy of the substances involved in a chemical reaction were tabulated, the standard free-energy change and, thus, K for a given reaction could be calculated directly.

Calculation of Equilibrium Conversion. In practically all engineering calculations, the evaluation of the equilibrium constant is merely a means to an end. The ultimate goal is the calculation of how far a reaction can proceed—the equilibrium conversion.

Single Isothermal Reaction between Ideal Gases. One of the simplest cases involving a calculation of equilibrium conversion is for an isothermal reaction between ideal gases. Consider the reaction

$$A \rightleftharpoons R + S$$

where A, R, and S are ideal gases.

The first step is to calculate K. The method involving the standard heat of reaction and the standard entropy change is usually used because these data are available for most substances. In the tables giving standard heats of formation (or standard heats of combustion) and absolute entropies, the standard state is usually specified as unit fugacity for all gases and is usually stated as the pure gas at 1 atm pressure. The calculation must be based upon the standard state specified by these tables and is not arbitrary, as many people are led to believe. If the standard state for each component is that of unit fugacity, the equilibrium equation becomes

$$K = \frac{p_R p_S}{p_A}$$

It is necessary to express each partial pressure in terms of the same variable—degree of conversion. If the initial gas consists of 1 mole of A, the conversion x at equilibrium may be expressed as follows:

$$\begin{array}{ccccc} A & \rightarrow & R & + & S \\ 1 - x & & x & & x \end{array}$$

BASIS: 1 MOLE OF A IN FEED

Constituent	Moles	Mole fraction	Partial pressure
A	$1 - x$	$1 - x/1 + x$	$\pi(1 - x)/1 + x$
R	x	$x/1 + x$	$\pi x/1 + x$
S	x	$x/1 + x$	$\pi x/1 + x$
Total.....	$1 + x$	1.0	

where π is defined as the total pressure on the system. Thus, the equilibrium equation becomes

$$K = \frac{\pi(x/1 + x)\,\pi(x/1 + x)}{\pi(1 - x/1 + x)}$$

or

$$K = \frac{\pi x^2}{1 - x^2}$$

or

$$x = \sqrt{\frac{K}{\pi + K}}$$

Correction for Nonideality. If the pressure were so high that the gases did not behave ideally, the equation would have to be corrected for nonideal behavior. Since the standard states are still unit fugacity, the equilibrium equation would be

$$K = \frac{f_R f_S}{f_A} = \frac{\nu_R p_R \nu_S p_S}{\nu_A p_A}$$

The fugacity coefficients (ν) would have to be evaluated. Since in this case

$$K_\nu = \frac{\nu_R \nu_S}{\nu_A}$$

the equation becomes

$$\frac{K}{K_\nu} = \frac{p_R p_S}{p_A}$$

Solving for conversion as in the previous example.

$$x = \sqrt{\frac{K/K_\nu}{\pi + K/K_\nu}}$$

The only difference between the nonideal case and the previous case is that the ratio K/K_ν replaces K in the equation for x.

Reactions Involving Gases and Solids. We have demonstrated how to calculate the equilibrium composition for a reaction involving all gases. Let us consider the case where a gas reacts with a solid such as in the reaction

$$C + CO_2 \rightleftharpoons 2CO$$

Here

$$K = \frac{f^2_{CO}}{f_{CO_2}} = \frac{\nu^2_{CO} p^2_{CO}}{\nu_{CO_2} p_{CO_2}}$$

The term f_C does not appear for carbon because the carbon remains in the solid state right up until the time it reacts and, therefore, is present only in its standard state, that is, as the pure solid at unit fugacity. It so happens that, in the tabulating of enthalpy and entropy data for solids, the standard state used is the pure substance at the standard temperature. The calculation which corrects ΔH° and ΔS° for temperature automatically provides for the correction of the fugacity of the solid from the standard temperature to the temperature of the system. Thus, the standard state for solids is the temperature of the system at one atmosphere pressure. However, the fugacity of solids is almost independent of pressure, and so the fugacity of a solid at the pressure of the system is for all practical purposes the same as that at 1 atm. Thus, the activity of any solid (carbon, in this reaction) is practically unity, and the term does not appear in the equilibrium equation. It should be noted, however, that the thermal properties of carbon must be used in calculating the value of $-\Delta G^\circ$ for the reaction and, hence, the value of K.

Simultaneous Reactions. When two isothermal reactions take place simultaneously, the calculation is slightly more involved, but may be solved readily. The solution of this type of problem involves two unknowns. The procedure is to set up the equations involving the equilibrium constant for each reaction and to solve the simultaneous equations graphically.

Assume that the following two ideal gas reactions occur simultaneously and are isothermal:

$$A + B \rightleftharpoons R \qquad K_1 = \frac{p_R}{p_A p_B} \tag{1}$$

$$A + R \rightleftharpoons S \qquad K_2 = \frac{p_S}{p_A p_R} \tag{2}$$

Compound A is the limiting reactant, B the excess reactant.

r = mole ratio of B to A in the feed
x = degree of conversion of A by reaction (1)
y = degree of conversion of A by reaction (2)

BASIS: 1 MOLE OF A IN FEED

Component	Moles at equilibrium	Mole fraction
A	$1 - x - y$	$\frac{1 - x - y}{1 + r - x - y}$
B	$r - x$	$\frac{r - x}{1 + r - x - y}$
R	$x - y$	$\frac{x - y}{1 + r - x - y}$
S	y	$\frac{y}{1 + r - x - y}$
Total...........	$1 + r - x - y$	

In the case where the total pressure is 1 atm, the partial pressures are equal to mole fractions and the two equations become

$$K_1 = \frac{(x - y)(1 + r - x - y)}{(r - x)(1 - x - y)}$$

$$K_2 = \frac{y(1 + r - x - y)}{(x - y)(1 - x - y)}$$

Since the K's are constant and may be calculated from thermal data and r is usually specified, the two equations can be solved simultaneously. The easiest method is, generally, to plot y versus x in both equations, and the point of intersection gives the desired x and y values.

Adiabatic Reactions. In the cases thus far considered, we have shown how to calculate the equilibrium conversion for reactions that take place at a constant temperature. In many industrial practices, no heat is added or removed during the process and the heat of reaction must originate from or be dispersed in the reacting system itself. Thus, the temperature of the reacting mass will change continuously during the reaction, and a calculation of the equilibrium composition will also involve the calculation of the final temperature. This type of problem is solved most easily by a graphic method.

The method of solution for adiabatic reactions presented here will be for the simplified case in which it may be assumed that ΔH_T° and ΔS_T° are relatively constant over the temperature range involved. If this is the case, a plot of $\log K$ versus $1/T$ will result in a straight line. The calculation involves two relationships between T and x, the degree of conversion. One is a simplified energy balance; the other is the relation involving the equilibrium constant. The procedure is as follows:

1. By methods previously discussed, calculate K for two temperatures and plot $\log K$ versus $1/T$. This will be a straight line if ΔH° and ΔS° are assumed to remain constant.

2. Assume even values of conversion, x, from 0 to 1, and calculate the corresponding partial pressure of each gas present for each value of x.

3. Using these ratios of partial pressures, calculate the values that K would have for each value of x.

4. Using the $\log K$ versus $1/T$ plot, evaluate T for each value of x and plot x versus T (line ab in Fig. 1-4).

5. Use a simple energy balance to obtain the other relationship between T and x.

$$x\,\Delta H = C_p\,(T - T_0)$$

where C_p = molal heat capacity
ΔH = heat of reaction

From this equation it is seen that at

$$x = 0 \qquad T = T_0$$

and where $x = 1$ $\qquad T_1 - T_0 = \dfrac{\Delta H}{C_p}$

$$T_1 = \frac{\Delta H}{C_p - T_0}$$

The line connecting T_1 and T_0 is drawn in.

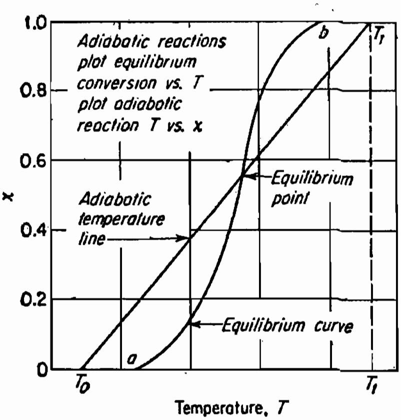

FIG. 1-4. Adiabatic reactions: equilibrium conversions vs. temperature, adiabatic T vs. x.

6. The intersection of the two lines gives the desired values of x and T. This procedure is illustrated in Fig. 1-5.

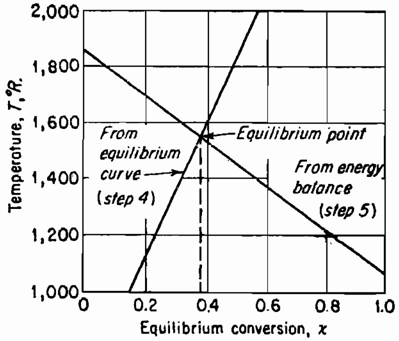

FIG. 1-5. Equilibrium conversion.

Thermodynamics and Unit Processes. The major purpose of presenting a review of thermodynamics principles in this volume is to emphasize the importance of thermodynamics to a fundamental understanding of unit processes. It is, therefore, appropriate to discuss some specific methods of application.

These practical applications generally involve three phases of thermodynamics. They are thermal effects, chemical equilibrium, and physical equilibrium. Thermal calculations involve only the first law of thermodynamics and are used for calculating:

1. Heat of reaction and the effect of temperature on heat of reaction.
2. Sensible heat transferred in preheating and cooling.
3. Heat of solution and adsorption.
4. Heat effects in phase transformations (vaporizing, melting, and crystallizing).

Chemical-equilibrium calculations, the subject of this chapter, are probably the most important application. They involve:

1. Calculating the equilibrium constants of both the major and secondary reactions of a process.
2. Calculating the effect of temperature on these constants.
3. Calculating how far a reaction can go at a given set of conditions.
4. Calculating the concentration of the desired product in the reactor effluent for various process conditions. (This applies to fast reactions.)
5. Determining the effects of solvents, inert diluents, or recycle streams on product yields.

Physical equilibrium is also a very important aspect of thermodynamics which applies to the chemical-process industries. It is more often used, however, in those phases of a process which involve the separation and purification of the product once it is formed. The physical-equilibrium portion is applied almost entirely to the unit operations. It is used to calculate phase compositions, vapor-liquid equilibria, absorption, adsorption, extraction, and distillation and to estimate solubilities. This phase of chemical engineering is covered adequately in other texts.

Chemical Equilibrium Applied. The major use of the principles of this chapter is to calculate the equilibrium composition of a system. This application in vapor-phase homogeneous reactions has been discussed above.

But what about other systems? Do the methods equally apply? The answer is "yes," provided that certain factors are considered.

Vapor-phase Catalytic Reactions. Since a catalyst does not change the equilibrium of a reaction, the calculated composition should be the same with a catalyst present as without. This is generally the case, but there are exceptions to bear in mind. One is the case of a possible competing reaction which is too slow to have any effect in the homogeneous system but which is speeded up by the catalyst to a greater extent than the main reaction. Consider, for example, the reactions

$$A \rightleftharpoons R$$

with the potential side reaction

$$A \rightarrow S$$

Suppose that the equilibrium conversion of the first reaction is 98 per cent and that the second is nonreversible but infinitely slow in the vapor phase. The yield will be 98 per cent. If the catalyst speeds up both reactions so that the second reaction is about the same speed as the first reaction, the yield will drop. The chemical-equilibrium calculation would not have predicted this since the second reaction was not considered.

Liquid-phase Reactions. There are times when the calculated equilibrium composition of a liquid-phase reaction does not compare at all with the actual measured value. This does not mean that the theory is wrong —just that there is not enough of it. Here is the reason. The rigorous equilibrium equation for the reaction

$$A + B \rightleftharpoons C + D$$

in the liquid phase is

$$K_a = \frac{a_C a_D}{a_A a_B}$$

where the a's represent the activities of the components. But, since we do not know the actual activities, we generally use the expression

$$K = \frac{x_C x_D}{x_A x_B}$$

where the x's are the mole fractions. This means that we are assuming the mixture to be an ideal solution. If the solution really were ideal, the calculated composition would match the measured one. If the solution should deviate much from ideality, the calculated composition will not be correct. Theoretically this could be taken care of by using the activity coefficient of each component. Unfortunately, our knowledge of physical equilibrium has not progressed far enough to allow us to calculate activity coefficients of complex liquid mixtures (more than two or three components).

Thermodynamics Is Not Infallible. Chemical-equilibrium calculations are useful, but they do not always give the whole answer. If a chemical reaction is fast, thermodynamics calculations may tell all we need to know about the reaction. In these cases the rate of reaction is not important, just product distribution and temperature control. If the reaction is not possible at all or not economically feasible because of too low a product concentration in the reactor effluent, thermodynamics can tell us so.

If, on the other hand, the reaction is not extremely fast, if the time spent in the reactor is important, or if rapid competing reactions are involved, the chemical engineer can turn to another tool—kinetics.

SOURCES OF THERMODYNAMIC DATA

Thermodynamic data must be sought from many sources. The American Petroleum Institute and Manufacturing Chemists Association have large projects to determine and collect thermodynamic data. Several governmental agencies, such as the National Bureau of Standards and the Bureau of Mines, determine, collect, and publish thermodynamic data. Some of the best and most readily available sources of thermodynamic data are listed below.

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(A collection of a series of 19 articles that appeared in the *Petroleum Refiner* from January, 1949, to December, 1951. Additional papers have appeared at intervals since 1951. Tables of heat capacity, mean heat capacity, and relative enthalpy are given in °C, °K, °F, and °R. Other thermodynamic data are given.)

Rossini, F. D., and others: "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(Lithographed sheets are being issued at intervals by API Project 44 to complete and extend this material.)

Rossini, F. K., and others: "Tables of Selected Values of Chemical Thermodynamic Properties," *Natl. Bur. Standards Circ.* 500, 1952.

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Sage, B. H., and W. N. Lacey: "Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide, and Carbon Dioxide," American Petroleum Institute, New York, 1955.

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Stull, D. R., and G. C. Sinke: "Thermodynamic Properties of the Elements," American Chemical Society, *Advances in Chemistry*, 1957.

Zeise, H.: "Thermodynamik," Band III/1 Tabellen, S. Hirzel Verlag, Leipzig, 1954.

(Tables of heat capacities, enthalpies, entropies, free energies, and equilibrium constants.)

The following special references are used throughout this volume.

The Office of Technical Services (O.T.S.), U.S. Department of Commerce, Washington 25, D.C., has a complete record of all declassified reports of the British Intelligence Objectives Sub-committee (B.I.O.S.), the Combined Intelligence Objectives Sub-committee, SHAEF (C.I.O.S.), and the Field Information Agency Technical (F.I.A.T.). The O.T.S. can arrange for delivery of copies, photostats, or microfilms of these reports for a fee. The Office of the Publication Board (O.P.B.) reports are also available from the O.T.S.

CHAPTER 2

CHEMICAL KINETICS

BY T. E. CORRIGAN AND JOHN J. MCKETTA

What Is Chemical Kinetics? Chemical kinetics is a study of the rates of chemical reaction and the effect that process conditions have on these rates. These process conditions are temperature, pressure, and reactant concentration. The application of kinetics in the selection and design of commercial reactors is of specific interest in the study of unit processes.[1]

Assume in the following consecutive reaction that the desired product is B and that C is valueless:

$$A \rightarrow B \rightarrow C$$

A thermodynamic calculation may show that the reaction is not practicable because at equilibrium there is an excess of C. Yet a kinetic study may show that the rates are such that a high yield of B may be obtained by quenching the reaction at the proper time. This is shown clearly in Fig. 2-1.

Review of Basic Principles.[2] The mass-action law, in equation form, states that for the reaction

$$A + B \rightarrow R$$

the rate of reaction may be expressed in the following manner:

$$r = kC_A C_B$$

This law is an empirical one based on observation and, unlike the thermodynamic expression for the equilibrium constant, is not a derived equation founded on theory.

Order of Reaction.[3] One method of describing homogeneous reactions is by the order of reaction, which is the sum of exponents of the concentration terms. In the equation

$$r = kC_A^a C_B^b$$

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[1] CORRIGAN, *Chem. Eng.*, **61**, July, 1954.

[2] CORRIGAN, *Chem. Eng.*, **61**, August, 1954; LAIDLER, "Chemical Kinetics," McGraw-Hill Book Company, Inc., New York, 1950; DANIELS, "Chemical Kinetics," Cornell University Press, Ithaca, N.Y., 1938; FROST and PEARSON, "Kinetics and Mechanism," p. 153, John Wiley & Sons, Inc., New York, 1953.

[3] **Nomenclature for Chaps. 2 and 3 will be found at the end of Chap. 2.**

the order of reaction is $a + b$. The molecularity of a reaction is the number of *reactant* molecules in the stoichiometric equation. If the reaction is

$$A + B \rightarrow R$$

and the rate is

$$r = kC_A^{1/2} C_B$$

the molecularity is 2 and the order of reaction is 1½. The order of a reaction is *not* determined by the molecularity. Chemical reactions in which the order of reaction is the same as the molecularity are called simple-order reactions.

Mechanism. A reaction usually does not occur in the single step which may be represented by the over-all stoichiometric equation but rather in a series of steps which add up to the over-all equation. These steps are the "mechanism" of the reaction. For example, the reaction

$$2A + B \rightleftharpoons R + S$$

might take place as follows:

$$\begin{array}{rl} A + B \rightleftharpoons AB & \text{(Step 1)} \\ A + AB \rightleftharpoons A_2B & \text{(Step 2)} \\ A_2B \rightleftharpoons AB + R & \text{(Step 3)} \\ AB \rightleftharpoons S & \text{(Step 4)} \\ \hline 2A + B \rightleftharpoons R + S & \end{array}$$

The slowest step controls the rate of the reaction and may also determine the form of the over-all rate equation. The rate equation, rather than the mechanism, is important to engineers.

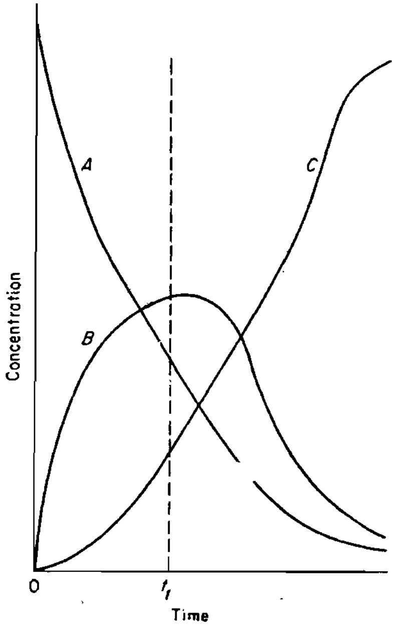

FIG. 2-1. Kinetic data may show that by quenching a reaction economic recoveries are feasible.

First-order Reaction. If the following is a first-order reaction

$$A \rightarrow B$$

a plot of $\Delta C_A/\Delta t$ against C_A will give a straight line since the rate equation for a first-order reaction is

$$-\frac{dC_A}{dt} = kC_A \tag{1}$$

Equation (1) integrates to the form

$$\ln C_A = -kt + I \tag{2}$$

where I is integration constant. Thus, if the reaction is first order, a plot of the term $\ln C_A$ versus time will give a straight line of negative slope.

Second-order Reaction. If a chemical reaction has a rate equation of the following form, it is of second order:

$$-\frac{dC_A}{dt} = kC_A^2 \tag{3}$$

A plot of $\Delta C_A/\Delta t$ against C_A^2 is a straight line. It is better to use the integral form of Eq. (3):

$$\frac{1}{C_A} = kt + \frac{1}{C_{A_0}} \quad \text{or} \quad \frac{1}{C_A} - \frac{1}{C_{A_0}} = kt \tag{4}$$

Thus, a plot of $1/C_A$ against t will give a straight line with a slope equal to k.

For a reaction of the form

$$A + B \rightarrow C + D$$

with the rate equation

$$-\frac{dC_A}{dt} = kC_AC_B \tag{5}$$

the integral form may be expressed in terms of conversion (x) and initial concentrations; thus[1]

$$\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = kt \tag{6}$$

A plot of the term $1/(a-b)\ln b(a-x)/a(b-x)$ against t will give a straight line with a slope equal to $-k$. If a and b are equal, the equation reverts to the integrated form

$$\frac{x}{a(a-x)} = kt \tag{7}$$

Thus, a plot of $x/a(a-x)$ against t would give a straight line with a slope of k.

Third-order Reaction. If the reaction

$$A \rightarrow B$$

were a third-order reaction, the rate equation would be

$$-\frac{dC_A}{dt} = kC_A^3$$

In terms of conversion, the rate equation is now

$$\frac{dx}{dt} = k(a-x)^3 \tag{8}$$

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[1] FROST and PEARSON, *op. cit.*

and the integrated form is

$$\frac{2ax - x^2}{2a^2(a - x)^2} = kt \tag{9}$$

A plot of the quantity $(2ax - x^2)/2a^2(a - x)^2$ against t would be a straight line.

Zero-order Reaction. In some chemical reactions the rate of reaction is independent of the reactant concentration. The rate equation would be

$$-\frac{dC_A}{dt} = k \tag{10}$$

and a plot of reactant concentration against time would be a straight line.

General Case. The general rate equation for a reaction involving a single reactant is

$$\frac{dC_A}{dt} = kC_A^n$$

or

$$\frac{dx}{dt} = k(a - x)^n$$

where n may be any positive number. In most cases, n is a fraction. The integral form of this equation[1] is

$$\frac{1}{(n - 1)}\left(\frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}}\right) = kt \tag{11}$$

Limitations of Methods. All the plots discussed above for determining the order of a reaction are valid either for nonreversible reactions or at low values of conversion.

The methods which can be used to determine the order of reaction may be summarized as follows:

1. Plotting $\Delta C_A/\Delta t$ versus concentration.
2. Calculating k from the data and taking the order which gives the most nearly constant value of k.
3. Plotting the proper integral function for each order and selecting the one which gives a straight line.

Table 2-1 is a summary of the differential and integral equations for each order of reaction.

Effect of Temperature on Chemical Reactions. The basic reaction-rate equations discussed above are defined only by concentration and time. The effect of temperature appears only in the variation of k.

The relationship between the reaction-rate constant (k) and temperature was first observed by Arrhenius to be

$$k = se^{-E/RT}$$

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[1] LAIDLER, *op. cit.*

TABLE 2-1. SUMMARY OF EQUATIONS FOR ORDER OF REACTION

Order	Chemical equation	Rate equation	Integrated equation	Units of k
0	$A \rightarrow$ products	$dx/dt = k$	$x = kt$	conc./time
1	$A \rightarrow$ products	$dx/dt = k(a - x)$	$\ln a/(a - x) = kt$	1/time
2	$A \rightarrow$ products	$dx/dt = k(a - x)^2$	$x/a(a - x) = kt$	1/(time) (conc.)
2	$A + B \rightarrow$ products	$dx/dt = k(a - x)(b - x)$	$\frac{1}{a - b} \ln \frac{b(a - x)}{a(b - x)} = kt$	1/(time) (conc.)
3	$A \rightarrow$ products	$dx/dt = k(a - x)^3$	$\frac{2ax - x^2}{2a^2(a - x)^2} = kt$	1/(time) (conc.)^2
3	$A + B \rightarrow$ products	$dx/dt = k(a - x)^2(b - x)$	$\frac{1}{(a - b)^2} \ln \frac{b(a - x)}{a(b - x)} +$ $\frac{1}{a - b} \frac{1/a - 1}{a - x} = kt$	1/(time) (conc.)^2
Fractional or general	$A \rightarrow$ products	$dx/dt = k(a - x)^n$	$\frac{1}{n - 1} \left[\frac{1}{(a - x)^{n - 1}} - \frac{1}{a^{n - 1}} \right] = kt$	$\frac{1}{(\text{time})\ (\text{conc.})^{n - 1}}$

When ln k is plotted against $1/T$, the values of E/R and of s may be determined from the slope and intercept of the line.

Types of Chemical Reactions.[1] Some of the classifications of reactions deal only with the chemistry of the reactions, and some are concerned with the environment in which the reaction takes place.

Some of the criteria which are used in classifying reactions are:

1. Heterogeneous or homogeneous reactions. This classification refers to the number of phases in the reacting system. A homogeneous reaction is one which takes place in only one phase. A heterogeneous reaction involves more than one phase.

2. Mechanism of reaction, such as chain reactions, regular molecular reactions, or photochemical reactions.

3. Catalytic or noncatalytic reactions.

4. The method of operating the reactor, such as adiabatic, isothermal or nonadiabatic-nonisothermal.

5. The stoichiometric chemical equation. Reactions may be divided in this manner into five major types: simple reactions, parallel reactions, series reactions, complex series reactions, and reversible reactions.

Simple Reactions. A simple reaction is where only one reaction is considered to take place. The more common simple reactions are represented by the following types:

$$\begin{array}{l} A \rightarrow R \\ A + B \rightarrow R \\ A \rightarrow R + S \\ A + B \rightarrow R + S \\ 2A \rightarrow R \\ A \rightarrow 2R \end{array}$$

A typical concentration-time curve is shown in Fig. 2-2 on page 30.

Some industrially important examples of simple reactions are:

1. $A \rightarrow R$. Isomerization of butane which is discussed in Chap. 14.

2. $A + B \rightarrow R + S$. Acylation of amines.

$$\begin{array}{l} RNH_2 + RCOOH \rightarrow RNHCOR + H_2O \\ RNH_2 + RCOCl \rightarrow RNHCOR + HCl \end{array}$$

3. $A \rightarrow R + S$. Production of vinyl chloride from ethylene dichloride.

$$ClCH_2CH_2Cl \rightarrow CH_2{=}CHCl + HCl$$

When only one reaction is taking place, the only variables to be considered are time and conversion. The reaction $A \rightarrow R$ is the simplest of this type. It represents a molecular rearrangement. The basic rate equation for this reaction is

$$-\frac{dC_A}{dt} = kC_A^n \qquad (12)$$

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[1] CORRIGAN, *Chem. Eng.*, 61, September, 1954.

where n is the order of reaction. The integrated forms of the equation for various reaction orders are given in the accompanying table.

Order	Differential form	Integral form
0	$-dC_A/dt = k$	$C_{A_0} - C_A = k$
1	$-dC_A/dt = kC_A$	$\ln C_{A_0}/C_A = kt$
2	$-dC_A/dt = kC_A^2$	$(1/C_{A_0}) - (1/C_A) = kt$
½	$-dC_A/dt = kC_A^{\frac{1}{2}}$	$2(C_{A_0}^{\frac{1}{2}} - C_A^{\frac{1}{2}}) = kt$
n	$-dC_A/dt = kC_A^n$	$\frac{1}{n-1}\left\{\frac{1}{C_A^{n-1}} - \frac{1}{C_{A_0}^{n-1}}\right\} = kt$

If the rate for a reaction involving two reactant molecules, such as the reaction $A + B \rightarrow R$, is given by the equation

$$-\frac{dC_A}{dt} = kC_AC_B$$

the equation can be integrated into one in terms of conversion and time only, as shown in Eq. (6).

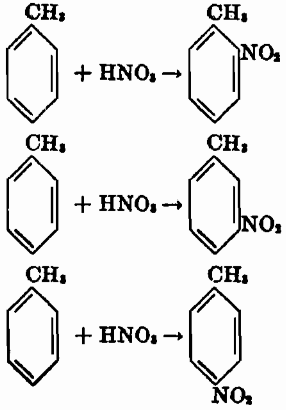
Parallel Reactions. Parallel reactions are those in which more than one product is formed by separate reactions and where the products, once formed, do not react again. Some typical parallel reactions are

$$\begin{cases} A \rightarrow R \\ A \rightarrow S \end{cases}$$
$$\begin{cases} A + B \rightarrow R \\ A + B \rightarrow S \end{cases}$$
$$\begin{cases} A \rightarrow R \\ A + B \rightarrow S \end{cases}$$

An example of a set of parallel reactions of the type

$$A + B \rightarrow R$$
$$A + B \rightarrow S$$
$$A + B \rightarrow T$$

is in the nitration of toluene, which is discussed fully in Chap. 4.



The basic rate equations for the reaction

$$\begin{cases} A \rightarrow R \\ A \rightarrow S \end{cases}$$

are

$$\frac{dC_R}{dt} = k_1 C_A^n$$

$$\frac{dC_S}{dt} = k_2 C_A^m$$

$$-\frac{dC_A}{dt} = k_1 C_A^n + k_2 C_A^m \tag{13}$$

If the reactions are both the same order,

$$\frac{dC_A}{dt} = -(k_1 + k_2)\, C_A^n \tag{14}$$

If both reactions are first order,

$$C_A = C_{A_0} e^{-b} \tag{15}$$

$$C_R - C_{R_0} = \frac{k_1}{k_1 + k_2} C_{A_0}(1 - e^{-b}) \tag{16}$$

$$C_S - C_{S_0} = \frac{k_2}{k_1 + k_2} C_{A_0}(1 - e^{-b}) \tag{17}$$

where $b = (k_1 + k_2)t$

The concentrations of R and S are related by the simple ratio of the rate constants

$$\frac{C_R - C_{R_0}}{C_S - C_{S_0}} = \frac{k_1}{k_2}$$

Figure 2-3 shows a concentration-time curve for a parallel reaction.

Series Reactions. Series reactions are those in which the product of the reaction goes on to react further. The simplest example is

$$A \rightarrow R \rightarrow S$$

An example of commercial interest is the liquid-phase chlorination of benzene.

From a typical plot of concentration versus holding time, it can be seen that the concentration of R passes through a maximum value and also that there is an inflection point in the curve for the concentration of S (Fig. 2-4).

The rate equations for reactions of this type are

$$-\frac{dC_A}{dt} = k_1 C_A^n$$

$$\frac{dC_R}{dt} = k_1 C_A^n - k_2 C_R^m \tag{18}$$

$$\frac{dC_S}{dt} = k_2 C_R^m$$

Integral reaction-rate equations have been worked out for the case of first-order reactions. These are discussed in the standard texts on physical chemistry.

The first-order rate equations are

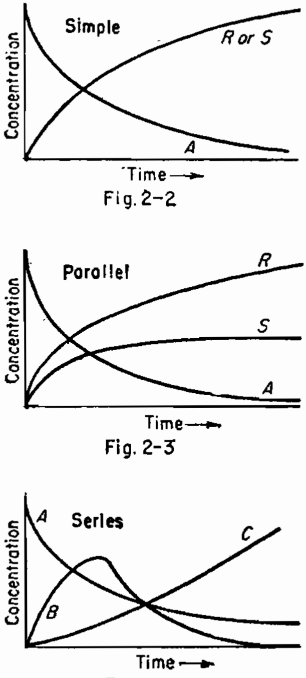


Fig. 2-2

Fig. 2-3

Fig. 2-4

FIGS. 2-2 to 2-4. Time-concentration curves for simple, parallel, and series reactions.

Differential	*Integral*
$-\dfrac{dC_A}{dt} = k_1 C_A$	$C_A = C_{A_0} e^{-k_1 t}$
$\dfrac{dC_R}{dt} = k_1 C_A - k_2 C_R$	$C_R = \dfrac{C_{A_0}}{1 - \kappa}(e^{-k_1 t} - e^{-k_2 t})$

where $\kappa = k_2/k_1$ for the case where neither R nor S is recycled. The concentration of S is determined by material balance

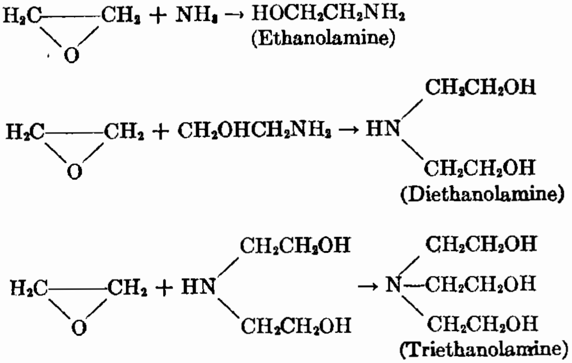
$$C_S = C_{A_0} - C_A - C_R$$

Complex Series Reactions. Complex series reactions are those in which there is further reaction between one of the reactants and one of the products so that both series and parallel reactions take place simultaneously. An example of this is

$$\begin{aligned} A + B &\rightarrow R \\ A + R &\rightarrow S \\ A + S &\rightarrow T \end{aligned}$$

This is a series reaction with respect to B, R, and S, but it is a parallel reaction with respect to A. A concentration-time curve is shown in Fig. 2-5.

An industrial operation exemplifying a complex series liquid-phase reaction is in the conversion of alkylene oxides to the alkanolamines, which is discussed in Chap. 8.



Among many similar liquid-phase reactions of the complex series type, the following are shown later in this book:

1. Glycol ethers,
2. Dimethylol urea,
3. Glycines.

An example of a vapor-phase complex series reaction is the chlorination of propane, which is discussed in Chap. 6.

A complex series reaction, such as the one above, is more complicated than the corresponding series reaction. The reactant ratio C_{B_0}/C_{A_0} is an added variable which is not present in the straight series reaction. The fact that A reacts with each of the products as well as with B results in a more complicated relationship between C_A and time. The presence of two reactants makes the control of the reaction easier than for a series reaction because in both cases, if R is the desired product and S is valueless, the best way to obtain the highest yield of R would be to run the reactor so as to obtain a fairly low conversion in each pass and to recycle the unreacted A. If this were the case, the lower limit to the conversion of A per pass in either case would be regulated only by the economics of the reactor and recovery equipment cost. However, a high yield could be obtained for either type of reaction.

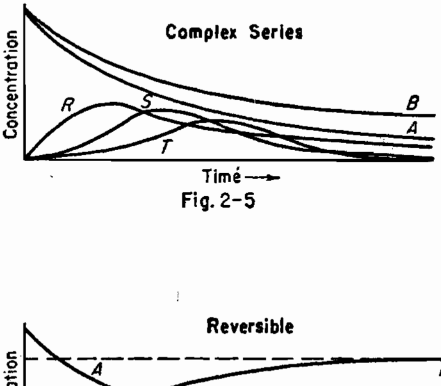


Fig. 2-5

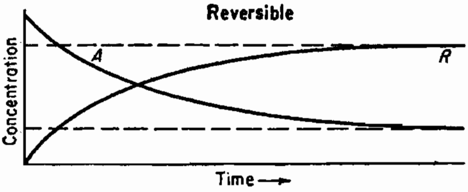


Fig. 2-6

FIGS. 2-5 and 2-6. Time-concentration curves for complex series and reversible reactions.

If reactant A happens to be a material which is so easily decomposed that it cannot be recovered in a recycle system, nothing can be done to obtain a high yield of the desired product in the case of the straight series reaction. In the case of the complex series reaction, the yield of R can be increased by using a high ratio of B to A in the feed.

Thus, higher yields of R can be obtained for the complex series reaction if B can be recovered and recycled. If B cannot be recycled, the same problem holds for the complex series reaction as for the series reaction.

Fortunately, in the commercial reactions listed above, the compound B either can be recovered and recycled (as in the reaction of alcohols with ethylene oxide) or is of low value (such as in the reaction of water and ethylene oxide).

Reversible Reactions. Reversible reactions are those in which the forward and reverse reactions take place simultaneously. Any of the above types of reactions can also be reversible (Fig. 2-6). If the reaction is reversible, this is taken into account in the rate equation. For a simple-order reversible reaction of the type

$$A + B \rightleftharpoons R + S$$

the net rate equation can be written

$$r = k\left(C_A C_B - \frac{C_R C_S}{K}\right) \tag{19}$$

where K is the equilibrium constant. The numerical value of K corresponding to concentration must be used in this equation.

Examples of the reversible reactions are:

1. Nitration of cellulose.
2. Water-gas shift reaction.
3. Sulfonation of naphthalene.
4. Esterification of ethyl alcohol.
5. Alkylation of benzene.

Calculation of Conversion and Reactor Size.[1] The most important use of kinetics for the engineer is in the calculation of reactor size. In the batch-reactor calculations, the typical kinetic equations involving concentration terms can be used without alteration. In this type of calculation it is usually desirable to calculate either the length of time per batch for a reactor of a given size or the amount of initial charge needed if the production rate is specified for a given degree of conversion.

Heterogeneous Reactions. Heterogeneous reactions are those in which more than one phase is involved. Some important types of heterogeneous reactions of industrial interest are:

1. Gas-phase reactions promoted by solid catalysts.
2. Noncatalytic reactions involving gases and solids.
3. Reactions between gases and liquids.
4. Two- (or more) phase liquid reactions.
5. Reactions between liquids and solids.

The first of these is particularly important to the chemical-process and petroleum-refining industries. An example is in vapor-phase catalytic cracking. The second type is particularly important in fuel technology since the combustion of any solid fuel falls in this category. The third type is very important in the chemical-process industries. An example would be the chlorination of a liquid hydrocarbon. Since the degree of contact of the two phases is of major importance, reactors are designed by the same methods used for absorption processes.

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[1] CORRIGAN, *Chem. Eng.*, 61, October, 1954.

Vapor-phase Catalytic Reactions.[1] When a gaseous reaction is promoted by a catalyst, the reactants are first adsorbed upon the catalyst surface. The actual transformation from reactants to products takes place in the adsorbed phase. Therefore, the adsorption characteristics of the catalyst toward each of the reactants and products are important factors in rate determination.

Adsorption may be either physical or chemical. The theory of physical adsorption assumes that the adsorbed phase is a condensed liquid-phase layer of molecules of the vapor on the solid surface. Chemical adsorption is the chemical combination of a vapor molecule with a portion of catalyst surface. This portion of surface is called an *active center*. In the application of adsorption to catalysis, chemical adsorption is of major importance.

Adsorption Equations.[2] There are three important equations relating the concentration of adsorbate on the solid with its partial pressure in the gas phase. One of these is entirely empirical, while the other two have a theoretical basis.

Freundlich's isotherm is the empirical relationship and is

$$c_A = ap_A^n$$

where p_A = partial pressure of A in vapor phase
c_A = concentration of adsorbed material on solid
a and n are empirical constants

An equation of more interest in catalytic kinetics is Langmuir's isotherm

$$c_A = \frac{k_1 p_A}{1 + k_2 p_A}$$

which was derived for the simplest possible case of chemical adsorption. Other isotherms of a similar nature, but more complicated, can also be derived for similar cases.

A general equation for a single adsorbate has been derived by R. A. Koble[3] and can be written in general terms:

$$c_A = \frac{L'K'p_A^n}{1 + K'p_A^n}$$

where L' and K' are constants related to K and L (see below) and n is an exponent which may be fractional, 1, or greater than 1. The special case where n equals 1.0 is the Langmuir isotherm.

Catalytic Rate Equations.[4] Catalytic rate equations based upon the order-of-reaction concept are not recommended because they do not ac-

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[1] Hougen and Watson, "Chemical Process Principles," John Wiley & Sons, Inc., New York, 1947.

[2] Corrigan, *Chem. Eng.*, **61**, November, 1954.

[3] Corrigan, *Chem. Eng.*, **61**, December, 1954; Koble and Corrigan, *Ind. Eng. Chem.*, **44**, February, 1952.

[4] Corrigan, *Chem. Eng.*, **62**, January 1955; **62**, February, 1955.

count for adsorption on the catalyst. A rate equation for catalytic reactions which has more theoretical basis is one which includes the effect of adsorption of the reactants and products on the catalyst. Equations of this type were derived by treating the adsorption and desorption as chemical steps.

Taking as an example the reaction

$$A \rightleftharpoons R + S$$

the following steps are encountered:

$$A + l \rightleftharpoons Al \qquad K_1 = \frac{c_A}{p_A c_l} \tag{20}$$

$$Al + l \rightleftharpoons Rl + Sl \qquad K_2 = \frac{c_R c_S}{c_A c_l} \tag{21}$$

$$Rl \rightleftharpoons R + l \qquad K_3 = \frac{p_R c_l}{c_R} \tag{22}$$

$$Sl \rightleftharpoons S + l \qquad K_4 = \frac{p_S c_l}{c_S} \tag{23}$$

In the above equations K_1, K_2, and K_4 represent the equilibrium constants for the individual steps.[1]

Assuming that the total number of active centers l, L (occupied or unoccupied) is independent of conversion, a relation for c_l can be obtained.

$$L = c_l + c_A + c_R + c_S$$

or

$$L = c_l + \frac{p_R p_S c_l}{K_2 K_3 K_4} + \frac{p_R c_l}{K_3} + \frac{P_S c_l}{K_4}$$

Therefore,

$$c_l = \frac{L}{1 + p_R p_S / K_2 K_3 K_4 + p_R / K_3 + p_S / K_4}$$

With this value of c_l, the rate equation for the first step of the reaction becomes

$$r = \frac{k_1 L (p_A - p_R p_S / K)}{1 + p_R p_S / K_2 K_3 K_4 + p_R / K_3 + p_S / K_4}$$

or

$$r = \frac{k(p_A - p_R p_S / K)}{1 + K_{RS} p_R p_S + K_R p_R + K_S p_S} \tag{24}$$

where

$$k = k_1 L$$

$$K_R = 1/K_3$$

$$K_{RS} = 1/(K_2 K_3 K_4)$$

$$K_s = 1/K_4$$

The rate equation for the second step would be

$$r = k_2 c_A c_l - k_2' c_R c_S \tag{25}$$

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[1] HOUGEN and WATSON, *op. cit.*

Elimination of the terms which cannot be measured experimentally leads to the following equation:

$$r = \frac{k(p_A - p_R p_S/K)}{(1 + K_A p_A + K_R p_R + K_S p_S)^2} \tag{26}$$

The squared term in the denominator appears because two active centers are involved in the rate-controlling step.

If the third step were controlling, the starting equation for it would be

$$r = k_3 c_R - k_3' c_R c_l \tag{27}$$

and the finished equation

$$r = \frac{k(p_A/p_S - p_R/K)}{1 + K_A p_A + K_S p_S + K_{RS}\,(p_A/p_S)} \tag{28}$$

The assumptions made in the above derivations are:

1. Adsorption of all materials is in accord with the Koble equation.
2. The resistance to diffusion is negligible.
3. Only one step is slow enough to be rate determining.
4. The specific rate constants and equilibrium rate constants are independent of total pressure.

Selection of Equations and Evaluation of Constants.[1] Several techniques making use of initial rates have been employed in the interpretation of experimental data to select the proper equation for a given reaction. To use this method, initial rate data have to be obtained at several different pressures. If Eq. (24) is rewritten for the initial rate (zero conversion),

$$r_0 = kp_A$$

or

$$r_0 = k\pi$$

where π is the total pressure and the feed is pure A, it can be seen that a plot of r_0 versus π is a straight line passing through the origin. It can also be seen that the ratio π/r_0 is independent of pressure.

For the case where the surface reaction is the controlling step [Eq. (26)], the initial rate is

$$r_0 = \frac{k\pi}{(a + b\pi)^2} \tag{29}$$

or

$$\frac{\pi}{r_0} = (a + b\pi)^2$$

or

$$\left(\frac{\pi}{r_0}\right)^{1/2} = a + b\pi$$

Therefore, a plot of $(\pi/r_0)^{1/2}$ versus π will give a straight line of positive slope. It may also be seen from Eq. (29) that a plot of r_0 versus π will pass through a maximum value.

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[1] CORRIGAN, *Chem. Eng.*, **62**, April, 1955; **62**, May, 1955.

If the controlling step involved only one active center, its chemical equation would be

$$Al \rightleftharpoons Rl + S$$

The rate equation, then, would be

$$r = \frac{k(p_A - p_R p_S/K)}{1 + K_A p_A + K_R p_R + K_S p_S} \tag{30}$$

and

$$r_0 = \frac{k\pi}{1 + K_A \pi} \tag{31}$$

A plot of r_0 versus π becomes asymptotic to a positive value, but does not pass through a maximum. Also, since

$$\frac{\pi}{r_0} = a + b\pi \tag{32}$$

a plot of π/r_0 against π would be a straight line of positive slope. If the controlling step is that of desorption

$$Rl \rightleftharpoons R + l$$

the rate equation would be

$$r = \frac{k(p_A/p_S - p_R/K)}{1 + K_A p_A + K_S p_S + K_{RS}(p_A/p_S)} \tag{33}$$

and

$$r_0 = \frac{k}{K_{RS}} = k''$$

Therefore, r_0 is independent of π and a plot of r_0 versus π is a straight line of positive slope passing through the origin.

Plots of r_0 versus π and of π/r_0 versus π may be quite helpful in determining which step is controlling. Correlations involving the same variable in both ordinate and abscissa must be regarded with caution, and the π/r_0 plots should not be relied upon if the variation of r_0 is small compared with that of π.

The values of initial rate r_0 may be determined by any of four methods:

1. By measuring the slope of the tangent to the total conversion curve at zero conversion.
2. By plotting rate versus time factor[1] (W/F) and extrapolating to zero.
3. By plotting $x/(W/F)$ versus x and extrapolating to $W/F = 0$.
4. By fitting an empirical equation to the conversion curve and differentiating the equation.

After the initial rates have been used to give an indication of the mechanism, the constants can be evaluated by using a plot of the appropriate

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[1] The time factor W/F is a term which is often used in catalytic flow reactions in place of contact time. W is the weight of catalyst in pounds and F is the feed rate in pound moles per hour.

group of terms[1] versus p_A. For instance, if the controlling step were

$$Al \rightleftharpoons Rl + S$$

a plot of $(p_A - p_R p_S/K)/r$ versus p_A would be a straight line. If the controlling step were

$$Al + l \rightleftharpoons Rl + Sl$$

a plot of $[(p_A - p_R p_S/K)/r]^{1/2}$ versus p_A would be a straight line.

From the shapes of the above plots the experimenter can usually eliminate all but one or two of the proposed mechanisms. The final test of the rate equation is whether or not it fits the experimental data. The equation should be tested not only against the data that were used to obtain the constants, but also against new data which had not been used previously in obtaining the equation.[2]

Use of Rate Equations in Reactor Design.[3] The method of using the rate equations for catalytic reactions to calculate the reactor size and amount of catalyst needed for a specified conversion and feed rate is very similar to the method used for noncatalytic reactions. The calculations may be divided into three types, namely, those for isothermal reactors,[4] adiabatic reactors,[5] and nonisothermal nonadiabatic reactors.[6] In all three cases where the feed rate F and the desired conversion x are specified, the weight of catalyst needed can be calculated from the expression

$$\frac{W}{F} = \int_0^x \frac{dx}{r} \tag{34}$$

The size of reactor is calculated from the weight and bulk density of the catalyst. The methods of calculation for the three cases differ only in the evaluation of the term on the right of Eq. (34).

Where the temperature may be assumed constant throughout the reactor, the values of r may be calculated directly for various values of x. $1/r$ is then plotted against x, and the area under the curve up to the desired conversion is measured. This area is equal to $\int_0^x \frac{dx}{r}$. The amount of catalyst needed W may then be calculated.

In the case of the adiabatic reactor, the heat of reaction causes a change

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[1] CORRIGAN, *Chem. Eng.*, **62**, May, 1955; BARKLEY, CORRIGAN, WAINWRIGHT, and SANDS, *Ind. Eng. Chem.*, **44**, 1,066 (1952); COCHRANE, Master of Science Thesis, Chemical Engineering Department, West Virginia University, Morgantown, W.Va., 1951; CORRIGAN, GARVER, RASE, and KIRK, Kinetics of Catalytic Cracking of Cumene, *Chem. Eng. Progr.*, **49**, 603 (1953).

[2] CORRIGAN, *Chem. Eng.*, **62**, June, 1955; **62**, July, 1955.

[3] CORRIGAN and MILLS, *Chem. Eng.*, **63**, April, May, and June, 1956.

[4] CORRIGAN and MILLS, *Chem. Eng.*, **63**, July, 1956.

[5] CORRIGAN and MILLS, *Chem. Eng.*, **63**, August, 1956.

[6] CORRIGAN and MILLS, *Chem. Eng.*, **63**, September, 1956.

in temperature. This, in turn, causes the constants of the rate equation to change. To solve a problem of this type, it is necessary to use the rate equation and a heat balance. The heat balance is used to establish a relationship between conversion and temperature. A working curve of T versus x is plotted. Then as each value of x is assumed, its corresponding temperature is obtained from the working curve. The constants of the rate equation can then be evaluated from plots of the log of each constant versus $1/T$ (usually straight lines), and $1/r$ can be calculated. Then $1/r$ is plotted against x, and the area is determined as in the isothermal case.

The nonadiabatic nonisothermal case cannot be solved by plotting $1/r$ versus x. Since heat may be transferred in or out along the length of the reactor, there can be no direct relation between x and T which does not involve reactor length. Since the relationship between x and reactor length is the object of the problem, it is not known. A relation between the heat transferred q and the reactor length must be known. The problem may then be solved by a trial-and-error method.

NOMENCLATURE FOR CHAPTERS 2 AND 3

A, B, C, R, S, etc.	(1) Symbol of chemical species involved in chemical reaction (2) Used in relative rate equations to represent moles of A, B, etc.
Sub A, B, C, etc.	Refers to chemical species A, B, C, etc., viz., p_A
a, b, c, etc.	Moles of species A, B, C, etc., in reactor charge
Exponent a, b, c, etc.	Power of concentration function, viz., C_A^a
b	$(k_1 + k_2)t$ in Eqs. (16) and (17)
C_A, C_B	Concentration of A, B, etc.
C_{A0}, C_{B0}	Initial concentrations
c_A, c_B, etc.	Concentration of adsorbate on surface of adsorbent
c_l	Hypothetical term expressing an "effective concentration" of unoccupied active centers
E	Activation energy in Arrhenius expression
e	Base of natural logarithm
F	Rate of feed to the reactor
I	Integration constant
K	Reaction equilibrium constant
K_1, K_2, K_3, etc.	Equilibrium constant of individual reaction steps
K_A, K_B, K_R, etc.	Adsorption equilibrium constants
K'	Constant in Koble equation
k	Over-all specific rate constant

k_1, k_2, k_3, etc.	Specific rate constant of individual reaction step
k'	Specific rate constant for reverse step of a reaction
L	Total concentration of active centers involved in a catalytic reaction
L'	Constant in Koble equation
l	Unoccupied active center
ln	Natural logarithm
M	Mole ratio of B to A in the feed C_{B_0}/C_{A_0}
m, n	Exponent in general order of reaction expression
p	Partial pressure
R	Universal gas constant
R, S	Component R, S; also moles of component R, S
r	Reaction rate
r_0	Initial reaction rate
r'	Rate of reverse reaction
s	Frequency factor in Arrhenius expression
T	Absolute temperature
t	Time
V	Reactor volume
W	Weight of catalyst
W/F	Pounds of catalyst per pound mole of feed to a vapor-phase catalytic reactor
κ	Ratio of rate constants, viz., $k_2 : k_1$
x	Degree of conversion of limiting reactant
π	Total pressure

CHAPTER 3

CHEMICAL-PROCESS KINETICS

BY THOMAS E. CORRIGAN AND JOHN J. MCKETTA

Chemical-process kinetics is a study of the influence of the physical factors that affect chemical reactions. Examples of these factors are:

1. The type and shape of reactor used.
2. The method of operation.
3. Temperature control.
4. Batch or flow process.
5. Batchmixing.
6. Fixed or fluidized bed (in the case of catalytic reactions).

These factors are characteristics of the reacting system. This classification may appear arbitrary, but it is helpful in discussing the subject of reactor design.

Factors That Affect a Chemical Process

Problems in Choice of a Reactor. When a process engineer is faced with the problem of designing a commercial or semicommercial unit, he must first choose the reactor to be used. The type of reactor (tube, tower, or tank), the type of operation (batch, continuous, recycle, or once-through), and the means of temperature control (isothermal or adiabatic) may depend on the type of reaction involved. In order to choose the best reactor and method of operation, the specific type of reacting system must be considered.

Backmixing. Backmixing is an extremely important phenomenon which must be considered carefully in all process-reactor design. Backmixing can occur only in flow reactions in a chemical process. Backmixing is the mixing of the reactants and products of a chemical reaction by upstream diffusion and reaction while the main flow is in the downstream direction. Later, in Fig. 3-2, it will be seen that in some cases of reactor design the failure to consider backmixing may result in an error of one hundredfold in the calculated reactor size.

Type and Shape of Reactor. The most common types of chemical reactors can be classified according to the scheme shown in Table 3-1.

TABLE 3-1. CLASSIFICATION OF CHEMICAL REACTORS

1. Simple batch homogeneous reactors
    - Closed tank
    - Rocking autoclave (laboratory tool, not used commercially)
    - Stirred kettle
    - Kettle with outside recirculation but with no material added or removed
    - Coil with outside recirculation but with no material added or removed
2. Semibatch reactors
    - Batch with continuous addition of one reactant:
        - Gas-phase addition
        - Liquid addition
        - Solid addition
    - Batch with continuous removal of one product:
        - Gas formation
        - Solid precipitation
        - Formation of immiscible liquid
    - Batch with combined addition of reactant and removal of one product
3. Continuous homogeneous reactors
    - Longitudinal tubular reactor (no backmixing)
    - Stirred-tank reactor (complete backmixing)
    - Tubular reactor with some backmixing
    - Tower reactors:
        - Packed tower
        - Empty tower
        - Baffled reactor
    - Baffled-tank reactor
    - Longitudinal reactor with multiple injection of one reactant
4. Continuous heterogeneous reactors
    - Packed-tower countercurrent reactors
    - Fixed-bed catalytic reactors
        - Longitudinal
        - Backmixing
    - Moving- and fluidized-bed catalytic reactors
        - Longitudinal
        - Backmixing
    - Distillation column

The *simple batch reactor* for homogeneous reactions is the most common type. From this kind of reactor, many kinetic data have been obtained. All the reactants are charged in at the beginning of the reaction, with no mass transfer occurring until the reaction is complete. Examples of batch reactions are the ammonolysis of nitrochlorobenzenes, hydrolysis of esters, and polymerization of butadiene and styrene in aqueous suspension. These will be treated in more detail in later chapters.

The *semibatch reactor* with continuous addition of one reactant is one in which one reactant is first charged and another is continuously added as the reaction proceeds. Examples of semibatch reactions are the production of high-molecular-weight polyglycols or of detergents by the reaction of ethylene oxide with ethylene glycol in the first case and alkylated phenols in the second. In these cases a large amount of ethylene oxide is added to a smaller amount of a less active reactant. By using the semibatch method wherein ethylene oxide is added gradually to the second reactant, large concentrations of hazardous ethylene oxide are avoided.

Another classification of a semibatch reactor is one in which a gas forms or a solid precipitates during the reaction. Here, also, a volatile product may be fractionated off continuously. An example is batch esterification with continuous distillation. An example of this type of reaction, which will be dealt with later in this text, is the esterification of ethyl alcohol with acetic acid to form ethyl acetate.

Of the *longitudinal tubular reactors* the most common type is the single-pass long tube such as those used in thermal cracking furnaces. Another type consists of a number of single tubes in parallel. In both cases, the ratio of length to diameter of the tube is large. In this reactor the reacting mass is carried through the reactor in plug flow with no diffusion in the longitudinal direction.

In the *stirred-tank continuous reactor* (the case of complete backmixing), reactants are fed and products withdrawn continuously. Continuous stirred-tank reactors are currently used in liquid-phase nitration of hydrocarbons or polyhydric alcohols. A diagram of such a reactor is shown in Fig. 4-10.

In a *tubular reactor*, if the ratio of length to diameter is not large enough, there will be some backmixing and the reactor will deviate from the hypothetical plug flow. This is usually true in most commercial tubular reactors. The most important processes using a tubular reactor are the thermal cracking of ethane and of propane to form ethylene. An example, dealt with in Chap. 6, is the dehydrochlorination of ethylene dichloride.

Tower reactors may consist of an empty tower, a packed tower, or a baffled tower. Where a large volume is needed, this type of reactor is less expensive than a tubular reactor. However, the amount of backmixing is much greater. An example of the use of a packed-tower reactor, which will be discussed in Chap. 14, is in the German process for the production of the ethers of ethylene glycol from ethylene oxide and alcohol. In this process, ethylene oxide and alcohol are fed to a pressure tower packed with iron Raschig rings.

The *baffled-tank reactor* is usually a horizontal tank with a low ratio of length to diameter. It has about the same advantages and disadvantages as the tower reactor.

The *longitudinal reactor*, with multiple injection of one reactant, is a special case and corresponds to the semibatch reactor.

The most common heterogeneous reactors are the *fixed-*, *moving*, and *fluidized-bed catalytic reactors*. One example of vapor-phase catalytic reactions is in the catalytic vapor-phase reduction of nitroxylene to xylidene. This process is discussed in Chap. 5 (Figs. 5-16 and 5-17).

Reaction System. Reaction systems can be divided into the following groupings:

1. Homogeneous liquid phase, only mutually soluble liquids are involved. This is represented by the hydrolysis of ethyl acetate, which will be discussed in Chap. 13.
2. Heterogeneous liquid phase, involving two or more immiscible liquids. Examples of this are in the nitration of toluene, hydrolysis of chlorobenzene to phenol, and ammonolysis of ethylene dichloride.
3. Reaction of a liquid with a gas, as in the liquid-phase chlorination of benzene or acetaldehyde.
4. Reaction of a liquid with a solid, as the sulfonation of anthraquinone.
5. Liquid-phase reaction forming a solid, as in saponification of glycerides.
6. Liquid-phase reaction forming a gas, as in the Friedel-Crafts reaction liberating HCl.
7. Homogeneous gas-phase reaction, as in the vapor-phase nitration of paraffins or in the dehydrochlorination of ethylene dichloride.
8. Heterogeneous gas-phase catalytic reaction, such as the hydrogenation of carbon monoxide to form methanol.
9. Heterogeneous gas-phase noncatalytic reaction, as represented by the gasification of coal or coke to form synthesis gas.

There are three general methods of operation for chemical reactors, namely, isothermal, adiabatic, and nonisothermal nonadiabatic.

In the *isothermal* case, just enough heat is added or removed to keep the temperature constant throughout. In the *adiabatic* reactor, no heat is added or removed during the course of the reaction. In the *nonisothermal nonadiabatic* reactor, some heat is either added or removed during the reaction but the temperature does not remain constant. Almost all commercial reactors are operated as nonisothermal nonadiabatic reactions.

Reactor Shape and Effect of Backmixing

The type and shape of a reactor, because of their effect on backmixing, have a profound effect on the process kinetics. For the purpose of kinetic calculations, reactors may be classified into three basic types. These are:

1. Batch reactor.
2. Longitudinal flow reactor.
3. Stirred-tank flow reactor.

The longitudinal reactor with zero backmixing, and the stirred-tank reactor with 100 per cent backmixing, are the two extremes between which most actual flow reactors will lie. The process engineer who designs a flow reactor will first use kinetics to calculate the extreme cases and then must estimate from empirical data how the actual reactor will behave. The batch reactor and the longitudinal reactor are treated the same mathematically.

The kinetic behavior of these basic reactor types is indicated in the concentration-time curves of Fig. 3-1, which shows concentration histories within the reactors (second row) and concentration-time curves for reactor effluents (third row). The kinetic equations for the three basic reactor types are shown in Table 3-2 for some of the more common reaction types. Figure 3-2 illustrates the effect of backmixing on first- and second-order reactions.

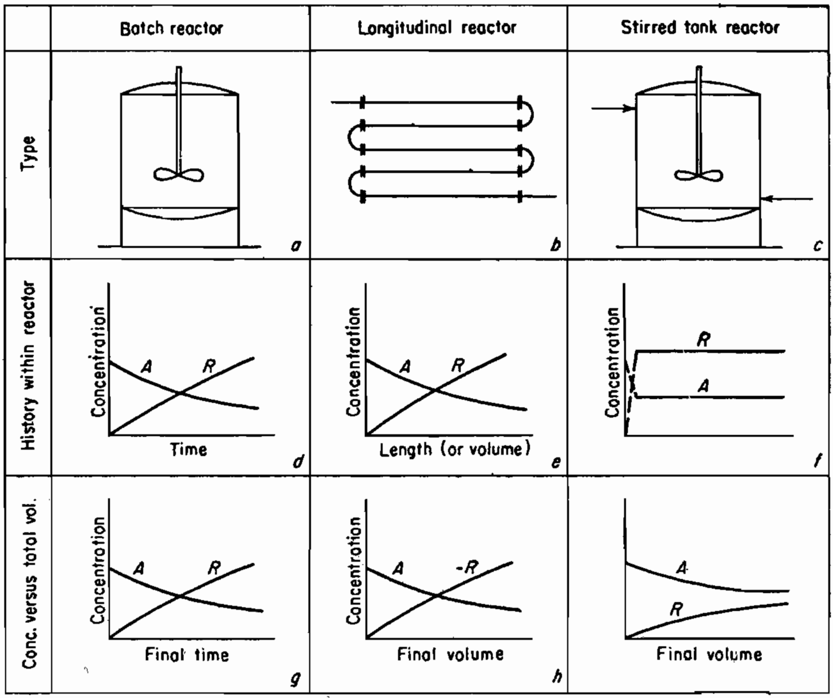

FIG. 3-1. Kinetic behavior in basic reactor types.

Two important items which must be known about backmixing in order to design a reactor are:

1. If backmixing is present in the process, what additional holding time or reactor volume is needed to compensate for it?

2. If the compensation is not made, what would be the decrease in production or yield due to the backmixing?

TABLE 3-2. EFFECT OF BACKMIXING ON SIMPLE REACTIONS

Reaction type	Reaction order	Basic differential Equation	Batch or longitudinal	Backmixing
$A \rightarrow R$	1	$-\frac{dC_A}{dt} = kC_A$	$C_A = C_{A_0}e^{-kt}$	$C_A = \frac{C_{A_0}}{kt - 1}$
	2	$-\frac{dC_A}{dt} = kC_A^2$	$\frac{1}{C_A} = \frac{1}{C_{A_0}} + kt$	$C_A = a^2 + 2aC_{A_0}^{0.5}; a = \frac{2k}{t}$
	½	$-\frac{dC_A}{dt} = kC_A^{1/2}$	$C_A = [C_{A_0}^{0.5} - 0.5kt]^2$	$C_A = C_{A_0} + 0.5a^2 - a\left[C_{A_0} - \frac{a^2}{4}\right]^{0.5}; a = kt$
$A + B \rightarrow R$ $A + B \rightarrow R + S$	2	$-\frac{dC_A}{dt} = kC_AC_B$ or $\frac{dx}{dt} = k(1 - x)(M - x)$	where $M \neq 1$ $\frac{1}{1 - M} \ln\left[\frac{M(1 - x)}{M - x}\right] = C_{A_0}kt$ where $M = 1$ $\frac{x}{1 - x} = C_{A_0}^2kt$	where $M \neq 1$ $\frac{x}{(1 - x)(M - x)} = C_{A_0}kt$ where $M = 1$ $\frac{x}{(1 - x)^2} = C_{A_0}kt$

The graphs in Fig. 3-2[1] show how important the effect of backmixing can be, especially at high conversions. It can be seen that for the extreme case of 99 per cent conversion at a mole ratio of 1:1 the reactor volume required for a stirred-tank reactor is 100 times as great as for either a longitudinal or a batch reactor. From the above discussion it is clear that backmixing has a considerable effect on reactor size and conversion.

Effect of Backmixing on Product Distribution.[2] The type and shape of a reactor, because of backmixing, also have a great effect on the yield or product distribution. In some processes, especially those which require only a small reactor, the effect of backmixing on yield is much more important than the effect on reactor size.

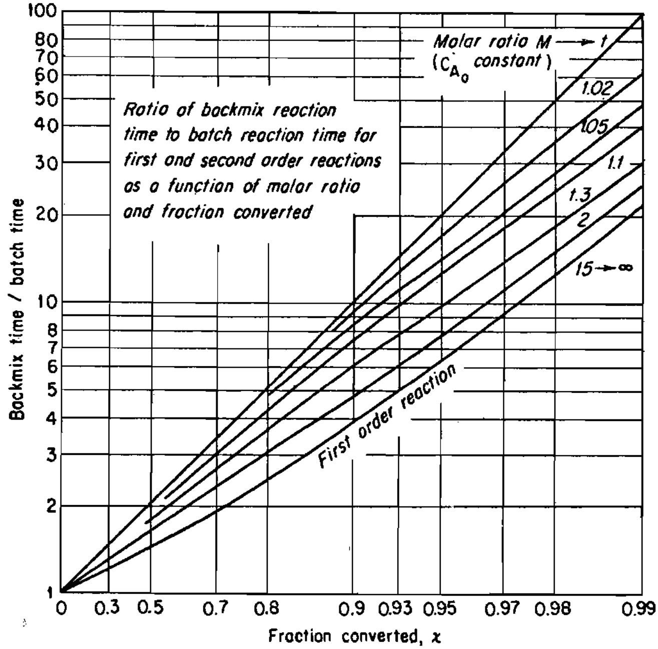

FIG. 3-2. Relation of backmixing to design and size of reactor.

For cases in which product distribution is important and reactor size is secondary, equations have been worked out for the batch, longitudinal, and backmixing reactors. These equations will be presented for the three major types of complex reactions, namely, parallel, series, and complex series.

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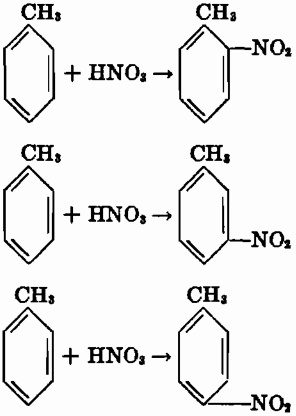
[1] LESSELS, Olin Mathieson Chemical Corporation, Brandenburg, Ky., personal communication; also *Chem. Eng.*, **64** (8), 251–256 (1957).

[2] MACMULLIN and WEBER, *Trans. Am. Inst. Chem. Eng.*, **31** (2), 409–458 (1935).

Parallel Reactions. The simplest case of parallel reactions $A \rightarrow R$ and $A \rightarrow S$ is used here to simplify the explanation. A more common type of parallel reaction is

$$\begin{gathered} A + B \rightarrow R \\ A + B \rightarrow S \\ A + B \rightarrow T \end{gathered}$$

An example of this type is in the nitration of toluene, discussed in Chap. 4. Here the parallel reactions are



The basic differential equations and the concentration-time relations for parallel reactions for longitudinal and backmixing reactions are shown in Table 3-3, and the corresponding product-distribution equations are shown in Table 3-4. It can be seen from these equations that backmixing does not effect the product distribution for parallel reactions of the same order.

Series (Consecutive) Reactions. The simplest example of series reactions which will be used for illustration is the reaction type

$$A \rightarrow R \rightarrow S$$

The basic differential equations, as well as the integral equations for both longitudinal and backmixing reactors, are shown in Table 3-3. The corresponding product-distribution equations are shown in Table 3-4. From these equations it can be seen that backmixing, and thus reactor shape, has a considerable effect on product distribution as well as on required holding time.

A specific example of the kinetics of the series reaction

$$A \rightarrow R \rightarrow S \rightarrow T$$

is in the liquid-phase chlorination of benzene where the gaseous materials Cl_2 and HCl can be eliminated from consideration in the calculation of

TABLE 3-3. PARALLEL AND SERIES REACTIONS. EQUATIONS RELATING TO CONVERSION AND HOLDING TIME

Reaction class	Reaction type	Reaction order	Basic differential equation	Batch or longitudinal*	Backmixing*
Parallel. . .	$A \xrightarrow{k_1} R$		$-\frac{dC_A}{dt} = k_1C_A + k_2C_A$	$C_A = C_{A_0}e^{-(k_1+k_2)t}$	$C_A = \frac{C_{A_0}}{1+(k_1+k_2)t}$
		1	$\frac{dC_R}{dt} = k_1C_A$	$C_R = \left(\frac{k_1}{k_1+k_2}\right)C_{A_0}\left[1 - e^{-(k_1+k_2)t}\right]$	$C_R = \frac{k_1tC_{A_0}}{1+(k_1+k_2)t}$
	$A \xrightarrow{k_2} S$		$\frac{dC_S}{dt} = k_2C_A$	$C_S = \left(\frac{k_2}{k_1+k_2}\right)C_{A_0}\left[1 - e^{-(k_1+k_2)t}\right]$	$C_S = \frac{k_2tC_{A_0}}{1+(k_1+k_2)t}$
Series.	$A \xrightarrow{k_1} R$		$-\frac{dC_A}{dt} = k_1C_A$	$C_A = C_{A_0}e^{-k_1t}$	$C_A = \frac{C_{A_0}}{1+k_1t}$
		1	$\frac{dC_R}{dt} = k_1C_A - k_2C_R$	$C_R = \left(\frac{1}{\kappa-1}\right)C_{A_0}\left(e^{-k_1t} - e^{-k_2t}\right)$	$C_R = \frac{k_1tC_{A_0}}{(1+k_1t)(1+k_2t)}$
	$R \xrightarrow{k_2} S$		$\frac{dC_S}{dt} = k_2C_R$	$\kappa = \frac{k_2}{k_1}$	

* Equations in this column are for the case with no recycle.

TABLE 3-4. PRODUCT DISTRIBUTION EQUATIONS FOR PARALLEL, SERIES, AND COMPLEX-SERIES REACTIONS

Reaction class	Reaction type	Basic differential equation	Material balance equations	Product distribution*	
				Batch and longitudinal	Backmixing
Parallel.	$A \xrightarrow{k_1} R$ $A \xrightarrow{k_2} S$	$\frac{-dC_A}{dt} = k_1C_A + k_2C_A$ $\frac{dC_R}{dt} = k_1C_A$	$A_0 - A = R + S$	$\frac{S}{R} = \kappa$	$\frac{S}{R} = \kappa$
Series.	$A \xrightarrow{k_1} R \xrightarrow{k_2} S$	$\frac{-dC_A}{dt} = k_1C_A$ $\frac{-dC_R}{dt} = k_1C_A - k_2C_R$	$A_0 - A = R + S$	$R = \frac{A^\kappa - A}{1 - \kappa}$	$R = \frac{A}{1 + \kappa}$
Complex series.	$A + B \xrightarrow{k_1} R$ $A + R \xrightarrow{k_2} S$	$\frac{-dC_B}{dt} = k_1C_AC_B$ $\frac{dC_R}{dt} = k_1C_AC_B - k_2C_AC_R$	$A_0 - A = R + 2S$ $B_0 - B = R + S$	$R = \frac{B^\kappa - B}{1 - \kappa}$	$R = \frac{B - B^2}{B + \kappa(1 - B)}$

* No recyle.
$\kappa = k_2/k_1$.
A,B,R = mole ratios.

product distribution. This application was developed by MacMullin,[1] and the results of his kinetic work are shown in Fig. 6-7.

Complex-series Reactions. In most industrial reactor designs, the problem is usually that of obtaining the highest yield possible while using the smallest reactor that will give the conversion and yield desired. There are some cases where product distribution is so much more important than reactor size that holding time is an insignificant problem. Examples are:

1. When the reaction is extremely rapid, taking place in a matter of seconds or a fraction of a second, but where the yield is important.
2. When the reactants and products are so expensive that even for moderate reactions the depreciation of the reactor has an extremely small effect on total product cost.
3. When the cost of the equipment for separation of the reactor effluent, recycle, and purification of the products is of a higher order of magnitude than for the reactor itself.

For these cases the integral equations, which present a complete picture of product distribution for any given feed ratio or degree of conversion, need not involve holding time and are, therefore, easier to use.

There are many important industrial applications of complex-series reactions. Some of the more important examples are:

1. The chlorination of benzene or toluene.
2. The chlorination of either saturated or unsaturated hydrocarbons.
3. The manufacture of ethylene glycol from ethylene oxide and water.
4. The manufacture of ethanolamines.
5. The manufacture of alkylamines from either the corresponding alcohols or halides and ammonia.
6. The manufacture of glycol ethers, polyglycols, and nonionic detergents.
7. The vapor-phase nitration of paraffins.
8. The liquid-phase nitration of higher paraffins.
9. The reaction of carbon tetrachloride and hydrogen fluoride to form Freons.
10. The manufacture of chloral.
11. The catalytic reaction of acetylene and HCl.
12. The reaction of ethylene with hydrogen chloride and oxygen.
13. The Raschig synthesis of chlorinated benzenes.
14. The manufacture of chloral by the chlorination of ethyl alcohol.
15. The amination of chloroacetic acid to form glycines.

The above examples of complex-series reactions are described in subsequent chapters, but the kinetics of product distribution are not discussed. For this reason the following section in this chapter is presented to explain

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[1] MacMullin, *Chem. Eng. Prog.*, **44** (3), p. 183 (1948).

the application of kinetic theory to the study of product distribution. The effect of backmixing on product distribution is very important to the study of unit processes.

The manufacture of ethylene oxide derivatives is an especially good example of the industrial application of complex series.

High-molecular-weight polyglycols are formed by the reaction of ethylene oxide with ethylene glycol or diethylene glycol. Some nonionic detergents are formed by the reaction of ethylene oxide with fatty alcohols or alkyl phenols. In both cases, a large amount of ethylene oxide (which is highly reactive and may polymerize with explosive violence) is added to a small amount of another reactant. In this type of reaction, the semibatch reactor is superior. The relatively inert reactant is charged to the reactor first, and then ethylene oxide is added gradually as it reacts. Thus, there is no large concentration of oxide at reaction conditions.

Glycol ethers are manufactured by adding ethylene oxide to alcohols. In these reactions, both reaction rate and product distribution are important. Reaction rate is important because the reaction is slow enough to require a large, costly reactor. Product distribution is important because the yields based on oxide and alcohols are lowered if an excess of the higher-molecular-weight by-products is formed. In this type of reaction, a tubular reactor would be desirable because it would give a better control of product distribution than a tank or tower reactor.

The reaction of ethylene oxide with aqueous ammonia to form ethanolamines is an example of a process where the kinetics of product distribution is most important. In this process, the reaction is fast and the reactor required is very small compared to the separation and finishing equipment needed in the process. For this reason the absolute rate of reaction is of minor importance. The relative rates of the reactions to form mono-, di-, or triethanolamine are extremely important for economic yield and product distribution.

The derivation of the product-distribution equations for the complex-series reaction of the type

$$A + B \rightarrow R$$
$$A + R \rightarrow S$$

is shown in Table 3-5 for both longitudinal and backmixing reactions. A simplified flow sheet for a typical continuous process for this type of reaction is shown in Fig. 3-3.

Equations shown in Table 3-5 can be used to determine the yield of desired product R, for any given feed ratio ($C_{B_0}:C_{A_0}$) and for any desired per cent conversion for a batch, longitudinal-flow, or stirred-tank reactor.

An example would be in the evaluation of laboratory batch data for a

TABLE 3-5. SUMMARY OF PRODUCT-DISTRIBUTION EQUATIONS FOR COMPLEX-SERIES REACTIONS

	Batch and longitudinal	Backmixing
Reaction type	$A + B \rightarrow R$ $A + R \rightarrow S$	$A + B \rightarrow R$ $A + R \rightarrow S$
Differential equations	$\frac{-dC_B}{dt} = k_1C_AC_B$ $\frac{dC_R}{dt} = k_1C_AC_B - k_2C_AC_R$	Same as for batch
Ratio	$\frac{dC_R}{dC_B} = \frac{k_1C_AC_B - k_2C_AC_R}{-k_1C_AC_B}$ or $\frac{dC_R}{dC_B} = \frac{k_2C_R}{k_1C_B} - 1$	Same as for batch
Using mole ratios; $C_R/C_{R_0} = R; CB/CB_0 = B; k_2/k_1 = \kappa$	$\frac{dR}{dB} = \kappa\frac{R}{B} - 1$	$\frac{dR}{dB} = \kappa\frac{R}{B} - 1$
Integrating factor	$R = e^{\int -\frac{\kappa}{B} dr}$ *Solution:* $e^{-\int -\frac{\kappa}{B} dr} \int e^{\int -\frac{\kappa}{B} dr} (-1)\, dr + Ie^{\int -\frac{\kappa}{B} dr}$	
General equation	$R = \left(\frac{1}{\kappa - 1}\right)B + IB^{\kappa}$ or $R = \frac{B^{\kappa} - B}{1 - \kappa} + R_0B$	$\frac{R - R_0}{B - B_0} = \kappa\frac{R}{B} - 1$
For no recycle, $R_0 = 0$	$R = \frac{B^{\kappa} - B}{1 - \kappa}$	$R = \frac{B - B^2}{B + \kappa(1 - B)}$
Material balance	$A_0 - A = R + 2S$ $B_0 - B = R + S$	$A_0 - A = R + 2S$ $B_0 - B = R + S$

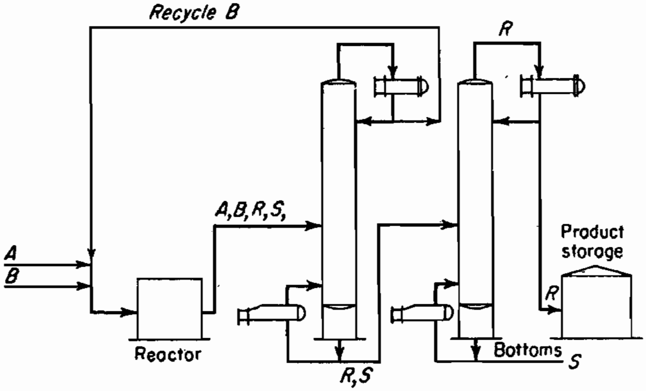

FIG. 3-3. Flow diagram for a typical continuous process involving complex-series reactions.

reaction which goes to completion with respect to reactant A. In this case, the procedure would be:

1. Obtain the experimental product distribution in a laboratory or pre-pilot-plant batch reactor.
2. Use an appropriate *equation* from Table 3-5 and a material balance to calculate the rate-ratio constant κ from the batch data.
3. Use the value of κ and the same *equation* used in step 2 to calculate the yield of R at other mole ratios, and plot R values against feed ratio $(C_{B_0}:C_{A_0})$. This gives the curve for a longitudinal flow reactor.
4. Calculate the yield of R, and plot R values against feed ratio.

This gives the curve for a backmixing reactor. Figure 3-4 shows a typical plot for the reaction

$$A + B \rightarrow R$$
$$A + R \rightarrow S$$

All actual reactors would operate in the shaded area between the two lines. Tubular reactors would be close to the upper line, stirred-tank reactors would be close to the lower line, and packed-tower reactors would be approximately halfway between.

Selection and Sizing of Homogeneous Reactors. One of the first decisions to be made when designing a reactor is which reactor type is best for the specific process. If a large-scale process is considered, then a continuous reactor will have a larger capacity and is preferable. If the process involves small quantities, intermittent products, a complicated sequence of operations, or extremely long holding times, a batch reactor may be preferable. If a flow process is used, the flow reactor could be a long coil, a bundle of parallel tubes, an empty, packed, or baffled tower, or a stirred tank or vessel.

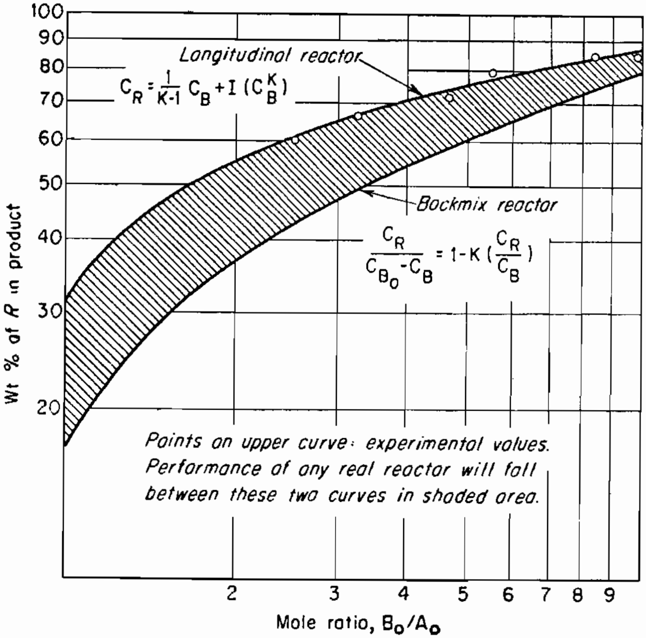

FIG. 3-4. Product distribution as a function of type of reactor.

For a single-phase reaction with a low holding time, a single coil is preferable. This gives high velocities and very little backmixing. A bundle of parallel tubes can also be used in place of a single tube. This type will give a lower velocity for the same holding time.

For tubular reactors with high holding time, the cost of tube or pipe is quite high per unit volume. A tower will provide a large reactor volume at a much lower cost. The disadvantage is that there is considerable backmixing in a tower or tank reactor unless packing is used.

The stirred-tank continuous reactor may be used where a high degree of agitation is necessary, possibly where a solid is held in suspension, where the reaction requires a relatively low holding time, and where backmixing is not detrimental to the yield.

If either the batch or the tubular type of reactor is chosen, the reactor size and product distribution can be calculated by using the batch or longitudinal-flow equations. For a stirred-tank continuous reactor, the backmixing equations can be used. If a packed or baffled tower is used, then the calculations must be made for both the longitudinal and backmixing cases. Proper extrapolation must then be made from empirical data or previous experience.

Calculation of Product Distribution. *Problem.* Assume a process is to produce the hypothetical compound R from the raw materials A and B. It is a liquid-phase reaction, and the equations of the reaction are

$$\begin{aligned} A + B &\rightarrow R \\ A + R &\rightarrow S \end{aligned}$$

Assume that S does not react further with A to form any more products in the series. Figure 3-3 is a simplified flow diagram of the process. R is the desired product, and all the S that is formed must be thrown away. The unreacted B which passes through the reactor may be recovered and recycled, but there is a 6 per cent loss in the recovery process. Any unreacted A which passes through the reactor is lost in the recovery process and cannot be recycled. The reaction time is several hours, and a large reactor is needed.

A catalyst has been discovered that will increase the reaction rate one hundredfold. It is estimated that this would save \$100,000 in the reactor cost. You, as a process engineer, are asked to determine whether the catalyst should be used in the process. For a preliminary comparison of economics, calculate the raw-material costs of R as a function of mole ratio of B to A in the feed for longitudinal reactors with and without catalyst.

The production rate of the plant is 10 million lb of R per year. The raw-material costs are 10 and 20 cents per pound for A and B, respectively. The values of κ are 0.5 without catalyst and 1.5 with catalyst. Molecular weights and physical properties of A, B, R, and S are available.

Solution (equations are taken from Table 3-5): Since R is the desired product, there is no reason to use a recycle stream in the process and, thus, the following equation can be used:

$$R = \frac{B^{\kappa} - B}{1 - \kappa}$$

This equation is combined with the material balance equations

$$A_0 - A = R + 2S$$

and

$$1 - B = R + S$$

and values of R are solved for at assumed values of B. The quantity $R/(R + S)$ will give the yield of the reaction, and from this the raw-material cost can be calculated.

This method of solution can be used for the case where no catalyst is used ($\kappa = 0.5$) and where the catalyst is used ($\kappa = 1.5$). In both cases the loss of raw material B from the recycle stream per mole of product is $0.06\ B/R$. The results of these calculations are plotted in Fig. 3-5. It can be seen that when no catalyst is used the minimum raw-material cost is 20 cents per pound of R, but when the catalyst is used, the minimum raw-material cost is 23.5 cents per pound of R. Thus, in this particular case, the use of the catalyst would result in an increased raw-material cost of \$350,000 per year.

The raw-material cost for the case of a reactor with no catalyst but with complete backmixing is also plotted in Fig. 3-5 for comparison. It can be seen that the raw-material cost is higher because of backmixing.

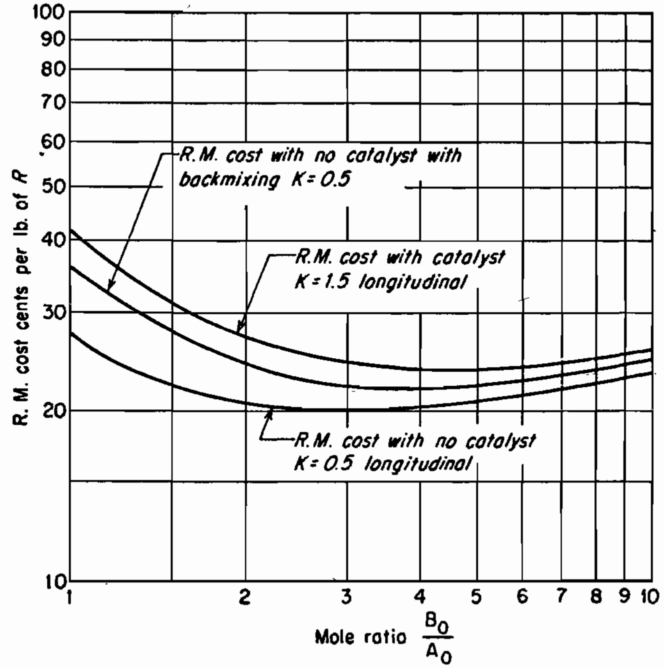

FIG. 3-5. Hypothetical raw-material costs related to use of a catalyst as a process variable.

Selection and Sizing of Catalytic Reactors. There are numerous examples of catalytic vapor-phase reactions in the organic-chemical industry. Some examples which are discussed in subsequent chapters are:

1. The vapor-phase reduction of nitrobenzene with hydrogen.
2. The manufacture of hydrogen by the reaction of steam and natural gas over a nickel catalyst followed by the shift reaction over an iron oxide catalyst.
3. The hydrogenation of nitroxylene to xylidene.
4. The reduction of nitrobenzene to aniline.
5. The chlorination of C_1–C_4 paraffins.
6. The catalytic hydroammonolysis of carboxylic acids to form nitriles.

7. The catalytic vapor-phase amination of methanol.

8. The direct oxidation of ethylene to form ethylene oxide.

9. The synthesis of methanol from carbon monoxide and hydrogen.

10. The hydrogenation of olefinic hydrocarbons to produce high-octane fuel components for aviation use.

Since there are so many applications of vapor-phase catalytic reactions in carrying out unit processes, the kinetics of this type of reaction are very important.

One of the most familiar of catalytic chemical reactors is the fixed-bed reactor. Here the catalyst particles remain in a fixed position and the reacting gases move through the catalyst bed. The catalyst particles are usually porous pellets, either cylindrical or spherical, ranging from $\frac{1}{8}$–$\frac{1}{4}$ in. or more in diameter. The physical structure of these pellets is usually such that the internal pore surface is infinitely greater than the actual pellet surface. Thus, the actual contact surface present is independent of pellet size.

Longitudinal versus Backmixing. Fixed catalyst beds may be classified roughly into longitudinal and backmixing types.

Two disadvantages of reactors which have backmixing are:

1. For a specified conversion, the amount of catalyst and the size of reactor required are much greater than in the case of the longitudinal reactor.

2. The ultimate yield of desired product will not be so great as in the case of the longitudinal reactor.

Fixed-bed reactors may be of either the longitudinal or the backmixing type, but in most cases the longitudinal reactor is preferred because of the advantages presented above. The catalyst chamber may consist of a series of relatively long catalyst tubes operating in parallel.

The major disadvantages of the fixed-bed reactor are:

1. It is difficult to transfer heat into or out of the catalyst bed fast enough to prevent large temperature gradients within the catalyst bed or even within the catalyst pellets themselves.

2. Where the rate of diffusion through the pores of the catalyst pellet is slow compared with the reaction rate, it is not possible to utilize the total surface area of the catalyst.

3. When the catalyst needs periodic regeneration, there is expense involved in taking the fixed-bed reactor out of service and of regenerating the catalyst.

In the fluidized-bed reactor, the catalyst bed is in the form of a fine powder which is suspended by the upward motion of the reacting gases passing through the bed. Difficulties which may occur in fluidization are slugging, channeling, and attrition of the catalyst. In most cases, circumventing these problems leads to a fluidized reactor which has a low height : diameter ratio and thus allows backmixing of the gas.[1] Thus, one of the major advantages of the fixed-bed reactors—that of longitudinal flow—is not present in the more common types of fluidized-bed reactors.

Calculation of Reactor Size. Assume that the hypothetical reaction

$$A + B \rightarrow R + S$$

is a vapor-phase reaction taking place on a solid catalyst. We can assume for the purpose of illustration that the rate equation for a specific case could be

$$r = \frac{k_1 p_A p_B}{1 + k_2 p_A + k_3 p_R}$$

If the above reaction were carried out in a longitudinal fixed-bed reactor, operating isothermally, at 1000°F, what amount of catalyst would be required to cause the reaction to be 95 per cent complete, using a stoichiometric feed ratio and no recycle? The desired production rate is 1,000 lb of R per hour. The reactor is to be operated at 2 atm and exhibits a negligible pressure drop.

Following is the general procedure for this type of problem:

1. Evaluate, or look up, the values of the constants k_1, k_2, and k_3 at the reaction temperature.
2. Calculate the values of p_A and p_B for various values of x from 0–0.95, using a material balance.
3. Calculate the value of r at each value of x.
4. Plot $1/r$ versus x.
5. Take the area under the curve of $1/r$ versus x from $x = 0$ to $x = 0.95$ (the direct conversion).
6. This area is the desired value of W/F, where F is the feed rate and W is the required weight of catalyst for 95 per cent conversion. Since F is known, calculate W.

Summary. The first three chapters of this book present a scientific approach to some of the principles involved in the selection and design of chemical reactors used in the unit processes. In many respects the selection of the proper type of reactor for a unit process is still as much an art as it is a science. It is recommended to the reader that, as he studies the unit processes presented in the remainder of this book, he try to justify the type of reactor used in each case.

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CHAPTER 4

NITRATION

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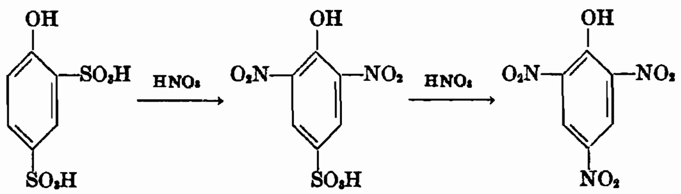
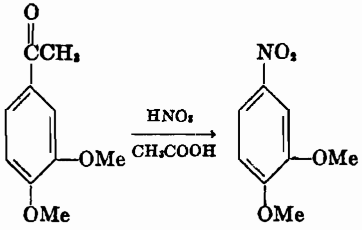
I. INTRODUCTION

The nitration reaction serves to introduce one or more nitro groups ($—NO_2$) into a reacting molecule. The nitro group may become attached to carbon to form a nitroaromatic or nitroparaffinic compound. It may become attached to oxygen to form a nitrate ester, or it may become attached to nitrogen to form a nitramine. In the nitration process the entering nitro group may replace a number of different monovalent atoms or groups of atoms. In this chapter we shall be concerned only with those nitrations in which the nitro group replaces a hydrogen atom, since these are the reactions of greatest technical importance. Among the reactions in which the nitro group replaces atoms or groups other than hydrogen, the following are shown by way of illustration. Certain alkyl halides can react with silver nitrate to form the corresponding nitrate esters or with silver nitrite to form the corresponding nitro compounds as shown below.

$$RCl + AgNO_3 \rightarrow RONO_2 + AgCl$$
$$RCl + AgNO_2 \rightarrow RNO_2 + AgCl$$

In the aromatic series the sulfonic acid or acetyl groups can, in certain instances, be replaced as shown in the accompanying equations.





Nitration is one of the most important reactions in industrial synthetic organic chemistry. Not only do nitration products find wide application as solvents, dyestuffs, pharmaceuticals, and explosives, but they also serve as useful intermediates for the preparation of other compounds, particularly amines which are prepared by the reduction of the corresponding nitro compound.

II. NITRATING AGENTS

A variety of reagents can be used to effect nitration. These include fuming, concentrated, and aqueous nitric acid and mixtures of nitric acid with sulfuric acid, acetic anhydride, acetic acid, phosphoric acid, and chloroform. Nitrogen pentoxide, N_2O_5, and nitrogen tetroxide, N_2O_4, are also used in certain instances. In order to make an intelligent choice of nitrating system for a particular nitration, it is desirable to know what species are present in the various systems and to understand the mechanism of the reaction under consideration.

The Nitryl Ion, NO_2^+.[1] The system nitric acid–sulfuric acid, commonly known as mixed acid, is the most important nitrating medium from a practical standpoint and is probably also the best understood. There is a large body of evidence that supports the belief that nitric acid exists in strong sulfuric acid as the nitryl ion, NO_2^+. From freezing-point depression measurements, the Van't Hoff *i* factor (the number of particles generated by one molecule of solute) of nitric acid in sulfuric acid is found to be 4, which indicates that the ionization of nitric acid can be represented by the equation

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

The *i* factors of ethyl nitrate, nitrogen pentoxide, and nitrogen tetroxide in sulfuric acid are 5, 6, and 6, indicating that these substances ionize to form nitryl ions according to the equations

$$C_2H_5ONO_2 + 3H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + C_2H_5OSO_3H + 2HSO_4^-$$
$$N_2O_5 + 3H_2SO_4 \rightarrow 2NO_2^+ + H_3O^+ + 3HSO_4^-$$
$$N_2O_4 + 3H_2SO_4 \rightarrow NO^+ + NO_2^+ + H_3O^+ + 3HSO_4^-$$

Each of these solutions is a powerful nitrating agent.

Solutions of nitric acid have three different ultraviolet-absorption spectra. In dilute aqueous solution, its spectrum is that of the nitrate ion, NO_3^-. In an inert weakly polar solvent such as chloroform, its spectrum is the same as that of ethyl nitrate, indicating that the nitric acid exists as unionized HNO_3. A third spectrum is characteristic of sulfuric acid solutions of nitric acid and its esters, indicating that here nitric acid does not exist as the nitrate ion or as unionized nitric acid. The Raman spec-

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[1] In the literature, this ion is more frequently called the nitronium ion. Here, the Chemical Abstracts nomenclature is used.

trum of nitric acid in sulfuric acid is even more informative. The nitryl ion, being isoelectronic[1] with carbon dioxide and the azide ion, N_3^-, should be a linear centrosymmetric ion; hence its Raman spectrum should consist of one strong and polarized line. From the known vibrational Raman frequencies of CO_2 and N_3^-, this line should have a frequency somewhat greater than 1,320 cm^{-1}. Solutions of nitric acid in sulfuric acid and in perchloric acid have only one Raman line owing to nitric acid which occurs at 1,400 cm^{-1} and which is polarized.

The fact that the ion derived from nitric acid in sulfuric acid is positively charged has been demonstrated by electrolysis experiments in which it was found that the nitric acid migrates from the anode to the cathode. Finally, it is noteworthy that several crystalline nitryl salts have been isolated and characterized, e.g., $NO_2^+NO_3^-$, $NO_2^+ClO_4^-$, and $NO_2^+HS_2O_7^-$.

The relationship between the amount of water present in sulfuric acid and the per cent of nitric acid molecules that are ionized to form nitryl ions is shown in Fig. 4-1.[2] In solutions weaker than 86 per cent sulfuric acid, the ionization of nitric acid is very slight but rapidly rises as the sulfuric acid becomes more concentrated. In about 94 per cent sulfuric acid, the nitric acid is practically completely ionized to nitryl ion.

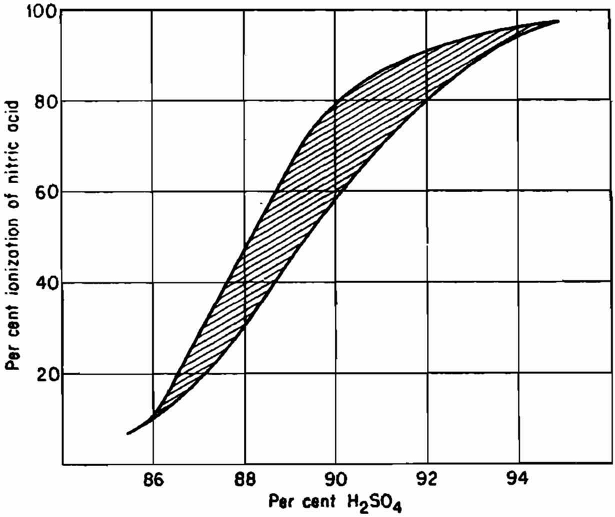

FIG. 4-1. The effect of water on the ionization of nitric acid in sulfuric acid.

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[1] Molecules, radicals, and ions having the same number of atoms and valence electrons are called isoelectronic. Species which are isoelectronic have similar shapes; thus since CO_2 and N_3^- are linear and centrosymmetric, the nitryl ion is likely to be linear and centrosymmetric.

[2] BONNER and WILLIAMS, *Chemistry & Industry*, **1951**, 820.

Nitryl ions have also been detected spectroscopically in 100 per cent nitric acid, but their concentration is very low. At −40°C, nitric acid is said to contain 1.2 per cent NO_2^+, 1.7 per cent NO_3^-, and 0.5 per cent H_3O^+. Nitric acid in acetic anhydride and nitric anhydride in 100 per cent nitric acid have been shown to yield NO_2^+ and NO_3^-.

III. AROMATIC NITRATION

The nitration of aromatic compounds[1] can be represented by the equation

$$ArH + HNO_3 \rightarrow ArNO_2 + H_2O$$

Orientation. The nitration agent is an electrophilic reactant; hence reaction will be favored at the carbon atom of the aromatic ring where the electron density is greatest. When the aromatic compound to be nitrated contains a substituent, the nitro group can enter at the ortho, meta, or para positions. The relative amounts of these isomeric products will depend upon the substituent, since the substituent has a profound effect on the electron densities around the various carbon atoms. Certain substituents cause the electron density to be greater at the ortho and para positions than at the meta positions; hence they yield nitration products in which the ortho and para isomers predominate. Other substituents cause the electron density to be greater at the meta positions than at the ortho and para positions. These are therefore meta directing. The isomer distribution arising from the nitration of various monosubstituted benzenes is shown in Table 4-1.

TABLE 4-1. NITRATION OF VARIOUS MONOSUBSTITUTED BENZENES*

Group already present	Percentage of		
	Ortho	Meta	Para
F	12.4	Trace	87.2
Cl	30.1	Trace	69.9
Br	37.6	Trace	62.4
I	41.1	Trace	58.7
CH_3	58.8	4.4	36.8
CH_2Cl	40.9	4.2	54.9
$CHCl_2$	23.3	38.8	42.9
CCl_3	6.8	64.5	28.7
$COOC_2H_5$	28.3	68.4	3.3
COOH	18.5	80.2	1.3
NO_2	6.4	93.2	0.25

* HOLLEMAN, *Chem. Revs.*, 1, 187 (1925).

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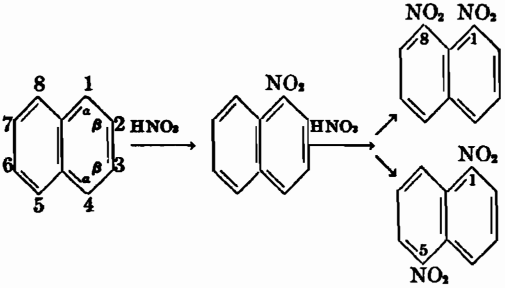
[1] For excellent discussions on aromatic nitration, see GILLESPIE and MILLER, *Quart. Rev.*, 2, 277 (1948); INGOLD, "Structure and Mechanisms in Organic Chemistry," p. 269, Cornell University Press, Ithaca, N.Y., 1953.

Naphthalene Series. In the naphthalene series, it is possible to have two different mononitro derivatives, viz., the alpha and beta compounds, also known at 1-nitronaphthalene and 2-nitronaphthalene. Upon nitration, the first nitro group enters almost exclusively into the alpha or 1 position; a second nitro group enters into position 5 or 8.

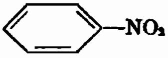
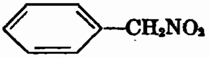
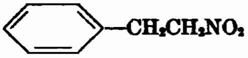


Anthraquinone Series. In the anthraquinone series, nitration with mixed acid containing a slight excess over one equivalent of nitric acid results in the formation of three nitro derivatives. These are the alpha-substituted 1-nitroanthraquinone and the 1,5-and 1,8-dinitroanthraquinones. Unless the nitric acid ratio and concentration are sufficient to ensure considerable dinitration, some anthraquinone remains unreacted.

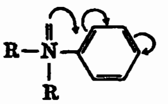
Theory of Aromatic Substitution. The development of the theory of orientation in aromatic substitution, which was due largely to R. Robinson and C. K. Ingold and their coworkers, is one of the most interesting chapters in organic chemistry. According to the theory, a substituent influences the electron density in two important ways—by the inductive effect (−I when it attracts electrons and +I when it repels electrons) and by the mesomeric effect (−M or +M). The inductive effect is associated with the dipole moment of the compound $C_6H_5 - X$. If X is at the negative end of the dipole, it will draw electrons from the ring and produce a −I effect, indicated by a straight arrow $C_6H_5 \rightarrow X$. If X is at the positive end of the dipole, it will increase the electron density in the ring and produce a +I effect. Groups which produce a −I effect in order of decreasing strength are $-NMe_3^+$, $-NO_2$, −COOEt, −halogen. Groups which produce a +I effect are $-O^-$ and alkyl. The +I effect causes all the positions in the ring to be more reactive than in unsubstituted benzene, the ortho and para positions being made somewhat more reactive than the meta. The −I effect reduces the reactivity of all positions in the ring relative to benzene, the effect being greater in the ortho and para positions, leaving the meta positions to be more reactive. Thus the nitration of toluene produces predominantly ortho- and para-nitrotoluene, while the nitration of nitrobenzene produces predominantly meta-dinitrobenzene.

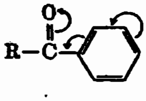
The effect of a side chain between the substituent and the ring is to reduce the effect of the substituent. This is illustrated in Table 4-2.

Table 4-2 Percentage of Meta Derivatives Formed in the Mononitration of Nitrobenzene and Its Side-chain Homologues

		
93%	67%	13%

Substituents which have an unshared pair of electrons can increase the electron density in the ring by the mesomeric effect, +M, which is indicated by curved arrows. Other substituents can decrease the electron density in the ring by the −M effect. These effects are illustrated in the accompanying diagrams.





Substituents which show a +M effect activate all the positions in the ring relative to unsubstituted benzene, the effect being more pronounced at the ortho and para positions than at the meta positions. Similarly, the substituents exhibiting the −M effect deactivate all the positions, the meta being less deactivated than the ortho and para. Groups which show a +I and +M effect will obviously facilitate substitution and be ortho-para directing, and groups which have a −I and −M effect will make substitution more difficult and be meta directing. When the two effects are in opposition, i.e., +I and −M or −I and +M, the net result will be more difficult to predict. The acetoxy, methoxy, and acetamino groups all show the −I, +M effects. The +M effect is much more powerful than the −I effect, and so phenyl acetate, anisole, and acetanilide are readily nitrated and the products are predominantly the ortho-para nitro derivatives. The halogens also produce the −I and +M effects, but in these cases the two effects are of comparable importance. The halogenated benzenes are nitrated more slowly than benzene itself because of the −I effect, but the nitro group enters the ortho and para positions because of the +M effect. Table 4-3 contains a classification of orienting substituents.

Ortho:Para Ratios. In the preceding paragraphs, the substituents were classified as ortho-para directing or meta directing, the difference being explained in terms of +I and −I effects and +M and −M effects. The effect of a substituent on the ratio of ortho to para nitration products is also explained by these factors and an additional factor, the size of the substituent, which we shall call the steric factor.

A substituent will make the ortho positions less accessible to the incoming nitro group according to its size. The larger the substituent, the less

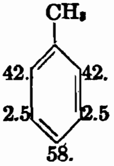
TABLE 4-3. CLASSIFICATION OF ORIENTING SUBSTITUENTS

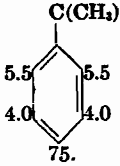
Type	Electronic mechanism	Example	Effect on orientation	Reactivity
+I	$Ph \leftarrow R$	$Ph \leftarrow CH_3$	Ortho, para	Activation
+I, −M	$Ph \overset{\curvearrowright}{\leftarrow} R$	$Ph \overset{\curvearrowright}{\leftarrow} COO^-$	Ortho, para, or meta	Activation or deactivation
−I	$Ph \rightarrow R$	$Ph \rightarrow NH_3^+$	Meta	Deactivation
−I, −M	$Ph \overset{\curvearrowright}{\rightarrow} R$	$Ph \overset{\curvearrowright}{\rightarrow} COOEt$	Meta	Deactivation
		$Ph \overset{\curvearrowleft}{\rightarrow} SMe_2^+$	Meta	Deactivation
−I, +M	$Ph \overset{\curvearrowleft}{\rightarrow} R$	$Ph \overset{\curvearrowleft}{\rightarrow} Cl$	Ortho, para	Deactivation
		$Ph \overset{\curvearrowleft}{\rightarrow} OMe$	Ortho, para	Activation
+I, +M	$Ph \overset{\curvearrowleft}{\leftarrow} R$	$Ph \overset{\curvearrowleft}{\leftarrow} O^-$	Ortho, para	Activation

accessible will the ortho positions be and the smaller will be the ortho:para ratio of the products. Evidence for this effect can be seen from the results of the mononitration of alkylbenzenes which are shown in Table 4-4. As the alkyl group is increased in size, the yield of ortho-substituted product decreases and the ortho:para ratio decreases. The rate of attack on the individual nuclear positions of toluene and *t*-butylbenzene (the rate for one position of benzene being taken as unity) presents the following comparison:

TABLE 4-4. PROPORTION OF PRODUCTS FORMED IN THE NITRATION OF ALKYLBENZENES

	$PhCH_3$	PhC_2H_5	$PhCH(CH_3)_2$	$PhC(CH_3)_3$
Ortho	57	55	14	11.8
Meta	3.2	0	0	8.7
Para	40	45	86	80





The polar effects I and M influence the ortho:para ratio because they are transmitted to the ortho and para positions to different extents. The inductive effect is as strong or stronger at the ortho positions than at the para position, whereas the mesomeric effect is much stronger at the para than at the ortho positions. Thus a compound in which the +I effect is dominant will, upon nitration, yield a larger ortho:para ratio of products than will a compound in which the +M effect is dominant. Similarly, a compound in which the −I effect is dominant will give a lower ortho:para ratio of nitration products than will a compound in which the −M effect is dominant. By way of illustration, the products of the nitration of phenyl halides shown in Table 4-5 are cited. The −I effect decreases in going from PhF to PhI; hence the corresponding increase in yield of ortho isomer.

TABLE 4-5. NITRATION PRODUCTS OF PHENYL HALIDES

	PhF	PhCl	PhBr	PhI
Per cent ortho	12	30	38	41
Per cent para	87	70	62	59

The ortho:para ratio is also influenced by the nitration medium in a manner which cannot be explained by the Robinson-Ingold theory. The isomer distribution which results from the nitration of aniline and anilides in several nitrating media is shown in Table 4-6.

The nitration of acetanilide with mixed acid yields nitroacetanilides in which the ortho:para ratio is less than 0.1. When the nitration medium is nitric acid, this ratio is 0.7, when acetyl nitrate in acetic anhydride is used, the product is almost entirely *o*-nitroacetanilide. No satisfactory explanation has been given for these results. The 40–50 per cent yield of *m*-nitroaniline that results from the nitration of aniline in mixed acid or in nitric acid can be explained in the following manner. In the strong acids, nitric and sulfuric acid, aniline is largely ionized.

$$C_6H_5NH_2 + HA \rightarrow C_6H_5NH_3^+ + A^-$$

TABLE 4-6. NITRATION OF ANILINE AND ANILIDES*

Nitration with 80 Per Cent HNO_3 in Glacial Acetic Acid

Amine	Per cent			Ratio ortho:para
	Para	Ortho	Meta	
Free amine	64	36	..	1:1.8
Acetyl	70	30	..	1:2.3
Benzoyl	72	28	..	1:2.6
Formyl	74	26	..	1:2.8
Chloroacetyl	75	25	..	1:3.0
Amino oxalyl	79	21	..	1:3.8
Toluenesulfonyl	84	16	..	1:5.3

* According to LAUER, *J. prakt. Chem.*, **137**, 175 (1933).

TABLE 4-6. NITRATION OF ANILINE AND ANILIDES (*Continued*)

Nitration with 94 Per Cent HNO_3 in Concentrated H_2SO_4

Amine	Per cent			Ratio ortho:para
	Para	Ortho	Meta	
Free amine	50	1	49	
Acetyl	92	8	..	1:11.5
Benzoyl	93	7	..	1:13.3
Formyl	94	6	..	1:15.6
Chloroacetyl	96	4	..	1:24.0
Amino oxalyl	98	2	..	1:49.0
Toluenesulfonyl	98	2	..	1:49.0

Nitration in HNO_3

Amine	Per cent			Ratio ortho:para
	Para	Ortho	Meta	
Aniline nitrate	56	4	40	
Acetyl	58	42	..	1:1.4
Benzoyl	60	40	..	1:1.5
Formyl	65	35	..	1:1.9
Chloroacetyl	73	27	..	1:2.7
Oxalyl	85	15	..	1:5.7
Toluenesulfonyl	88	12	..	1:7.3

Temperature, 20°C; time, 24 hr.

The anilinium ion is strongly deactivated because of the $-I$ effect of the $-NH_3^+$ substituent. Its nitration will yield the meta isomer. The free amine will be strongly activated because of the $+M$ effect of the $-NH_2$ group, and it will yield the para isomer. In the relatively weak acid, acetic acid, the concentration of the anilinium ion will be much less than in the stronger acids; hence no significant amount of the meta isomer is formed.

IV. KINETICS AND MECHANISM OF AROMATIC NITRATION

The kinetics of the nitration reaction depend upon the reaction medium. Let us consider first the reactions in strong sulfuric acid. Compounds which are nitrated at a conveniently measurable rate in this system are those which have strong $-I$ and $-M$ effects such as nitrobenzene, anthraquinone, and ethyl benzoate. The rate of all these nitrations is proportional to the concentration of added nitric acid and of organic substrate

$$\text{Rate} = k\,(HNO_3)\,(ArH)$$

The effect of the amount of water present upon the reaction rate is shown in Fig. 4-2. The reaction rate rises sharply with increasing sulfuric acid concentration and reaches a maximum at about 90 per cent H_2SO_4 and then falls off at higher acid concentrations. It was first suggested by Westheimer and Kharasch[1] that the rise in rate with increasing acid strength when the acid in less than 90 per cent is due to the increase in concentration of nitryl ion. It was shown that the equilibrium constant for the ionization of *tris* *p*-nitrophenylcarbinol increases in the same way as the rate constant, as shown in Fig. 4-2. Since triphènylcarbinols ionize in sulfuric acid to yield carbonium ions in a manner analogous to the formation of nitryl ions from nitric acid

$$(Ar)_3COH + 2H_2SO_4 \rightarrow (Ar)_3C^+ + H_3O^+ + 2HSO_4^-$$

it was believed that both ionization constants would show a similar dependence on acid strength. This conclusion seems justified in view of the strong evidence for the nitryl ion given in the paragraphs on nitrating agents.

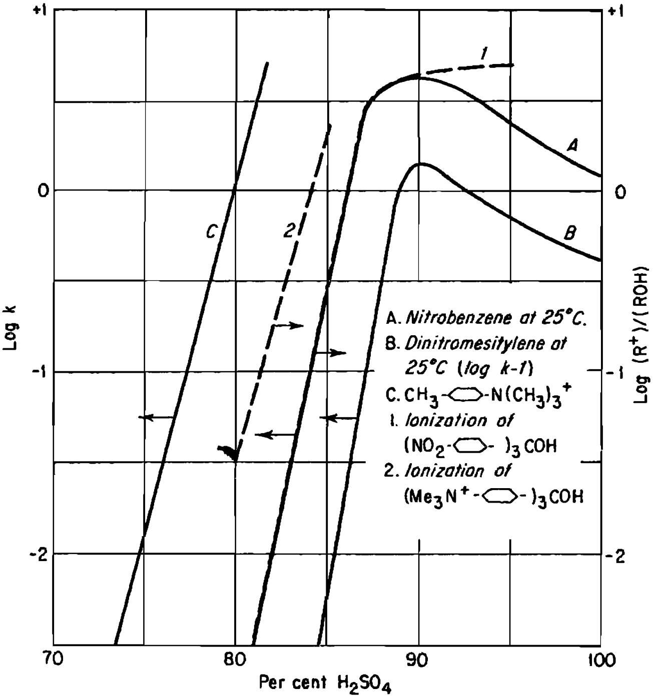


FIG. 4-2. The effect of water on the rate of nitration and on the ionization of triphenylcarbinols.

[1] KHARASCH and WESTHEIMER, *J. Am. Chem. Soc.*, **68**, 1871 (1946).

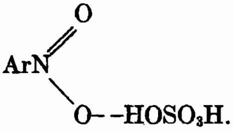
The generally accepted mechanism which is compatible with the data may be represented by the following series of reactions:

$$HNO_3 + 2H_2SO_4 \xrightarrow{\text{fast}} NO_2^+ + H_3O^+ + 2HSO_4^- \qquad \text{(Step 1)}$$

$$ArH + NO_2^+ \xrightarrow{\text{slow}} ArHNO_2^+ \qquad \text{(Step 2)}$$

$$ArHNO_2^+ + HSO_4^- \longrightarrow ArNO_2 + H_2SO_4 \qquad \text{(Step 3)}$$

There still remains to be explained the decrease in rate with increasing acid strength when $H_2SO_4 > 90$ per cent. It was originally thought that step 3 in the above mechanism was also slow and that the decrease in rate was due to the decrease in concentration of bisulfate ions which served to remove the proton from the positively charged intermediate formed in step 2. This theory was found to be untenable from experiments with isotopically labeled aromatic substrates. If the removal of hydrogen were a slow step, then the nitration of aromatic compounds in which the hydrogen was replaced by deuterium or tritium should proceed more slowly. It has been found experimentally that the tritium-containing compounds are nitrated at the same rate as the hydrogen-containing substances, indicating that the proton-transfer step could not be rate determining.

A plausible explanation for the decrease in rate at higher acidity has been given by Gillespie and Millen.[1] An interaction occurs between the organic substrate and the sulfuric acid which decreases the electron density in the ring and hence decreases the reactivity. The interaction is probably a hydrogen-bond formation. The hydrogen bond between nitrobenzene and sulfuric acid can be pictured  $ArN(=O)O{-}{-}HOSO_3H.$ The strength of a hydrogen bond increases with the acidity of the hydrogen donor, which in this case is sulfuric acid. Decreasing the water content of the acid would thus be expected to increase the interaction between acid and organic substrate, which would result in greater withdrawal of electrons from the ring.

Nitration in Organic Solvents. In the organic solvents nitromethane or acetic acid, with nitric acid in large excess, the kinetics of the nitration process depend upon the aromatic compound being nitrated. Compounds such as nitrobenzene or ethyl benzoate which possess strongly deactivating groups are nitrated at a rate which is proportional to the concentration of the substrate, i.e., the reaction is first order. Compounds which are more reactive than benzene, such as toluene, xylene, and *p*-chloranisole, react at a rate which is independent of the concentration of the substrate, i.e.,the reaction is zero order. The rate of the reaction with all substrates which show zero-order kinetics is the same. For substrates of intermediate re-

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[1] Gillespie and Millen, *loc. cit.*

activity, there is a dependence of rate on concentration, the kinetics being intermediate between first and zero order.

The most reasonable interpretation of these results is as follows. The formation of nitryl ions probably takes place thus:

$$2HNO_3 \rightarrow H_2NO_3^+ + NO_3^-$$
$$H_2NO_3^+ \rightarrow H_2O + NO_2^+$$

The first step, which represents the transfer of a proton from one nitric acid molecule to another, is very rapid. The rate at which the second step, the formation of the nitryl ion, takes place depends upon the medium. As we have seen, in a strongly acidic, highly polar solvent like concentrated sulfuric acid, this takes place very quickly. However, in less strongly acidic media such as acetic acid or nitromethane, this step can be relatively slow. The zero-order kinetics shown by highly reactive substrates in these solvents indicate that the nitration step

$$NO_2^+ + ArH \rightarrow ArNO_2^+ + H^+$$

is fast compared with the rate of formation of NO_2^+. In agreement with this hypothesis is the fact that all these highly reactive compounds are nitrated at the same rate, which is the rate of formation of the nitryl ion. In the nitration of the aromatic substrates of low reactivity, the formation of the nitryl ion is fast relative to the nitration step which is rate determining. Each compound in this class reacts at its own characteristic rate. In the nitration of compounds of intermediate reactivity, both steps occur at comparable rates.

Nitration in Aqueous Nitric Acid. A similar pattern of behavior is found in aqueous nitric acid.[1] Highly reactive substrates show zero-order kinetics, and less reactive compounds show first-order kinetics in about 40 mole per cent aqueous nitric acid. The rate of nitration of the reactive compounds is the same as the rate of exchange of O^{18} between HNO_3^{18} and H_2O^{16}. This constitutes the most convincing evidence for nitration by nitryl ion in aqueous solution. The rate-determining step in each reaction is the formation of the nitryl ion. The exchange of oxygen between nitric acid and water occurs in the following steps:

$$2HNO_3^{18} \xrightarrow{\text{fast}} H_2NO_3^{18+} + NO_3^{18-}$$
$$H_2NO_3^{18+} \xrightarrow{\text{slow}} H_2O^{18} + NO_2^{18+}$$

The nitryl ion after being formed by the above reactions reacts with water quickly:

$$NO_2^{18+} + H_2O^{16} \longrightarrow H_2NO^{16}O_2^{18+}$$

Effect of Nitrous Acid on Nitrations. Nitrous acid or nitrogen dioxide in certain instances exerts an inhibiting effect and in other instances exerts a catalytic effect on aromatic nitrations. The inhibiting effect is observed

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[1] Burton and Halevi, *J. Chem. Soc.*, **1952**, 4917.

in the nitration of compounds having no activating groups, which reactions are necessarily carried out either in strong nitric acid or in mixed acid. In these media the nitrous acid forms the nitrosyl ion, NO^+,

$$HNO_2 + HNO_3 \longrightarrow NO_3^- + NO^+ + H_2O$$
$$HNO_2 + 2H_2SO_4 \longrightarrow H_3O^+ + 2HSO_4^- + NO^+$$

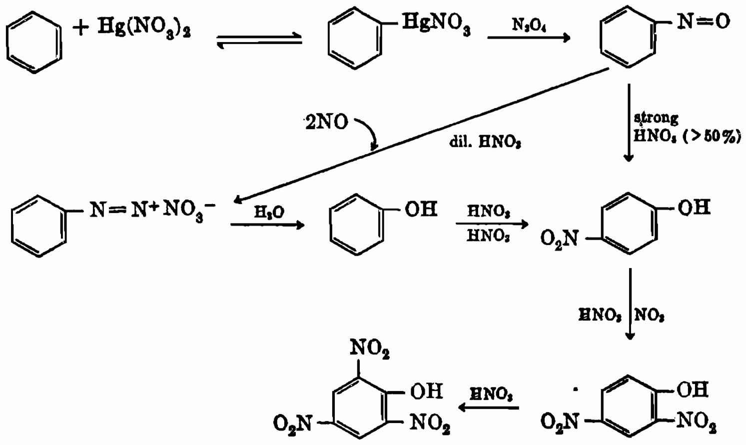
which decreases the concentration of nitryl ions (see equations, p. 61) and thus reduces the reaction rate. The catalytic effect is observed in the nitration of reactive substrates such as anisole or dimethylaniline, which are nitrated in relatively weak nitric acid where the nitryl ion concentration is low. The catalysis is due to the formation of a nitroso compound which is oxidized to the nitro compound according to the equations

$$ArH + NO^+ \longrightarrow ArNO + H^+$$
$$ArNO + HNO_3 \longrightarrow ArNO_2 + HNO_2$$

Because the nitrosyl ion is a much weaker electrophilic reagent than the nitryl ion, it is able to react only with very reactive aromatic compounds such as anisole or dimethylaniline.

Two conditions are therefore necessary for catalysis by nitrous acid: (1) The substrate must be sufficiently reactive so as to be susceptible to attack by nitrosyl ion, and (2) the reaction medium must be such that the concentration of nitryl ions is very low, thus allowing the nitrosyl ions to compete favorably for the substrate.

Oxynitration. An interesting reaction occurs between benzene and approximately 50 per cent nitric acid containing 0.2 molar mercuric nitrate which yields up to 85 per cent dinitrophenol and picric acid. This process is known as oxynitration. It has been shown by Westheimer and coworkers[1] that this reaction occurs in the following steps:



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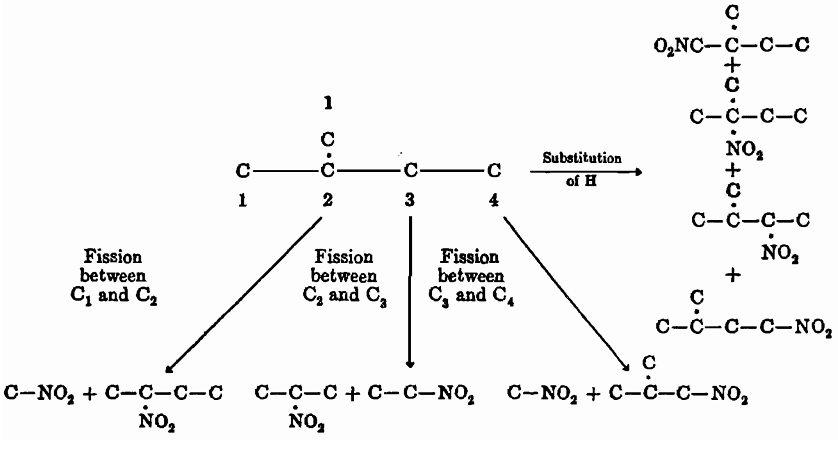
[1] Westheimer, Segal, and Schramm, *J. Am. Chem. Soc.*, **69**, 773 (1947).

The benzene is initially converted to phenylmercuric nitrate which reacts with nitrogen dioxide to yield nitrosobenzene. Each of these intermediates has been isolated from the reaction mixture. The nitrosobenzene can react in two ways. In nitric acid weaker than 50 per cent, it reacts with 2 moles of nitric oxide to form phenyldiazonium nitrate, a reaction first discovered by Bamberger. The diazonium salt is converted by water to phenol, which is nitrated in steps to the final products. In nitric acid of greater than 50 per cent concentration, the nitrosobenzene is converted directly to *p*-nitrophenol without going through the diazonium compound. The *p*-nitrophenol is then nitrated further to give the dinitrophenol and picric acid.

V. NITRATION OF PARAFFINIC HYDROCARBONS

Gas-phase Reactions. In contrast to aromatic hydrocarbons which are susceptible to attack by electrophilic reagents such as the nitryl ion, the paraffins are quite inert to such reagents. The paraffins, on the other hand, are susceptible to attack by certain atoms and free radicals. The nitration of these compounds as practiced commercially is carried out in the vapor phase and at temperatures of 350–450°C; it is undoubtedly a free-radical reaction. Nitric acid of 70 per cent strength or less is generally used, although nitrogen dioxide can also be used. A characteristic feature of reactions involving alkyl radicals is the great variety of products formed. This is clearly shown by the nitration of 2-methylpentane which yields all the possible mononitration products that might be formed by breaking any one of the bonds present and introducing a nitro group at the point of cleavage. The products are nitromethane, nitroethane, 2-nitropropane, 2-nitrobutane, 1-nitroisobutane, 1-nitro-3-methylbutane, 2-nitro-3-methylbutane.

Nitration Products of Isopentane



The nitration produces only mononitroparaffins and no significant amounts of polynitro compounds. Although cleavage of the carbon skeleton occurs, as shown above, no rearrangement of the carbon skeleton has been found to occur.

The reaction is carried out by passing the reactants through the reaction chamber in a flow system. The products are condensed and distilled. As a a result of a systematic study, the following facts have emerged.[1]

1. There is an optimum temperature at which the highest yield is obtained. Using butane and concentrated nitric acid in molar ratio of 15:1, and a contact time of 1.6 sec, the results shown in the accompanying table were obtained.

Temperature, °C....................	405	425	435
% Conversion of nitric acid..........	15	36	22
% Yield of RNO_2: based on butane...	1	2.9	1.4

2. The addition of oxygen increases the yield based on nitric acid but also increases the oxidation of butane. These effects are shown in Fig. 4-3. Oxygen also increases the yield of nitromethane and nitroethane and

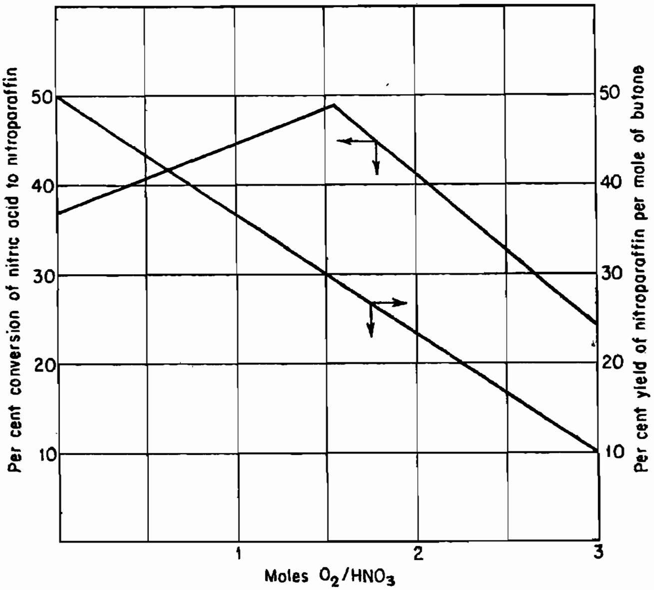


FIG. 4-3. The effect of oxygen on the nitration of butane. Butane:nitric acid ratio = 15. T = 425°C.

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[1] BACHMAN, HASS, and ADDISON, *J. Org. Chem.*, 17, 906 (1952).

decreases the yield of nitrobutane. Increasing the surface:volume ratio in the reactor to 300 makes possible slightly higher conversions of nitric acid and produces striking improvements in yield based on butane consumed. When $O_2:HNO_3 = 1$, the yield based on butane consumed is increased from 32 to 45 per cent. The use of steam as a diluent in the presence of oxygen also mitigates the oxidative effects of the oxygen and aids in raising the conversion still further.

3. Nitrogen dioxide also reacts with paraffins to yield nitroparaffins. At 325°C, a contact time of 1.9 min, and propane:NO_2 = 4.2, the per cent conversion of NO_2 is 16.6 and the yield based on moles of hydrocarbon is 51 per cent. The addition of oxygen lowers the optimum temperature and improves conversion and yields. At 285°C, contact time 3 min, and $O_2:NO_2 = 0.75$, the conversion is 29 per cent and the yield is 71 per cent. Table 4-7 shows the relative merits of NO_2 and nitric acid.

TABLE 4-7. RELATIVE MERITS OF NO_2 AND NITRIC ACID

	NO_2	HNO_3
Yield based on hydrocarbon	Higher	Lower
Yield based on N	Lower	Higher
Optimum temperature	Lower	Higher
Optimum contact time	Longer	Shorter
By-products:		
$CO + CO_2$	Higher	Lower
Olefins	Lower	Higher
Aldehydes and ketones	Lower	Higher
Nitrogen	Lower	Higher
Economy	Less	Greater

4. Bromine has a beneficial effect on both yields and conversions to nitroparaffins using nitric acid. At 423°C, a contact time of 1.5 sec, and the following ratios of reactants, propane: O_2 = 8.2, propane: nitric acid = 9.9, water: nitric acid = 15, and $Br_2:HNO_3 = 0.015$, the per cent conversion of nitric acid is 47.7 and the yield based on propane is 55.5 per cent. The yields of other products are as follows: $CO_2 = 0$, $CO = 3.6$, $C_3H_6 = 9.7$, $C_2H_4 = 4.1$, aldehydes and ketones = 27 per cent. The effect of chlorine is similar to that of bromine.

5. Highly branched hydrocarbons undergo less fission during nitration than do their less-branched isomers. Correspondingly, hydrogen substitution is favored when highly branched structures are nitrated. As can be seen from the data in Table 4-8, in which a comparison is made of the nitration of isomeric butanes and pentanes, the molar ratio of the product resulting from fission to that resulting from hydrogen substitution decreases as the carbon skeleton becomes more highly branched.

TABLE 4-8. NITRATION OF PARAFFINS: PRODUCTS OBTAINED AND EFFECT OF BRANCHING ON FISSION REACTION

Hydrocarbon	Temp, °C	Mole % of products		Ratio, fission products: substitution products
Butane	420	10.5	nitromethane	0.463
		15.8	nitroethane	
		5.3	1-nitropropane	
		44.2	2-nitrobutane	
		24.2	1-nitrobutane	
2-Methylpropane	420	5.8	nitromethane	0.407
		23.1	2-nitropropane	
		7.0	2-methyl-2-nitrobutane	
		64.1	2-methyl-1-nitropropane	
n-Pentane	400	2.3	nitromethane	0.745
		10.9	nitroethane	
		16.7	1-nitropropane	
		12.8	1-nitrobutane	
		18.9	1-nitropentane	
		18.2	2-nitropentane	
		20.2	3-nitropentane	
2-Methylbutane	420	3.9	nitromethane	0.628
		8.8	nitroethane	
		16.1	2-nitropropane	
		9.8	2-methyl-1-nitropropane 2-nitrobutane	
		12.2	2-methyl-2-nitrobutane	
		14.0	3-methyl-2-nitrobutane	
		24.1	2-methyl-1-nitrobutane	
		11.1	3-methyl-1-nitrobutane	
2,2-Dimethylpropane	410	14.0	nitromethane	0.370
		13.0	2-methyl-2-nitropropane	
		73.0	2,2-dimethyl-1-nitropane	

6. The temperature coefficients for hydrogen substitution are in the order primary > secondary > tertiary. The rate of substitution is in the reverse order at low temperature. As the reaction temperature is increased, the rates tend to approach equality.

The following steps are probably involved in the nitration of paraffins:

$$HONO_2 \rightarrow HO^{\cdot} + NO_2$$

Alkyl radical formation

$$RH + OH^{\cdot} \rightarrow R^{\cdot} + HOH$$

$$RH + NO_2 \rightarrow R^{\cdot} + HNO_2$$

Nitroparaffin formation

$$R^{\cdot} + NO_2 \rightarrow RNO_2$$

Oxidative and cleavage steps

$$RCH_2\cdot + NO_2 \rightarrow RCH_2O\cdot + NO$$

$$RCH_2O\cdot + NO_2 \rightarrow RCHO + HNO_2$$

$$RCH_2O\cdot \rightarrow CH_2O + R\cdot$$

$$RCHO + NO_2 \rightarrow RCO\cdot + HNO_2$$

$$RCO\cdot \rightarrow R\cdot + CO$$

$$CH_2O + NO_2 \rightarrow NO + H_2O + CO$$

Olefin formation

$$RCH_2CH_2\cdot + NO_2 \rightarrow HNO_2 + RCH{=}CH_2$$

$$2RCH_2CH_2\cdot \rightarrow RCH{=}CH_2 + RCH_2CH_3.$$

Liquid-phase Nitration. This reaction is of less importance than the gas-phase nitration because of low yields, lower conversions, and the occurrence of unwanted side reactions.

The principal liquid-phase nitration reaction of hydrocarbons is replacement of hydrogen atoms by nitro groups; there is no evidence for a nitration reaction involving replacement of alkyl groups as in the vapor phase. In general, the ease of formation of products follows the order tertiary > secondary > primary nitroparaffins. The reaction is usually slow because of the low mutual solubility of the paraffin and the nitration medium. Because of their higher boiling points, higher hydrocarbons can be nitrated at higher temperatures and, hence, more quickly than the lower-molecular-weight hydrocarbons.

The initially formed mononitroparaffin is more soluble in the nitric acid than is the hydrocarbon and undergoes further reaction to yield, on the one hand, polynitroparaffins, and on the other hand, decomposition and oxidative products including fatty acids, alcohols, and oxides of carbon.

The concomitant oxidation results in the reduction of much of the nitric acid to elementary nitrogen, which prevents recovery by reoxidation, and thus constitutes an economic barrier to the industrialization of the process.

Nitrocyclohexane has been prepared by E. I. du Pont de Nemours & Company by nitration of cyclohexane. Cyclohexane undergoes nitration and oxidation to give nitrocyclohexane and adipic acid along with smaller amounts of glutaric acid and succinic acid. Nitration is accelerated by the addition of nitrogen dioxide. The process may be operated continuously in the liquid phase with 45–75 per cent nitric acid at temperatures of 100–200°C and pressures of 2–10 atm. This process is of particular interest in that oxidation products from cycloalkanes are usually symmetrical dicarboxylic acids, which are of industrial importance.

Nitration of 2-nitropropane with nitric acid to give 2,2-dinitropropane has been conducted in pilot-plant quantities by the Commercial Solvents Corporation. Reaction may be effected in stainless-steel apparatus at

204–232°C at pressures of 900–1,200 psi, with a molar ratio of nitric acid (70 per cent) to 2-nitropropane of 1:1 and a space velocity of 1.0. Conversions of 2-nitropropane per pass range from 11–14 mole per cent under these conditions; the ultimate yields, on the basis of recycled 2-nitropropane, are well above 50 per cent. The most critical variable in this nitration is temperature: nitration does not occur at reflux temperatures at atmospheric pressure; at temperatures of 260–302°C, oxidation becomes pronounced and violent explosions occur. The yield of 2,2-dinitropropane is increased at elevated pressures; however, the efficiency of the process is not improved at pressures above 1,200 psi. Conversion to 2,2-dinitropropane is favored by the use of a lower molar ratio of 2-nitropropane to nitric acid; however, considerable oxidation and decomposition of 2-nitropropane occur, and the yield of 2,2-dinitropropane is decreased. The effect of increasing the molar ratio of nitric acid may be modified by increasing the amount of water as diluent; by this method, excellent conversions per pass can be maintained with little loss in yield.

When higher paraffins in the liquid phase are nitrated with nitric acid in the vapor phase, the reaction proceeds smoothly at relatively low temperatures. Mixing of the reactants is accomplished in a simple and efficient manner by feeding the nitric acid through a coil submerged in the paraffin undergoing reaction. The hydrocarbon is maintained above 121°C (the maximum boiling point of 65–70 per cent nitric acid), while the incoming vaporized acid is diffused through a porous plate and permitted to bubble up through the charge. Table 4-9 contains the results of the nitration of *n*-dodecane at 180–190°C by this procedure.[1]

TABLE 4-9. NITRATION OF DODECANE WITH HNO_3 VAPOR
Per Cent in Reaction Product

Ratio P:HNO_3	Dodecane	Nitrodecanes	Polynitrodecanes	Fatty acids
1:4	24	4	47	25
1:2	33	25	38	4
1:1	43	40	15	2
2:1	58	36	5	1

Temperature, 180–190°C; density, HNO_3 = 1.40.

A similar diversity of reaction products is obtained by nitrating decane, hexadecane, and octadecane at 160–180°C. The tabulated data show that a high ratio of nitric acid to paraffin results in the preponderant formation of polynitro compounds and fatty acids. When the acid:paraffin ratio is reduced to 1:2, it is found that only 42 per cent of the paraffin has been used up and the principal products are mononitrododecanes. Some of the

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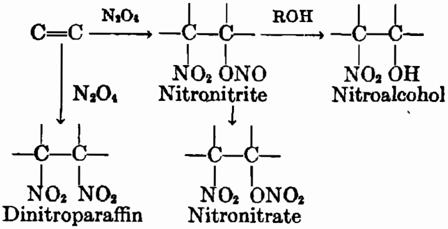
[1] GRUNDMANN, *Die Chemie*, **56**, 159 (1943).

paraffin (up to 19 per cent, depending on conditions) is destroyed through oxidative reaction.

Liquid-phase Nitration of Olefins. Although this reaction has been known for some time, it had never been of any preparative value until the work of Levy and Scaife,[1] who showed that under the proper conditions the work could be carried out safely and products could be obtained in good yield. Nitrogen dioxide is the nitrating agent, and air is added to oxidize any nitric oxide to the dioxide. The initial products are the dinitroparaffin and a nitronitrite. The latter is unstable and is partially oxidized to the stable nitronitrate by the air. The remaining nitronitrite is converted to the nitroalcohol by treatment of the reaction product with water or ethanol before distillation.

REACTION OF OLEFINS WITH NITROGEN DIOXIDE



The reactions are carried out by the slow addition of olefin to the nitrogen dioxide at temperatures of −10 to +25°C. The use of ether as a solvent minimizes oxidative side reactions. Although ethylene reacts slowly, higher olefins react more rapidly and molar equivalents can be made to react completely in 1–2 hr. Total yields of separated products are 65–85 per cent.

Nitration of Acetylene. The reaction of acetylene with nitric acid yields tetranitromethane, a compound that is useful in increasing the cetane number of diesel fuels and has interesting properties as a military explosive. In the first step of the process, acetylene is allowed to react at 50°C with highly concentrated nitric acid containing mercury nitrate in a reactor provided with cooling coils and a thermostat. At first, a solution of trinitromethane (nitroform) in 85 per cent HNO_3 containing NO_2 results, while CO_2 and NO_2 are generated as waste gases. In the second step, sulfuric acid is added to the solution, and upon heating, the nitroform is converted to tetranitromethane (TNM), which separates from the mixed acid. The resulting TNM, containing some nitric acid and nitrogen dioxide, is purified largely by a sulfuric acid rinse to give a product melting at 13.8–14.0°C.

[1] LEVY and SCAIFE, *J. Chem. Soc.*, **1946**, 1093.

In this process, the main reaction proceeds according to the following equations and gives a yield of about 60 per cent:

$$\begin{aligned}
&HC{\equiv}CH + 2HNO_3 \rightarrow (NO_2)_2CH{-}CHO + H_2O \\
&(NO_2)_2CH{-}CHO + HNO_3 \rightarrow (NO_2)_3C{-}CHO + H_2O \\
&(NO_2)_3C{-}CHO + 2HNO_3 \rightarrow (NO_2)_3C{-}COOH + H_2O + 2NO_2 \\
&(NO_2)_3C{-}COOH \rightarrow (NO_2)_3CH + CO_2 \\
&(NO_2)_3CH + HNO_3 \rightarrow (NO_2)_4C + H_2O \\
&HC{\equiv}CH + 6HNO_3 \rightarrow (NO_2)_4C + CO_2 + 4H_2O + 2NO_2 \text{ (over-all)}
\end{aligned}$$

A by-reaction (about 40 per cent) leads to the total oxidation of acetylene according to the following equation:

$$HC{\equiv}CH + 10HNO_3 \rightarrow 2CO_2 + 6H_2O + 10NO_2$$

VI. NITRATE ESTERS

Nitrate esters are prepared by the reaction of nitric acid and alcohol:

$$ROH + HNO_3 \rightarrow RONO_2 + H_2O$$

The nitrates of polyhydroxy compounds such as glycerol, pentaerythritol, and cellulose find extensive use as propellants and explosives. Cellulose nitrate is of course also widely used in the plastics and lacquer industries. Certain nitrates are used in the field of medicine as blood-pressure depressants. Although glyceryl trinitrate and cellulose nitrate are commonly called nitroglycerine and nitrocellulose, respectively, they are really not nitro compounds. The term nitro compounds should be reserved for compounds having the nitro group bound to carbon, whereas nitrate esters have their nitro group bound to oxygen.

The most commonly used nitrating medium is mixed acid, i.e., nitric and sulfuric acid mixtures, although mixtures of nitric with phosphoric acid, with acetic anhydride, and 100 per cent nitric acid are also used. The reaction usually proceeds readily at room temperature, and external cooling is frequently necessary to remove the heat of the reaction.

A fundamental difference between nitrate ester formation and nitration to form nitro compounds is the fact that the former is reversible whereas the latter is not. Thus a highly nitrated cellulose, say 13 per cent N, when immersed in a nitrating bath which, according to Fig. 4-4, gives a product of 11 per cent N, would become denitrated so that its nitrogen content would be reduced to 11 per cent. The nitrogen content depends only upon the composition of the medium. The same result will be obtained whether one starts with completely nitrated cellulose or with unnitrated cellulose, provided that the mixed acid is in sufficiently large excess so that its composition is not affected by the nitration process. The processes of nitration and denitration are special cases of the reactions of esterification and hydrolysis. Each is reversible, and one is the reverse of the other.

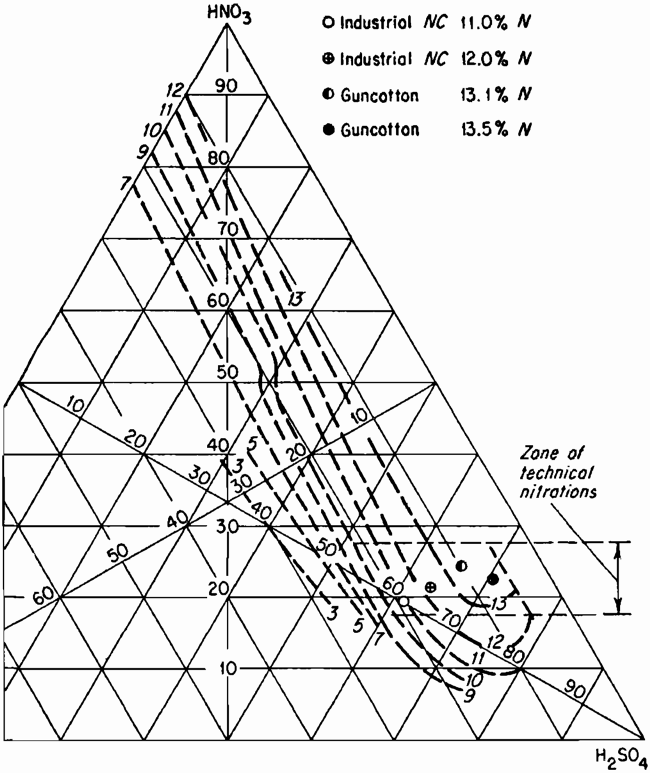
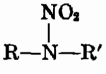


FIG. 4-4. Lines of constant nitrogen for nitrocellulose prepared in mixed acid. The dashed lines are lines of constant degree of nitration, namely, 3, 5, 7, 9, 10, 11, 12, and 13 per cent N. These lines are almost parallel to the lines of constant water concentration except in the regions of high sulfuric acid concentration at the lower right-hand corner. The zone of technical nitration is also indicated. The choice of composition for technical nitration in this concentration area is probably dictated by the economics of the recovery of spent acids. (*F. D. Miles, "Cellulose Nitrate," Interscience Publishers, Inc., p. 66, 1955.*)

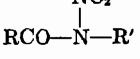
VII. N-NITRO COMPOUNDS

The N-nitro compounds include the nitramines, which have the structure (*A*), and the nitramides, which have the structure (*B*),

(*A*)



$$\begin{array}{c} NO_2 \\ | \\ R\text{—}N\text{—}R' \end{array}$$

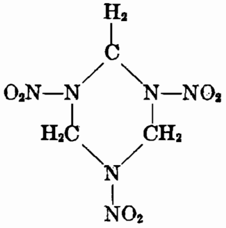


$$\begin{array}{c} NO_2 \\ | \\ RCO\text{—}N\text{—}R' \end{array}$$

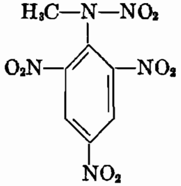
(*B*)

where R is an alkyl or aryl group and R′ is H, alkyl or aryl. The primary nitramines and nitramides are those in which R′ is H. N-nitro compounds find their greatest use as explosives and propellants. Trimethylenetrinitramine which is known as RDX is used as an explosive as is 2,4,6-

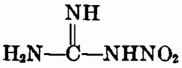
trinitro-N-nitro-N-methylaniline which is known as tetryl. Nitroguanidine is used in solid propellant formulations.



RDX



Tetryl



$$H_2N{-}\overset{\overset{\Large NH}{\|}}{C}{-}NHNO_2$$

Nitroguanidine

Methods of Preparation. Primary nitramines cannot be prepared by the direct nitration of primary amines. Because of their sensitivity toward acid, they probably do not survive in the strongly acidic environment of the nitration. They are generally made by alkaline hydrolysis of nitramides.

$$\begin{aligned}&RCONHCH_3 \xrightarrow{HNO_3} RCON(NO_2)CH_3 \xrightarrow{OH^-}\\&RCOOH + HN(NO_2)CH_3\end{aligned}$$

The nitramides are readily prepared by nitration of the amide with 100 per cent nitric acid or with nitric acid, acetic anhydride, acetic acid mixture.

Primary nitramines can also be prepared from the appropriate urethane

$$CH_3NH_2 \xrightarrow{ClCOOEt} \underset{\text{(Urethane)}}{CH_3NHCOOEt} \xrightarrow{HNO_3} CH_3N(NO_2)COOEt \xrightarrow{NH_3} CH_3NHNO_2 + NH_2COOEt$$

Secondary nitramines are prepared by the nitrolysis of secondary amides or of N,N-dialkyl ureas

$$RCON(CH_3)_2 \xrightarrow{HNO_3} RCOOH + (CH_3)_2NNO_2$$

$$R_2NH \xrightarrow{RCNO} \underset{\text{Dialkyl Urea}}{R_2NCONH_2} \xrightarrow{HNO_3} \underset{\textit{sec}\text{-Nitramine}}{R_2NNO_2}$$

In an interesting series of papers, G. Wright and coworkers[1] showed that nitramines can be obtained directly from secondary amines by using a nitrating mixture which contains chloride ions. Thus by treating the amine nitrate with acetic anhydride containing zinc chloride, the nitramines of dimethylamine, diethylamine, piperidine, and morpholine were obtained in yields of 60–70 per cent.

Aromatic nitramines undergo a rearrangement in which the nitro group migrates to the benzene ring. Such a rearrangement is believed to occur in the synthesis of tetryl, which is made by the nitration and nitrolysis

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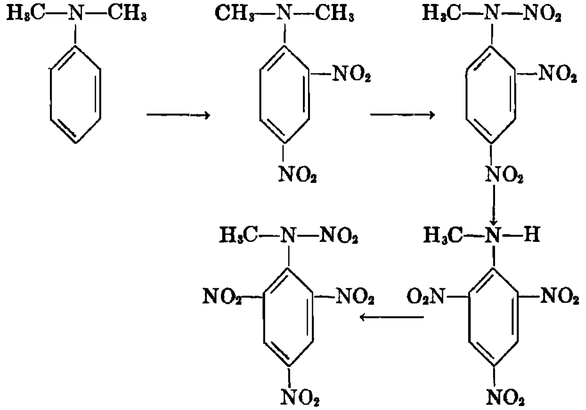
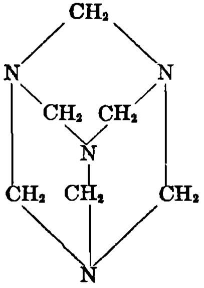
[1] WRIGHT et al., *Can. J. Research*, **26**, 89, 114 (1948).

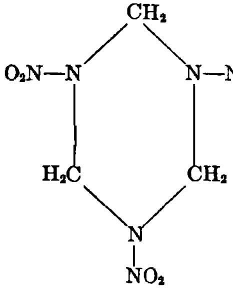
of dimethylaniline with mixed acid. The reaction steps are as follows:



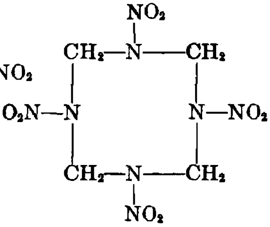
The earlier process for making RDX consisted of reacting hexamine (hexamethylenetetramine) or its dinitrate salt with 98–100 per cent nitric acid. The yields of this method are not good because the formation of RDX is accompanied by the formation of formaldehyde, which is oxidized by the nitric acid. Greatly improved yields (70–80 per cent) can be obtained by means of the Bachman process,[1] which employs hexamine, 98 per cent nitric acid, ammonium nitrate, and acetic anhydride. In the Bachman process a by-product having the structure I is also formed in yields up to 10 per cent. The mechanism of these reactions is not thoroughly understood.



Hexamine



RDX



I

VIII. THERMODYNAMICS OF NITRATIONS

By Cyrus G. Dunkle[2]

The nitration reaction is highly exothermic. The heat released, for example, in nitration of 1 lb of benzene is comparable to that released on

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[1] Bachman and Sheehan, *J. Am. Chem. Soc.*, 71, 1842 (1949).

[2] Picatinny Arsenal, Dover, N.J.

condensation of 1 lb of steam. *The heat problem is accentuated because of the heat of dilution of the nitrating acid and the low heat capacity of the medium.* A study of the thermal properties of nitrating acids is consequently essential for an adequate understanding of this unit process. The chemical engineer must, moreover, know how to develop and use thermodynamic data in designing nitrating equipment and providing safe and efficient operations.

A convenient function to use in such calculations is the enthalpy (H), sometimes called the heat content. This is a characteristic function; i.e., it has a definite value at any given state of a system. Its value is determined entirely by the temperature, pressure, composition, and any other thermodynamic coordinates concerned. The engineer is interested, however, not in the absolute value of H in any state but in its change ΔH, when the system passes from one state to another. The value of ΔH is determined solely by the magnitudes of H in the initial and final states and is not affected by any process through which the system passes from one to the other. In an exothermic change, the enthalpy decreases. The magnitude of the decrease equals that of the heat evolution, but this is true only when the reaction proceeds without performance of useful work and when the system is brought back to the initial temperature and pressure.

The assumption that these conditions hold is implicit in the usual manner of writing thermochemical equations, in which ΔH is understood to mean the heat actually absorbed in the reaction of the number of gram-formula weights indicated. For instance, the formation of benzene from its elements is written:

$$6C_{(\text{diamond})} + 3H_{2\,(\text{gas})} \rightarrow C_6H_{6(\text{liquid})} \qquad \Delta H_{295°\text{K}} = +9.7 \text{ kg-cal}$$

This indicates reaction of 6 g atoms or 72.1 g of carbon and 3 moles or 6 g of hydrogen to form liquid benzene. The enthalpy change as written is taken to mean that these quantities in reacting at constant pressure and at a constant temperature of 295°K (22°C or 71.6°F) absorb 9.7 kg-cal of heat from their surroundings. The positive enthalpy change indicates an endothermic reaction. Nitration, on the other hand, as already noted, is strongly exothermic and the enthalpy change is negative.

Heat of Nitration. The nitration reaction must be controlled by systematic cooling designed to withdraw the energy evolved. When all the energy set free by an exothermic reaction is forced to appear as heat, the quantity of it lost to the cooling mechanism equals the decrease in enthalpy:

$$Q = -\Delta H$$

Here Q, the heat of reaction, represents the total amount of heat lost by the reacting system from the start of the reaction till the products return to the initial temperature and pressure of the system.

The foregoing relationships enable the heat of any reaction to be calculated if the heats of formation of the reactants and products are known. For example, in the following equation for the nitration of benzene, heats of formation Q_f of the compounds concerned, in kilogram-calories per mole, are given immediately below their formulas:

$$\begin{array}{lcccccc} & C_6H_6 & + & HNO_3 \rightarrow & C_6H_5NO_2 & + & H_2O \\ Qf: & -9.7 \text{ kg-cal} & & +41.5 \text{ kg-cal} & -2.3 \text{ kg-cal} & & +68.4 \text{ kg-cal} \end{array}$$

Comparison of totals on both sides indicates that, in the nitration of a mole of benzene, $Q = -\Delta H = +34.3$ kg-cal. Since its molecular weight is 78.1, this heat evolution is equivalent to 439.2 cal per g of benzene or, multiplying calories per gram by the conversion factor 1.8, equals 790.6 Btu per lb. These are different ways of expressing the heat of reaction, in this case the *heat of nitration.* Heats of nitration of the more important classes of organic compounds are listed in Tables 4-10 to 4-12 (pp. 93-95).

This heat evolution is based, of course, on existence of both reactants and products in the "standard state," in this case that of the pure unmixed liquids at 22°C, or 71.6°F, and 1 atm pressure. Their actual state is usually far different.

Thermal Properties of Nitration Acids. *Heats of Solution.* To determine the heat evolved during the actual process of nitration of a hydrocarbon by mixed acids, it is necessary to consider not only the heat of nitration but also various heats of solution. These may be obtained from the enthalpy chart developed by McKinley and Brown[1] (Fig. 4-5). For each of the three components, the enthalpy is taken as zero at the standard state, consisting of the pure liquid component at a temperature of 32°F and a pressure of 1 atm. Plotted against the same abscissa but against different ordinates are the specific heat data for the system. From this figure, containing both 32°F relative enthalpies and specific heats, the enthalpy of any liquid mixtures of these components at ordinary temperatures can be readily calculated by reading the desired relative enthalpy at 32°F and the specific heat from the chart.

The location of all the relative enthalpy curves below zero shows that mixing of any two or all three of the pure liquids in any proportion involves decrease of enthalpy and hence evolution of heat. The negative values of the intercepts of all the mixed-acid curves on the 100 per cent total acid ordinate indicate that some heat is evolved even when the pure acids are mixed without any water present. Dilution with water then liberates an additional quantity of heat, the *heat of solution.*

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[1] McKinley and Brown, *Chem. Met. Eng.*, **49**, 142 (1942).

While the enthalpy curves of Fig. 4-5 show minima near 60 per cent total acid, there is still a decrease on forming more dilute solutions, for the dilu-

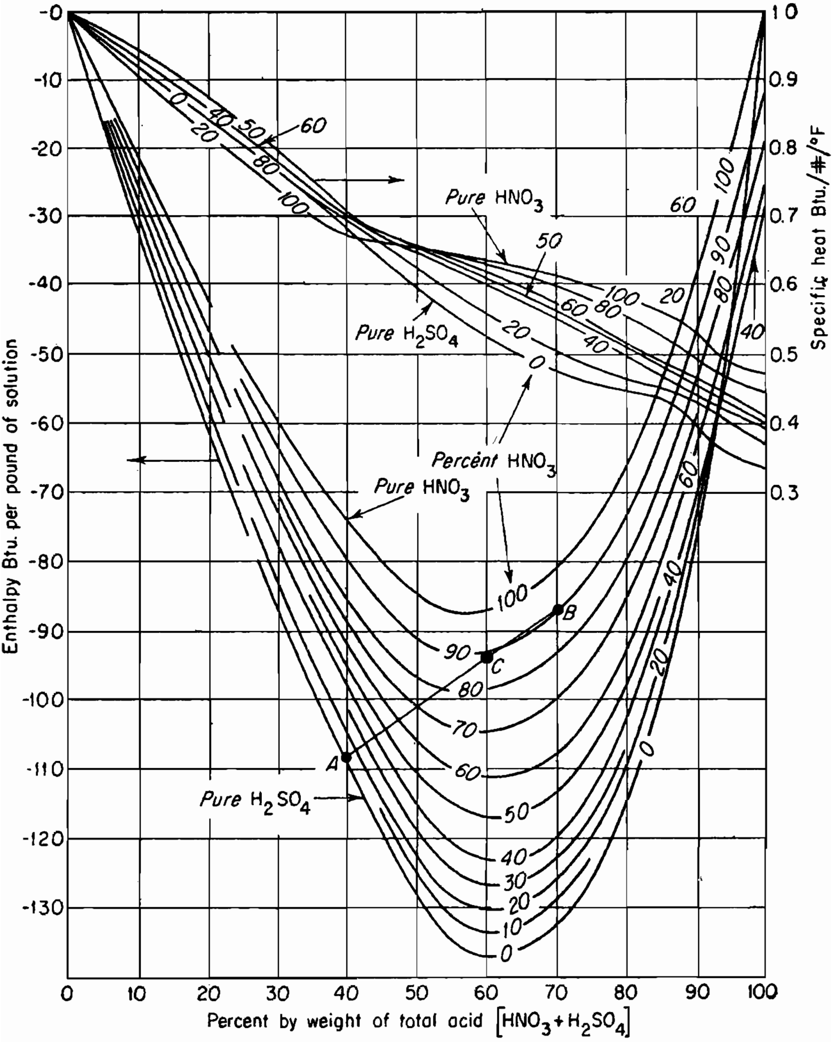

FIG. 4-5. Enthalpy of nitric acid, sulfuric acid, and water mixtures. The ordinate of Fig. 4-5 is enthalpy in "Btu per pound of solution," and its abscissa is "per cent by weight of total acid in mixed-acid solution." The enthalpy for a specific composition is obtained by interpolation between the lines of indicated nitric acid composition, being based on anhydrous $HNO_3 + H_2SO_4$. For example, the line of 60 per cent HNO_3 represents the enthalpy at 32°F of all mixtures of water with an acid containing 60 parts nitric acid to 40 parts sulfuric acid on the basis of anhydrous acid ($HNO_3 + H_2SO_4$).

tion itself increases the quantity of the mixture. To illustrate, consider initially 10 lb of a mixed acid of the following composition:

HNO_3, 48%; H_2SO_4, 32%; H_2O, 20%

$$HNO_3 \text{ on anhydrous or water-free basis} = \frac{48}{80} \times 100 = 60\%$$

Total acid = 80%

Read from the chart at 80 per cent on the abscissa and on the 60 per cent HNO_3 curve $H = -93$ Btu per lb of solution. The 10 lb of solution thus has an enthalpy of -930 Btu at 32°F.

Since the solution contains 8 lb acid and 2 lb water, the addition of 15 lb water will increase its total to 17 lb as against 8 lb anhydrous acid. The solution so diluted contains 32 per cent total acid, and its enthalpy at 32°F is -76 Btu per lb. However, there are now 25 lb of solution and the total enthalpy has decreased from -930 Btu to -1900 Btu. The heat evolution per pound of the original mixed acid on diluting to this extent equals the decrease in H divided by the original weight:

$$Q_s = -\Delta H = \frac{1900 - 930}{10} = 97 \text{ Btu per lb}$$

This can be considered the heat of solution of 1 part of the original mixed acid in 1.5 parts of water by weight.

Heats of Dilution. Diluting with an additional 75 lb water will produce 100 lb dilute solution with a total acid content of 8 per cent and an enthalpy of -21 Btu per lb, or a total enthalpy of -2100 Btu. Hence the total heat evolution on diluting the original 10 lb to 100 is 115 Btu per lb. The straightness of the enthalpy curve between 8 and 0 per cent total acid shows that any further addition of water will not change the total enthalpy further. Hence 115 Btu per lb can be taken as the *heat of dilution* of the mixed acid at 32°F, the heat evolved on diluting it at this temperature to zero acid concentration.

To find heats of dilution at other temperatures, it is necessary to consider the relationship $\Delta H = C_p \Delta t$, where ΔH represents the increase in enthalpy, C_p is the specific heat at constant pressure, and Δt is the over-all increase in temperature. Furthermore, the enthalpy contributed by the diluting water is no longer zero and must be taken into account.

The specific heat of the original 10 lb of mixed acid just discussed is read from the 60 per cent HNO_3 curve of Fig. 4-5 as 0.52 Btu per lb of solution per degree Fahrenheit. Hence the enthalpy at 65°F,

$$H_{65°} = -93 + (65 - 32)0.52 = -75.8 \text{ Btu per lb}$$

The 10 lb of mixed acid, therefore, has at this temperature a total enthalpy of -758 Btu before diluting, and the 90 lb of diluting water at the same temperature contributes 90 Btu per °F above 32, or $+2970$ Btu. The total enthalpy before mixing is thus $+2970 - 758$, or $+2212$ Btu.

After diluting,

$$H_{65°} = -21 + (65 - 32)0.945 = +10.2 \text{ Btu per lb}$$

The enthalpy of the 100 lb diluted acid is 1020 Btu, and its decrease on dilution is 1192 Btu. The heat of dilution of the original 10 lb mixed acid at 65°F is then 119 Btu per lb.

Heats of dilution at 18°C, or 64.4°F, of mixed acids that contain various known percentages of sulfuric acid, nitric acid, and water were measured by Rhodes and Nelson,[1] and their data are represented graphically in Fig. 4-6. For an acid of 60 per cent HNO_3 or weight ratio H_2SO_4:HNO_3 of 40:60, the intercept on the ordinate representing 20 per cent water indicates a heat of dilution of about 115 Btu per lb, in fair agreement with the foregoing calculations. The curves of Fig. 4-6 show in an impressive manner the pronounced lowering of the heats of dilution as the nitration progresses and as the water content of the nitrating acid increases. It is clear that, at the start of the reaction, the total heat liberated per pound of nitro compound formed is relatively great. Furthermore, owing to the lower specific heats of the more concentrated acids (Fig. 4-5), there is greater danger of violent or explosive reactions during the early stages of nitration.

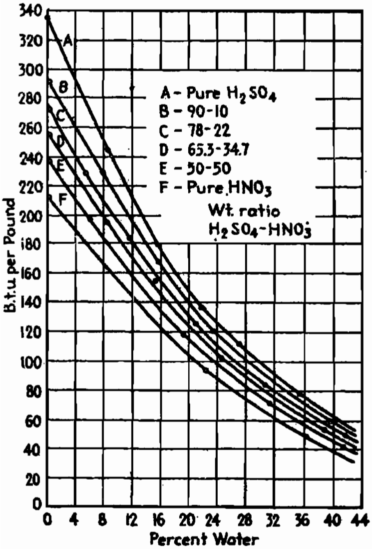

FIG. 4-6. Heats of dilution of mixed acid. Points on these curves indicate the heat of dilution per pound of acid of indicated H_2SO_4:HNO_3 weight ratio, containing the percentage of water shown on the abscissa. Heat evolved during actual nitration can be computed from data pertaining to composition of acids at the beginning and the end of reaction.

The curves of Fig. 4-6 indicate quite clearly why it is comparatively safe to make rapid nitrations at relatively high temperatures with spent acid or with nitric acid alone. The nitrating acids with lower heats of dilution and high heat capacity have an added economic advantage because of their lower boiling points. Smaller quantities of heat are, therefore, necessary for removal of the water of nitration in the integrated system.

Integrated Heats of Nitration. In the nitration of a hydrocarbon by means of a mixture of concentrated nitric and sulfuric acids, the total heat

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[1] RHODES and NELSON, *Ind. Eng. Chem.*, **30**, 648 (1938).

liberated is equal to the heat of solution of the initial mixed acid minus the heat of solution of the final spent acid minus the heat of solution of the nitric acid entering into reaction plus the heat of the nitration reaction. Although heats of nitration are relatively large, the control of the reaction is intimately related to the heats of dilution of the nitrating acid. The simplest way to integrate the heat effects involved is to sum up the enthalpies on both sides of the complete reaction equation by use of heats of nitration and the data of Fig. 4-5.

The method can be illustrated by use of typical operating data for the nitration of benzene in a Hough nitrator. The process follows that described as "indirect nitration" in Sec. IX. The Hough nitrator is characterized by two external tunnels, each of which is equipped with a stirrer. Circulation of cycle acid and fortified acid is up through the tunnels and by overflow through ports into the main body of the nitrator and past the cooling coils. The benzene to be nitrated is fed into unfortified cycle acid in the tunnels and floats above the cycle acid. The level of cycle acid or fortified acid is kept above the overflow level of the ports, and essentially it is acid which circulates through the tunnels as nitration proceeds. As soon as fortifying acid feed is begun into the tunnels, by the same method as the initial hydrocarbon feed, cycle acid is withdrawn through the bottom of the nitrator. The level in the nitrator is thus maintained constant. The cycle acid withdrawn contains a small amount of nitrobenzene and is later returned to the process as cycle acid for succeeding nitrations. A diagram of a Hough nitrator is shown as Fig. 4-7.

Based on a charge of 10,000 lb benzene, the weight of nitric acid required for nitration and the theoretical yields of nitrobenzene and water are calculated from the respective formula weights:

	C_6H_6 +	HNO_3 →	$C_6H_5NO_2$ +	H_2O
Formula wt:	78.1	63.0	123.1	18.0
Quantity, lb:	10,000	8,067	15,762	2,305

Since the reactants are cooked finally at 90°F, this is taken as the reaction temperature. An initial charge of 9,000 lb cycle acid

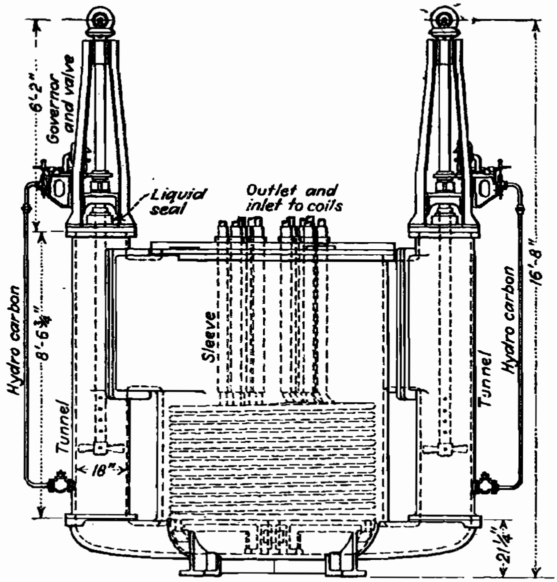
H_2SO_4	83.0%	$H_{32°} = -96$ Btu per lb
HNO_3	2.3%	$C_p = 0.44$ Btu per lb per °F
H_2O	14.7%	

$$H_{90°} = -96 + (90-32)0.44 = -70.5 \text{ Btu per lb } (-634{,}500 \text{ Btu})$$

was augmented by 23,300 lb mixed acid

H_2SO_4	62.8%	$H_{32°} = -31$ Btu per lb
HNO_3	36.1%	$C_p = 0.39$ Btu per lb per °F

$$H_{90°} = -31 + (90-32)0.39 = -8.4 \text{ Btu per lb } (-195{,}720 \text{ Btu})$$



Central Vertical Section

FIG. 4-7. Hough nitrator, cast iron, with external tunnels.

The composition which would be obtained by mixing these two acids can be deduced by summing up the quantities of the respective components, as given in the accompanying table.

Component	Quantity 9,000 lb cycle acid, lb	Quantity in 23,300 lb mixed acid, lb	Total quantity, lb	Composition obtained by mixing, %
H_2SO_4	7,470	14,632	22,102	68.4
HNO_3	207	8,411	8,618	26.7
H_2O	1,323	256	1,579	4.9

For a mixture of this composition:

HNO_3 on anhydrous or water-free basis = 28.05%

Total acid = 95.1%

$H_{90^\circ} = -49 + (90 - 32)0.405 = -25.5$ Btu per lb (−823,650 Btu)

Since the enthalpies of the two acid solutions separately total −830,220 Btu, this would indicate a slight cooling effect on mixing them together, but the difference is within the range of uncertainty of the graph readings.

Neglecting decomposition and losses, it is easy to compute the changes brought about in the proportions of the components of the nitrating acid during the reaction, as given in the accompanying table.

Component	Initial quantity, lb	Change due to nitrating reaction, lb	Quantity in spent acid, lb	Composition of spent acid, %
H_2SO_4	22,102	....	22,102	83.3
HNO_3	8,618	−8,067	551	2.1
H_2O	1,579	+2,305	3,884	14.6

For the spent acid:

HNO_3 on anhydrous or water-free basis = 2.4%

Total acid = 85.4%

$H_{90°} = -96 + (90 - 32)0.44 = -70.5$ Btu per lb (−1,870,859 Btu)

The sum of the enthalpies of the nitrating acids was −830,220 Btu. The heat evolution due to changes in acid concentration during the nitrating reaction, including any thermal effect of mixing of the acids, is, therefore, 1,870,859 minus 830,220, or 1,040,639 Btu.

The quantity of heat which must be removed during the nitration as actually carried out is obtained by adding this value to the heat of nitration. The latter was found to be 790.6 Btu per lb of benzene, or 7,906,000 Btu at 71.6°F. This value can be corrected to 90°F for consistency even though the correction is, in this instance, negligible. The specific heats of benzene, nitric acid, nitrobenzene, and water throughout this temperature range average 0.41, 0.42, 0.33, and 1.0 Btu per lb per °F, respectively. On heating from 71.6 to 90°F, therefore, the quantities concerned in the reaction, the enthalpy increases are, respectively, 75,440; 62,341; 95,706; and 42,412 Btu. Comparing the totals on the left and right sides of the reaction equation indicates an increment of +337 Btu in the enthalpy of the reaction due to this temperature increase. The heat of nitration at 90°F is thus 7,906,000 minus 337, or 7,905,663 Btu. Adding the 1,040,639 Btu evolved through changes in acid concentration gives a total of 8,946,302 Btu actually evolved during the nitration of 10,000 lb benzene by mixed acid at 90°F, or 894.6 Btu per lb of benzene as against 790.6 for the uncorrected heat of nitration.

Thermal Data Relating to the Preparation and Use of Nitro Compounds. From the previous paragraphs, it has become apparent that the nitration process is accompanied by the development of a considerable amount of heat. A discussion of nitration processes would, therefore, be incomplete without some consideration of the principal thermal factors involved in this reaction.

Garner and Abernethy found (Fig. 4-8) that certain regularities exist between the heats of formation and nitration of the benzene, toluene, and phenol series.[1] Their values of heats of nitration were calculated by use of the heat of formation of nitric acid at infinite dilution, 48.8 instead of the 41.5 kg-cal per mole heat of formation of the pure substance. Hence they give the heat of nitration of benzene as 27.0 instead of 34.3 kg-cal per mole (Table 4-10).

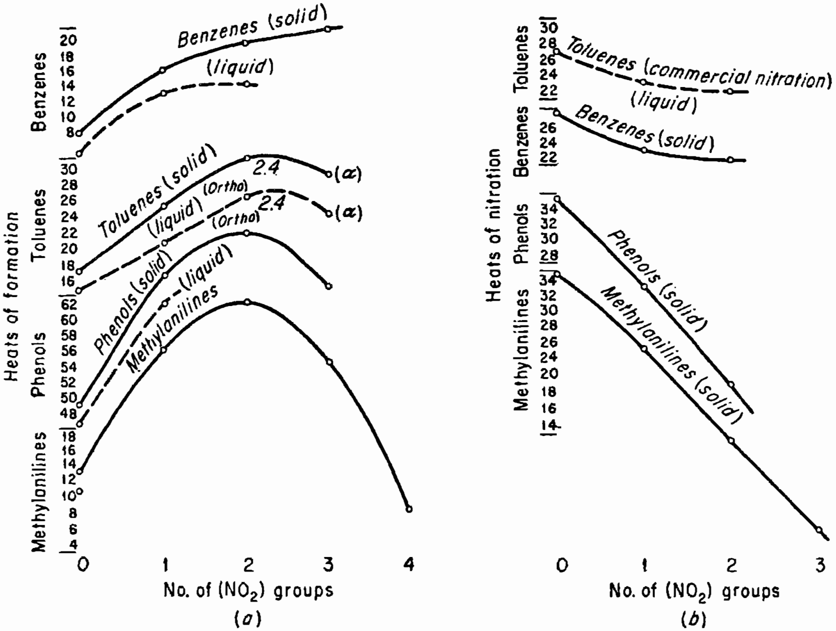


FIG. 4-8. Heats of (*a*) formation (kg-cal per mole) and (*b*) nitration (kg-cal per mole).

The basic heat of combustion values of Garner and Abernethy were confirmed in general by Rinkenbach of Picatinny Arsenal.[2] The heats of formation at constant pressure derived from these (Tables 4-10 to 4-12) are recalculated by use of Rinkenbach's more accurate basic data:

$R = 1.9885$

$T = 295°\text{K}$

Q_f of H_2O liq. = 68.4 kg-cal per mole

Q_f of CO_2 from diamond = 94.4 kg-cal per mole

Q_f of HNO_3 = 41.5 kg-cal per mole

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[1] GARNER and ABERNETHY, *Proc. Roy. Soc.* (*London*), **99A**, 213 (1921).

[2] RINKENBACH, *J. Am. Chem. Soc.*, **52**, 115 (1930).

TABLE 4-10. HEATS OF COMBUSTION, FORMATION, NITRATION, AND CRYSTALLIZATION
Benzene Series and Lower Paraffins

Substance	Mol. wt	Heat of combustion, kg-cal/mole		Heat of formation, kg-cal/mole		Heat of nitration, kg-cal/mole	Heat of crystallization, kg-cal/mole
		Const. vol.	Const. press.	C amorph.	C diamond		
Benzene	78	780.4	781.3	+ 6.5	−9.7	+27.0	2.35
Nitrobenzene	123	739.9	739.7	+13.9	−2.3	+25.6	2.78
o-Dinitrobenzene	168	703.8	702.6	+16.8	+0.6		
m-Dinitrobenzene	168	700.6	699.4	+20.0	+3.8	+21.4	4.87
p-Dinitrobenzene	168	693.7	692.5	+26.9	+10.7		
1,3,5-Trinitrobenzene	213	665.6	663.4	+21.8	+5.6		
1,2,4-Trinitrobenzene	213	675.9	673.7	+11.5	−4.7		
Methane* (g)	16	211.7	212.9	+21.0	+18.3	+30.3§	
Ethane* (g)	30	371.4	372.5	+26.5	+21.1	+40.2§	
Propane* (g)	44	528.8	530.6	+34.3	+26.2		
n-Butane* (g)	58	685.9	688.0	+42.4	+31.6		
i-Butane* (g)	58	684.2	686.3	+44.1	+33.3		
Nitromethane*	61	170.2	169.8	+29.9	+27.2		
Nitroethane†	75	325.6	325.4	+39.8	+34.4		
1-Nitropropane†	89	481.1	481.2	+44.1	+41.4		
2-Nitropropane†	89	477.3	477.5	+47.8	+45.1		
1-Nitrobutane†	103	637.2	637.6	+58.6	+47.8		
2-Nitrobutane†	103	633.6	634.0	+62.2	+51.4		
1,1-Dinitropropane†	166	447.2	446.3	+44.8	+42.1		
1,3-Dinitropropane†	166	434.5	433.6	+57.6	+54.9		
2,2-Dinitropropane† (s)	166	443.1	442.2	+48.9	+46.2		
Trinitromethane†	151	112.1	109.9	+21.8	+19.1		
Tetranitromethane‡	196	106.4	102.9	−5.7	−8.4		

* "Selected Values of Chemical Thermodynamic Properties," U.S. National Bureau of Standards.

† HOLCOMB and DORSEY, *Ind. Eng. Chem.*, **41**, (12), 2788–2792 (1949).

‡ ROTH and ISECKE, *Ber. deut. chem. Ges.*, **77B**, 537–539 (1944).

§ Calculation of heats of nitration of methane and ethane based on HNO_3 liq., heat of formation 41.5 kg-cal per mole.

g = gaseous, *s* = solid, others are liquid.

It is evident that the heats of nitration decrease with the increase in the number of nitro groups, but the heats of formation tend to a maximum for the second or third member of the series and then diminish. Values of heats of formation of picric acid and of α-TNT given by Rinkenbach, however, and corroborated by later determinations, indicate a leveling off rather than a decrease. Possibly here also, as in the benzene series, the maximum may appear at the fourth member of the series and a decline show up if more highly nitrated derivatives could be obtained. The following paragraphs, abstracted from the paper of Garner and Abernethy, note some interesting relationships.

TABLE 4-11. HEATS OF COMBUSTION, FORMATION, NITRATION, AND CRYSTALLIZATION
Phenol Series

Substance	Mol. wt	Heat of combustion, kg-cal/mole		Heat of formation, kg-cal/mole		Heat of nitration, kg-cal/mole	Heat of crystallization, kg-cal/mole
		Const. vol.	Const. press.	C amorph.	C diamond		
Phenol	94	736.9	737.5	+50.2	+34.0	+35.0	2.34
o-Nitrophenol	139	689.9	689.4	+64.3	+48.1	+24.5	4.30
p-Nitrophenol	139	687.0	686.5	+67.1	+50.9		
2,4-Dinitrophenol	184	650.2	648.7	+70.2	+54.5	+12.9	
Picric acid	229	623.7	621.2	+64.0	+47.8		
	...	615.5*	613.0*	+72.2*	+56.0*		

* RINKENBACH, *J. Am. Chem. Soc.*, **52**, 115 (1930).

In the paraffin, benzene, toluene, and phenol series, it is clear (Tables 4-10 to 4-12) that the nearer the nitro groups are to one another in the benzene ring, the greater is the strain in the molecule and the lower the heat of formation. Thus *o*-dinitrobenzene and the ortho-mononitro compounds of the toluene and phenol series have the smallest heats of formation. The differences between the ortho and the para derivatives are, however, greatest for the benzene and least for the phenol series. In the case of di- and trinitro derivatives also, the proximity of the groups has the same effect.

Some regularities have been observed in the heats of formation of members of the toluene series. Thus there appears to be a definite *increase* in the internal energy (lower value for heat of formation) associated with groups in the ortho position, and especially when nitro groups are ortho to one another. Thus, of the isomeric trinitrotoluenes, β-(2,3,4) trinitrotoluene (Table 4-12) has the lowest heat of formation, i.e., contains the greatest internal energy per gram, and α-(2,4,6) trinitrotoluene the highest heat of formation, i.e., contains the least internal energy per gram. If on detonation these two substances gave the same products of decomposition, β-trinitrotoluene would have an advantage over α-trinitrotoluene of 54 cal per g. For the same reason, the unsymmetrical trinitrobenzene should be a more powerful explosive than the symmetrical body. In general, the greater the number of adjacent groups in a molecule of high explosive, the greater will be the heat of detonation. There are, however, practical

TABLE 4-12. SUMMARY OF HEATS OF COMBUSTION, FORMATION, AND NITRATION PER MOLECULE, AND FIGURES OF INSENSITIVENESS

Substance	Mol. wt	Heat of combustion kg-cal/mole		Heat of formation kg-cal/mole		Heat of nitration, kg-cal/mole			Heat of crystallization, kg-cal/mole	Gas evolution at 120°C, cc/40 hr	Figure of insensitiveness (picric acid = 100)
						One NO₂ group inserted in the following positions relative to existing NO₂ groups					
		Const. vol.	Const. press.	C amorph.	C diamond	Ortho position	Meta position	Para position			
Toluene	92	935.9	937.1	+16.2	− 2.7	+25.3	+29.4	+33.7	2.4		
Mononitrotoluene:											
Ortho (liquid)	137	897.0	897.2	+21.9	+ 3.0	2:3 + 22.9	2:4 + 29.7 2:6 + 28.2	2:5 + 27.3			
Meta (liquid)	...	892.9	893.1	+26.6	+ 7.1	2:3 + 18.8 3:4 + 18.5	3:5 + 25.4	2:5 + 23.2	4.3		
Para	...	888.6	888.8	+30.3	+11.4	3:4 + 14.2	2:4 + 21.3				
Dinitrotoluene:											
2:3	182	860.5	859.6	+25.3	+ 6.4	2:3:4 + 12.1	2:3:5 + 12.2	2:3:6 + 19.7 2:3:5 + 21.2			
2:4	...	853.7	852.8	+32.1	+13.2	3:4:6 12.6 2:3:4 5.3	2:4:6 17.5	3:4:6 12.6	4.80		
2:5	...	856.1	855.2	+29.7	+10.8	2:3:5 16.8 3:4:6 15.0 2:3:6 15.3	2:3:5 16.8 3:4:6 15.0 2:3:6 15.3				
2:6	...	855.2	854.3	+30.6	+11.7	2:3:6 14.4	2:4:6 19.0	2:3:6 14.4			
3:4	...	860.8	859.9	+25.0	+ 6.1	2:3:4 12.4 3:4:5 17.2	3:4:6 19.7	3:4:6 19.7			
3:5	...	853.9	853.0	+31.9	+13.0	2:3:5 14.6 3:4:5 10.3	....	2:3:5 14.6			
Trinitrotoluene:											
α (2:4:6)	227	822.5	820.7	+30.0	+11.1	....	....	....	4.88	0.08	114
	...	817.2*	815.3	+35.4	+16.5						
β (2:3:4)	...	834.7	832.9	+17.8	− 1.1	....	....	....	....	0.73	92
γ (3:4:6)	...	827.4	825.6	+25.1	+ 6.2	....	....	....	....	1.40	102
δ (3:4:5)	...	829.9	828.1	+22.6	+ 3.7	....	....	....	....	1.60	95
ε (2:3:5)	...	825.6	823.8	+26.9	+ 8.0	....	....	....	....	0.40	101
ζ (2:3:6)	...	827.1	825.3	+25.4	+ 6.5						

* RINKENBACH, *J. Am. Chem. Soc.*, **52**, 115 (1930).

limitations to this choice on account of the greater reactivity and lower stability of the less symmetrical nitro compounds as well as difficulties in synthesis.

IX. PROCESS EQUIPMENT FOR TECHNICAL NITRATIONS

Types of Process Equipment. Nitrations, as technical industrial processes, have evolved from batch-type operations using stoneware vessels and hand operations to automatically controlled continuous-type processes carried out in gleaming stainless-steel vessels. The high heats of reaction and dilution involved in nitration, originally absorbed by placing the stoneware vessels in a water bath, are now taken up by coils or jackets cooled by refrigerated brine. Controls have evolved from none at all to completely automatic systems which may be so elaborate as to permit operation from remote locations. The idea of remote control has always appealed to the designer of equipment for the manufacture of hazardous, explosive compounds which often are the result of nitration processes.

It will be convenient to discuss technical nitrations from the standpoint, first, of batch processes and, second, of continuous processes. This is the historical order of development. However, it should not be concluded that batch processes have been rendered obsolescent by continuous ones or that they surely will be superseded. Each kind of process has advantages peculiar to itself.

In broad terms, batch processes have the following advantages compared to continuous processes:

1. *Flexibility.* Batch-process equipment possesses general usefulness because each batch of material passing through the process is separate, or nearly separate, from batches which have preceded or which will follow it. It is usually easier to introduce process variations into a batch process than into a continuous one. Furthermore, batch-processing equipment is often of such general applicability that a given plant may be readily converted from production of one nitrated material to another. Beginning production of a new compound or pilot production is conveniently done by the batch process because of operating flexibility, even though the use of a continuous process may be planned for the completely developed process.

2. *Labor Usage.* For high rates of production when large batches are used the labor efficiency of a batch process may be just as good as that for a continuous process. This appears to be true for the large-scale industrial production of nitroglycerine and nitrotoluene, for example.

Continuous processes, in general, will be found to have the following advantages over batch processes:

1. *Lower Capital Costs.* For a given rate of production, the equipment needed for a continuous process is smaller than for a batch process. This

is usually the most striking difference between the two types of process. The reason for this is obvious. Since it is not necessary to accumulate material in a continuous process anywhere, the vessels are designed with capacities dictated by the rate of the reaction process step which they must accommodate. Alternatively, because of the relatively small size of continuous-process equipment, it is often possible and advantageous to use materials of construction which would be excessively high in cost for batch-scale equipment. Thus, for example, corrosion-resistant alloys such as the appropriate stainless steels may be used for a continuous plant, whereas ordinary mild steel may be dictated for a batch plant because of cost. In the case of the stainless steel, corrosion problems may be completely eliminated.

2. *Safety.* Because of the relatively small size of continuous-process equipment, there is less material in process at any time than at certain times in a comparable batch process. For example, at the completion of a batch-process nitration and during its normal separation of the product from spent nitrating acid, the entire batch of an often hazardous compound will be present in the equipment. In the continuous process, only as much material need be present in hazardous conditions as needed to gain sufficient reaction or process time. In the case of high explosives made by nitration, such as nitroglycerine, this inherent safety factor of a continuous process is very attractive.

3. *Labor Usage.* In the nitration field, a continuous process is usually a more efficient labor user than a batch process. This is particularly true for small- or medium-scale production and for hazardous products. Since continuous processing minimizes the amounts of material in process on the average, it is often possible to handle operations at one place that require physical separation in a batch process and hence require additional labor. The discrepancy in labor efficiency tends to disappear as the scale of operations increases.

Batch Nitration. Nitration is usually done in closed cast-iron or steel vessels. Modern practice is to use mild carbon steel. When nitrating with mixed acid (nitric-sulfuric), the life of such nitrators is satisfactory, and any short life failures can usually be traced to excessive water or to low actual nitric acid content in the waste acid. By experience, it has been found that, when manufacturing mononitrotoluene, as the water content of the waste acid increases above 26 per cent or the actual nitric falls below 2.5 per cent the rate of corrosion on mild steel becomes very rapid. Such considerations would have less importance if modern alloy steels could be justified for construction of the nitrator. In general, the nitrator consists of an upright cylindrical vessel containing some kind of cooling surface, a means of agitation, feed inlet or inlets, and product outlet lines. Most nitrators are also equipped with a large-diameter quick dumping line for emergency use if the reaction gets out of hand or the temperature rises because of failure of agitation, cooling, or otherwise. In such an emergency the contents of the nitrator may be dumped rapidly into a large volume of water contained in a "drowning tub." A common accessory for a nitrator is a suction line in the vapor space above the liquid charge to remove the acid fumes and oxides of nitrogen which may be liberated.

The two factors of prime importance in the design of nitrators are (1) the degree of agitation and (2) the control of temperature. Agitation generally must be very efficient, even violent, in order to obtain smooth reactions and to avoid local overheating which could occur if stagnant spots were to exist in the nitrator. This also means that the material fed to the nitrator is quickly and thoroughly mixed with the contents of the nitrator, and so local concentrations of reactants which could lead to local overheating do not occur.

Cooling or other temperature control in nitrators is generally accomplished by coils of tubes through which either cold water or brine for cooling may be circulated or hot water or steam for heating. For control of temperature in nitrations, a wall jacket is not usually efficient enough except in the case of vessels of very small capacity. The need for large cooling surface and for high velocity of cooling medium and nitrator contents past the surfaces dictates use of cooling tubes. The thermal effects which are encountered and the heat-transfer characteristics of the various materials involved are generally well known so that efficient cooling-system design calculations may be made by the engineer. A good and detailed discussion of the problems involved and the design of typical nitration equipment is given by Coulson and Warner.[1]

Probably the most common type of agitating system used in nitrators consists of a vertical shaft with one or more propellers mounted on it. This shaft propeller is mounted in the cylinder-shaped center of one or more banks of cooling coils. An actual cylindrical sleeve is sometimes mounted in the center of the coil banks to ensure that circulation of the nitrator contents is as desired. When reactant feed to the nitrator is from the top into the center of the agitator sleeve, circulation by the propellers is usually down through the center and around and up through the cooling coils. When the feed is beneath the liquid level, at the bottom of the sleeve, and cycle acid is used, circulation may be up through the sleeve and around and down through the banks of coils. Good mixing and efficient heat transfer are obtained by this "sleeve-and-propeller arrangement." When cycle acid is not used, circulation is down through the sleeve so that the hydrocarbon fed into the sleeve near the bottom is quickly dispersed in the mixed acid and immediately passes over the cooling coils.

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[1] A Problem in Chemical Engineering Design: The Manufacture of Mononitrotoluol," The Institution of Chemical Engineers, London, 1949.

In batch nitrations of hydrocarbons such as benzene or toluene, it has been common past practice to nitrate by using cycle acid, as previously described. In this procedure, common practice involved charging a sleeve-and-propeller agitator with cycle acid to above the level of the top of the cooling coils. Hydrocarbon was then floated in on top of the cycle acid. With the agitation system running, nitrating acid was fed into the nitrator in the cycle acid near the bottom of the sleeve under the propeller. This fortified cycle acid then reacted at the interface of the hydrocarbon and acid in the top of the nitrator. Feed of nitrating acid and circulation were continued until all the acid had been added. Nitration was then completed by allowing the temperature to rise and eventually to emulsify the nitrated product and acid. More modern practice for this type of hydrocarbon involves no cycle acid but consists of feeding the hydrocarbon under the surface of the nitrating acid in the bottom of the sleeve where agitation is very thorough. This is called "direct" nitration and is now considered more satisfactory, both from a production and safety standpoint, than the older "indirect" method.

Commercial nitrating operations generally include the separation of nitric and sulfuric acids, manufacture of nitric and sulfuric acids, and separation of the nitrated product from the spent acids. Product purifications by such unit engineering operations as washing, distillation, and crystallization are also commonly employed.

Continuous Nitration. The initial well-known applications of continuous procedures for the nitrations of polyhydric alcohols such as glycerine and hydrocarbons such as benzene were made in Europe. In the United States the scale of operation of batch nitrations had become so large, and the techniques for safe operation so well established, that there did not exist as strong compulsion toward continuous processes here as elsewhere. The methods used for continuous production of products which are liquid, and hence can be separated from other immiscible liquids such as spent nitrating acids by decanting procedures, as well as nitrations which are fast and do not therefore require long reaction-time allowances, were first developed. Later, equipment for more complex processes have been worked out. At present it is safe to consider that most nitrations could be handled by continuous procedures.

The actual nitration reactions in a continuous process are carried out in the same type of vessels as those used for batch nitrations, with the exceptions that an overflow pipe or weir arrangement is provided for the continuous withdrawal of products and that continuous feed of all reactants is provided. Schematic diagrams of two typical nitrators for continuous operation are shown in Figs. 4-9 and 4-10. Figure 4-9 shows the kind of nitrator designed for the German Schmid-Meissner system. In this apparatus the material to be nitrated is fed into the top of the nitrator and is

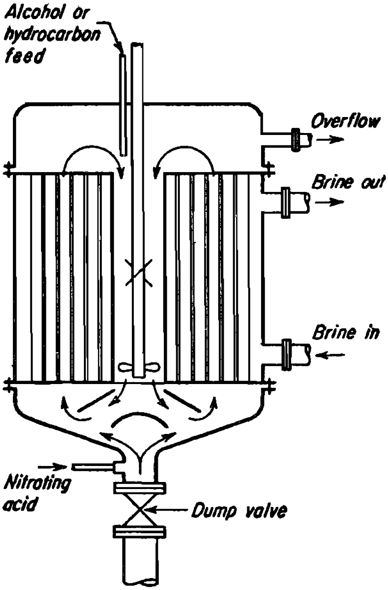


FIG. 4-9. Schmid nitrator.

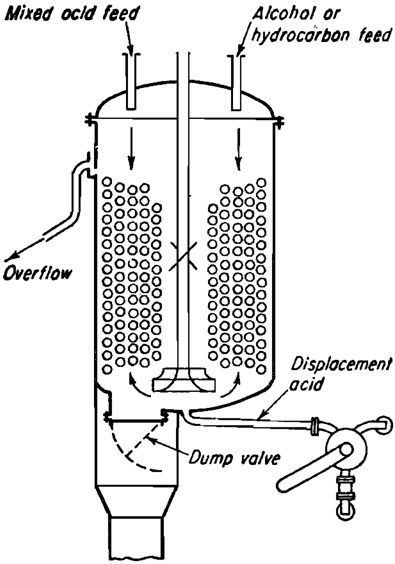


FIG. 4-10. Biazzi nitrator.

immediately drawn down through the sleeve and intimately and thoroughly mixed with the spent acid and reacting materials. In the bottom of the nitrator, fresh mixed acid is fed in and is immediately mixed with the other reactant by means of the high flow rate induced by the agitator and the baffles provided. The reacting materials then pass upward with high velocity through the tubes surrounded by refrigerated brine circulating in the jacket. Product and spent acid are withdrawn continuously from the nitrator through the overflow line.

Figure 4-10 shows a schematic diagram of the nitrating vessel designed by the Swiss firm of M. Biazzi. In this apparatus the turbine-type agitator provides intensive agitation. A vortex is formed in the center about the agitator shaft. The reactants, both of which are fed into the nitrator through the top, are immediately drawn into this vortex, thoroughly mixed, and circulated down through the center of the bank of cooling coils and back up through and around the coils. The high velocity imparted to the nitrator contents makes for efficient mixing and heat transfer.

In any continuous equipment, the designer must be careful to assure that no stagnant areas can exist. Also it is quite general to specify high finishes on the interior surfaces with complete freedom from surface pits or pockets which could trap product. It is especially desirable to have the apparatus completely drainable so that, if the contents must be dumped, no product contaminated with acid remains. Alternatively, upon shutdown of the equipment, it is common to displace all product from the apparatus by filling the nitrator from the bottom with spent or cycle acid. Only if the apparatus is completely free of traps or pockets can this displacement procedure be carried out with assurance that no nitrated product will be trapped and remain behind in the nitrator.

Continuous nitration demands accurate metering and control equipment. Such equipment as positive-displacement pumps, constant-head orifice flow controls, and rotameters are common accessories to continuous nitrators.

Safety measures which should be present in nitration operations are similar for both continuous and batch processes. It is common to provide for automatically stopping feed of the material to be nitrated in the event of an undue temperature rise in the nitrator, a failure of the refrigeration or brine circulation, or a failure of agitation. It is common to require that continuous observation of the nitrator temperature be maintained; the feed of reactant can then be conveniently controlled by a "dead-man" valve which can be kept open only by manual pressure. Solenoid-operated controls which are "fail-safe" are also commonly used. The expression "fail-safe" generally implies that the operation can be carried out only when all necessary services such as power, refrigeration, or agitation are functioning. For example, in the equipment designed by Biazzi for the nitration of glycerine (see Chap. 12), the glycerine-feed arm can be held in place, down over the nitrator-feed opening, only by an energized solenoid apparatus. Electric power failure then causes the solenoid coil to be deenergized, and when this happens the feed arm swings out of place and the feed of glycerine is cut off automatically.

To handle process variations such as those needed to accommodate slow reactions or those which require variations in temperature as the reaction proceeds, the practice is to multiply the reaction vessels and place them in series. By this means, successive vessels in a series may be operated at increasing temperatures, fortifying acid could be added part-way through the reaction, or other process variables could be introduced.

X. MIXED ACID FOR NITRATIONS

In order to comprehend the operations of a complete nitration plant, it is necessary to understand something of the processing of the mixed acid normally used, including its preparation, adjustment to the needs of the nitration, its handling as spent acid, and the disposal of the wastes recovered from it. Figure 4-11 shows the flow of acid in a typical acid operation. The compositions shown are those for mixed acids used to manufacture glyceryl trinitrate. The economics of acid operation are of great importance in the over-all operating costs of a nitration process.

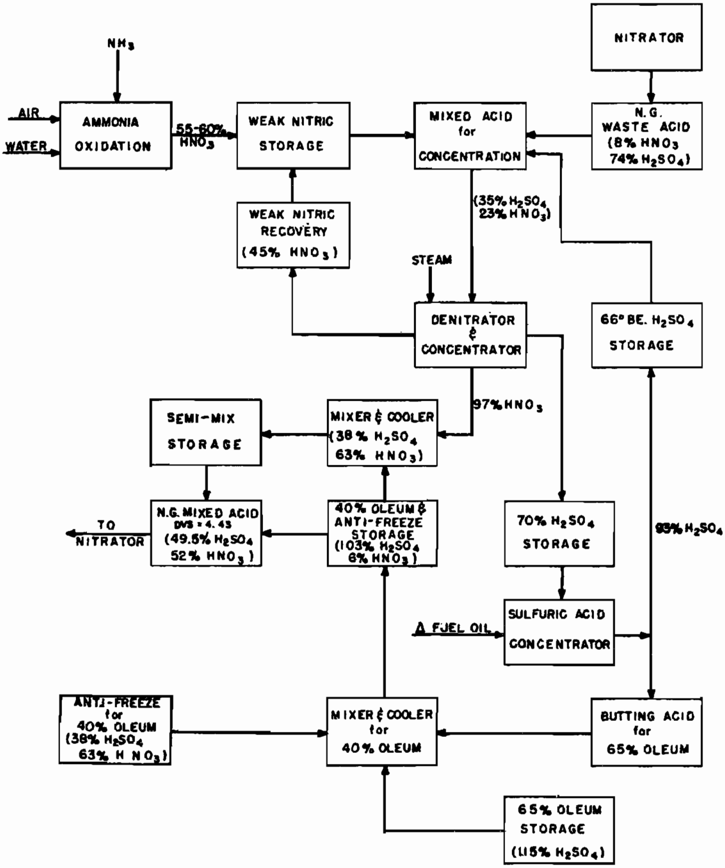


FIG. 4-11. Acid-operation flow chart.

Acid Processing. The materials entering the acid processing are 65 per cent oleum from a contact-process sulfuric plant, 56–60 per cent HNO_3 from an ammonia-oxidation plant, and spent acid from the nitration operation. The processing produces nitroglycerine mixed acid, concentrated HNO_3, and 93 per cent H_2SO_4. Normally the 93 per cent H_2SO_4 produced must be disposed of by sale to a fertilizer producer, to a user of technical acid for such purposes as metal pickling or, occasionally, to a sulfuric acid producer for use in a contact-process absorption system. The following brief description will serve to give reasons for the various steps indicated in the diagram of Fig. 4-11. The 65 per cent oleum is stored in a heated building upon receipt by tank car since it has a freezing point of about 41°F (5°C) and readily freezes during winter weather. In order to avoid this freezing nuisance, the strong oleum is diluted to a solution called 40 per cent oleum and antifreeze, with a nominal composition of about 103 per cent H_2SO_4, 6 per cent HNO_3 (by volumetric analysis), which solution remains liquid to well below 0°F (−18°C). This 40 per cent oleum is used first to mix with 97 per cent HNO_3 to make semimix acid and to make final adjustments of the semimix, after it has been analyzed, to the desired mixed acid ready for use in nitrations. The 97 per cent HNO_3 is made in a concentrator fed with concentrator mixed acid made from weak (55–60 per cent) HNO_3, 93 per cent H_2SO_4, and spent nitrating acid to a composition of about 35 per cent H_2SO_4, 23 per cent HNO_3. This mixed acid is fed to a denitrating and concentrating operation. One form of this process is indicated in Fig. 4-12.

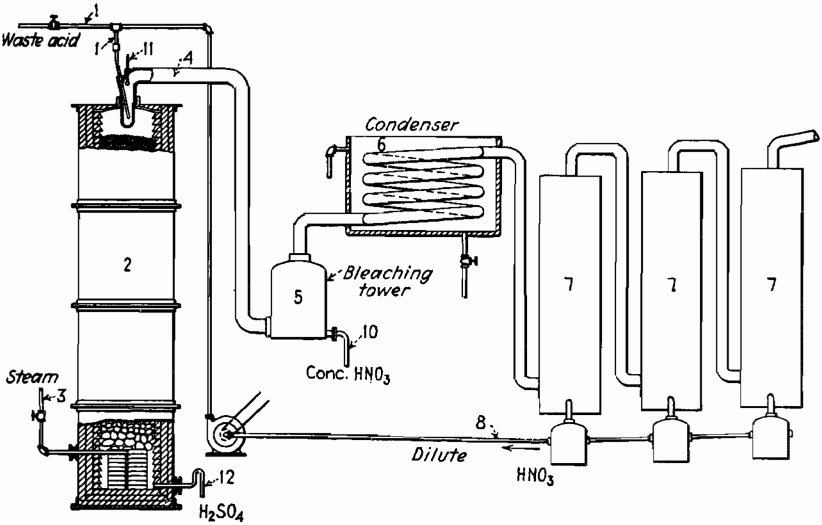


FIG. 4-12. System for the production of concentrated nitric acid.
1 Spent-acid delivery
2 Denitrating tower
3 Steam inlet
4 Outlet for nitric acid vapors
5 Bleaching tower
6 Chemical-ware condenser
7 Absorption towers
8 Dilute nitric acid—returned to denitrating tower
10 Outlet for concentrated nitric acid
11 Thermometer
12 Outlet for diluted sulfuric acid

In this process the first step involves feeding the dilute acid to the top of a packed tower. As the acid trickles down through the tower, it is heated by steam ascending from the bottom. There is enough H_2SO_4 present to hold back the water, and strong HNO_3 along with oxides of nitrogen are volatilized and pass from the top of the tower to bleaching and absorption vessels where the oxides have time to be oxidized by the air admitted and form dilute HNO_3. The strong HNO_3 produced by the initial condensation of the vapors from the tower is removed at the bleaching operation. The dilute HNO_3 produced in the absorption system is fed back to the denitrating tower. The other product of this denitrating and concentrating operation is dilute sulfuric acid, taken from the bottom of the denitrating tower at about 70 per cent strength. The dilute H_2SO_4 is then concentrated to 66°Bé strength in fuel-oil-fired drum concentrators.

In Fig. 4-12 the indicated bleacher and absorption towers are usually constructed of ceramic materials. The current trend is to replace these ceramic absorption towers with single-pass metal towers, which involve much less maintenance expense.

Another variation in acid processing occurs in the nitration processes for making nitrotoluenes. Here the mixed acid for carrying out the nitration to mononitrotoluene and dinitrotoluene does not require the use of very strong HNO_3, and the final spent acid from the mononitration is low in HNO_3. In this process the spent acid is denitrated by a similar process to the one described above, but the HNO_3 is all recovered as 55–60 per cent strength HNO_3 which is used to build up the mixed acid coming to the binitration and mononitration operations to required HNO_3 content. The only strong HNO_3 needed for the trinitration mixed acid is made fresh in the acid operations separate from the nitration process.

The products of the acid processing are thus mixed acid for nitrations and dilute H_2SO_4. In very large-scale nitration operations, the disposal of this dilute acid may be of prime importance in the locating of a plant.

Mixed-acid Compositions. In the operation of a plant, the specification of composition of the mixed acid used will have arisen originally from some process research or development. The theoretical considerations of the mechanism of nitrations, their kinetics and thermodynamics, which have been dealt with in the early part of this treatment, have clearly pointed out the governing processes and factors affecting nitrations. From the technical standpoint of using mixed nitric and sulfuric acids, there are two primary conditions that must be met. These are: (1) The amount of 100 per cent HNO_3 present in the nitration must be enough to satisfy the stoichiometric requirements of the nitration reaction. It is usually present in excess in order to maintain reasonably fast over-all reaction rates. (2) The amount of 100 per cent H_2SO_4 with, if necessary, its associate dissolved SO_3 (oleum) must be sufficient to promote the desired reaction regardless of the mechanism which is involved. Two values which are calculated from the reaction stoichiometry in one case and determined in the process development in the other are the practical control yardsticks. These values are the D.V.S. (dehydrating value of sulfuric acid) and the nitric ratio. D.V.S. is the ratio of H_2SO_4 to H_2O present at the end of the reaction. The nitric ratio (R) is the ratio of the weights of 100 per cent HNO_3 to weight of material being nitrated. R is set by the specifications of the process.

D.V.S. was used for mixed-acid calculations for many years before the presently held theories of nitration by the agency of the nitryl or nitronium ion, NO_2^+. It is still a valuable tool in such calculations and an important factor in setting up optimum conditions for nitrations so as to obtain maximum yields and productivity. From the practical standpoint, the accumulation of water, as a result of the nitration reaction, would be objectionable in the nitrating medium, and the function of the sulfuric acid is to render it ineffective, whether the effect of water be to repress the formation of the nitryl ion in aromatic nitrations or to exert an unfavorable influence on the equilibrium involved in the aliphatic esterification involved in preparing nitrates from alcohols. The ratio involved in the D.V.S. figure can be calculated for any stage of the nitration reaction. When high total acidity mixtures are involved in nitration such as at the trinitration stage of the process for TNT or in the preparation of nitroglycerine, the mixed acids are generally not made up to specified compositions. The compositions will vary somewhat because of normal variations in the strength of nitric acid and oleum used, especially the former. For these mixtures the final adjustment of the mix to make it ready for use is by adjustment of the D.V.S.

D.V.S. Calculations. A typical reported analysis of a mixed acid for preparing nitroglycerine is as follows:

Total H_2SO_4	49.99%
Total HNO_3	52.44%
Actual H_2SO_4	49.90%
Actual HNO_3	52.38%
$HNOSO_4$	0.12%
H_2O	−2.40%

By way of explanation, the figures given for total H_2SO_4, total HNO_3, and $HNOSO_4$ are determined directly by analysis. Actual H_2SO_4 and actual HNO_3 are obtained by correcting their corresponding totals by subtraction of the equivalents to each from the $HNOSO_4$. These factors are 0.772 for sulfuric acid and 0.496 for nitric acid. By using these factors the actual values listed are obtained. Total acidity is the sum of these two actuals plus $HNOSO_4$, in this example 102.40 per cent. The water content is then obtained by difference.

To calculate D.V.S. from the mixed-acid analysis the formula is:

$$\text{D.V.S.} = \frac{S}{EN/R + W}$$

where S = per cent actual H_2SO_4

N = per cent actual HNO_3
W = per cent water
E = water equivalent of material to be nitrated
R = nitric ratio

E is defined as parts by weight of water resulting from the nitration of 1 part of the starting material; it is made up of the water of reaction, plus the water present in the starting material, if any. If the calculation is based upon 100 lb of mixed acid, then the figures for percentages are in pounds and the factor EN/R may be readily understood. If the weight of starting material per 100 lb of mixed acid is called X, then by definition

$$R = \frac{N}{X}$$

and

$$X = \frac{N}{R}$$

hence

$$\frac{EN}{R} = EX$$

the pounds of water resulting from the nitration of the starting material proper for 100 lb of mixed acid. The denominator of the D.V.S. ratio thus represents the total water present at the end of the nitration, as required by the definition of D.V.S.

If the particular mixed acid discussed above is used to nitrate glycerine, the D.V.S. may be calculated as follows: In this nitration a nitric ratio of 2.30 has been widely used. Assume a value of 1 per cent of moisture in the actual glycerine.

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(ONO_2)_3 + 3H_2O$$

$$\text{Mol. wt: } 92.06 + 189.06 \qquad 227.06 + 54.06$$

The water equivalent for glycerine is then

$$\frac{54.06}{92.06} \times 0.99 = 0.581 \quad \text{lb per lb from nitration}$$

$$\text{plus } \underline{0.010} \quad \text{lb from moisture content}$$

$$E = 0.591 \quad \text{lb per lb}$$

The nitric ratio of 2.30 provides an excess of HNO_3 of about 13 per cent over theoretical as shown by this calculation of the stoichiometric ratio

$$\frac{189.06}{92.06} = 2.05 \qquad \text{stoichiometric ratio}$$

$$\frac{2.30}{2.05 \times 0.99} = 1.133$$

This ratio has been set by process-development studies. Then for the acid of our example,

$$\text{D.V.S.} = \frac{49.90}{(0.591 \times 52.38)/2.30 - 2.40}$$
$$= \frac{49.90}{11.06} = 4.51$$

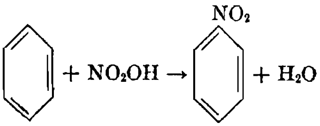
It is common practice for the plant-control chemist to report the D.V.S along with the mixed-acid analysis as though this value were a property of the acid only. It is important for a clear understanding to bear in mind that the D.V.S. applies to the situation which exists in the nitrator at the end of a nitration when the acid is used under certain specified conditions.

Relations between D.V.S. and Stability of Nitrator Charge. An important consideration in the nitration of glycerine and related compounds is the stability of the nitrator charge or the stability of the nitrated product in contact with its own spent or partially spent acid. Any condition which lowers the stability is obviously increasing the hazard because of firing in the nitrator. It can be demonstrated experimentally that increasing D.V.S. favors high stability of the nitrator charge, while decreasing the D.V.S results in lowering stability. This might be expected, since increasing D.V.S. tends to drive the nitration or esterification farther toward completion, whereas too low a D.V.S. would permit accumulation of incompletely nitrated material, along with increased dilution, and this would be favorable to oxidation reactions. It is also of interest to consider the instantaneous values of the D.V.S. ratio during the course of a nitration of glycerine in which the alcohol is fed into the mixed acid. Since the amount of sulfuric acid is constant throughout the nitration and there is no water present at the start of the nitration, the D.V.S. instantaneous ratio is infinity until enough water has been formed to balance the initial negative water content. In a typical glycerine nitration, this takes place after about 18 per cent of the nitration has been completed. From this point, the D.V.S. ratio falls rapidly at first and then more slowly, approaching the specified value which is reached at the finish of the nitration. Practically, the significance of this is that the D.V.S. ratio is always on the high, safer side, a kind of automatic safety factor.

XI. TYPICAL INDUSTRIAL NITRATION PROCESSES

This section presents commercially practical processes for the manufacture of some of the industrially important nitro compounds. In general, the examples have been selected to illustrate actual processes of the several types described earlier in this chapter.

Preparation of Nitrobenzene



In the following paragraphs, a study will be made of some of the more important details of nitrobenzene manufacture in order that the observations may be of value in the preparation of the other nitro compounds that will later be described.

Batch Nitration with Mixed Acid. The description that follows assumes the use of cycle acid, although this practice is not essential, particularly when the problem of heat transfer has been satisfactorily solved. The operation commences by delivering to the nitrator sufficient cycle acid, i.e., spent acid from a previous charge in which some nitrobenzene and nitric acid are still present. The amount of such acid required depends on the type of nitrator used. In the sleeve-and-propeller type, it should cover the cooling coils; in the Hough nitrator, it must cover and overflow through the ports of the machine. Cold water is then circulated through the heat-exchange medium; when the temperature is 50°C or lower, the charge of benzene is pumped from the scale tank into the nitrator.[1]

The mixed acid for nitration can be fed on top of the hydrocarbon or under the surface. When top feed is used in conjunction with a downflow propeller, there is a slight loss of benzene vapors because of the reaction with surface hydrocarbon accompanied by the local evolution of heat. When undersurface feed is used in conjunction with paddle-type agitators, the acid runs into a lead funnel placed on the agitator just above the top paddle. A lead pipe leads from the funnel to one of the lower paddles, where it makes a loop upward. The loop in the lead pipe is always full and prevents spluttering, as the mixed acid now comes in contact with the cycle acid at the lower part of the nitrator instead of making direct contact with benzene. A similar feeding arrangement is made for the sleeve-and-propeller type of machine by terminating the feed pipe just under the propeller. In the Hough nitrator, this is all taken care of in the design of the machine, as the mixed acid is forced in a small stream into the benzene–cycle acid mixture.

The temperature of nitration for benzene may vary within moderate limits. When no cycle acid is used, it is inadvisable to exceed 50°C; when fortified spent acid is employed, the nitration temperature may be kept between 50 and 55°C. The efficiencies of agitation and of heat exchange are also important considerations, which affect not only the control of temperature but also the rate of feed.

To arrive at the proper amount of mixed acid to be used per charge, it is necessary to multiply the weight of benzene by the acid factor that is used in making the calculations for the D.V.S., provision being made for the presence of a slight excess of nitric acid.

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[1] At Griesheim (I. G. Farbenindustrie) benzene is nitrated continuously with mixed acid, using two nitrators in series. All the materials are introduced into the first vessel. The second unit receives the overflow and serves as a finishing nitrator. SUDHOFF, *C.I.O.S.*, *Rept.* XXIV–18, Item 22 (Combined Intelligence Objectives Sub-Committee).

Separation and Neutralization. The separation of the nitrobenzene is accomplished in large conical-bottomed lead tanks, each capable of holding one or more charges. The nitrator charges are permitted to settle here for 4–12 hr, when the spent acid is drawn off from the bottom of the lead tanks and delivered to the spent-acid tanks for additional settling or for treatment with benzene next to be nitrated, in order to extract the residual nitrobenzene. The nitrobenzene is then delivered to the neutralizing house.

The neutralizing tub may be either a large lead conical-shaped tub containing an air-spider, which is used for agitating the charge of nitrobenzene during the washing process, or a standard cast-iron kettle similar to the nitrator with sleeve-and-propeller agitation. The neutralizing vessel is prepared with a "heel" of warm water, which is delivered from an adjacent vat, and the nitrobenzene is blown into it. The charge is thoroughly agitated and warmed with live steam for 30 min, or until neutral to Congo, and then allowed to settle for a similar period. The supernatant acid water is then run off through side outlets into a labyrinth where practically all the enmeshed nitrobenzene will settle out.

The charge is now given a neutralizing wash at 40–50°C with a warm sodium carbonate solution, until alkaline to phenolphthalein. When the nitrobenzene is intended for aniline production, this may be followed by a wash with aniline water from the reducer house if any has to be worked up. Otherwise, a final washing with a small quantity of warm water is made. The nitrobenzene is then delivered to its storage tanks, where it is again settled to remove final traces of water. The crude product can now be distilled for commerce or used directly for the preparation of aniline. In some plants where the nitrobenzene is used almost exclusively in the aniline plant, the neutralizing and subsequent washes are omitted. The nitrobenzene delivered to the reducer houses is consequently acid. No harmful effects on the equipment are noticeable, provided the acidity is kept below 0.5 per cent.

Operating Losses in Nitrobenzene. *Loss in Waste Acid.* When the nitrobenzene in the spent acid is not extracted by countercurrent washing with benzene next to be nitrated, it is recovered by permitting the acid to settle in large lead-lined vats for 8–24 hr, the duration depending on production schedules. The percentage of nitrobenzene removed in waste acid depends upon the temperature and efficiency of separation and is approximately 0.5 per cent of the yield. These losses are in excess of the true solubility losses (Fig. 4-13), being caused by incomplete separation of the nitrobenzene from the spent acid.

Loss in Wash Waters. The losses incidental to the neutralization of the nitrobenzene are directly proportional to the number of washes given and the amount of water used. In neutralizing, three washes may be given, the second of which contains sodium carbonate. The washes are made at a

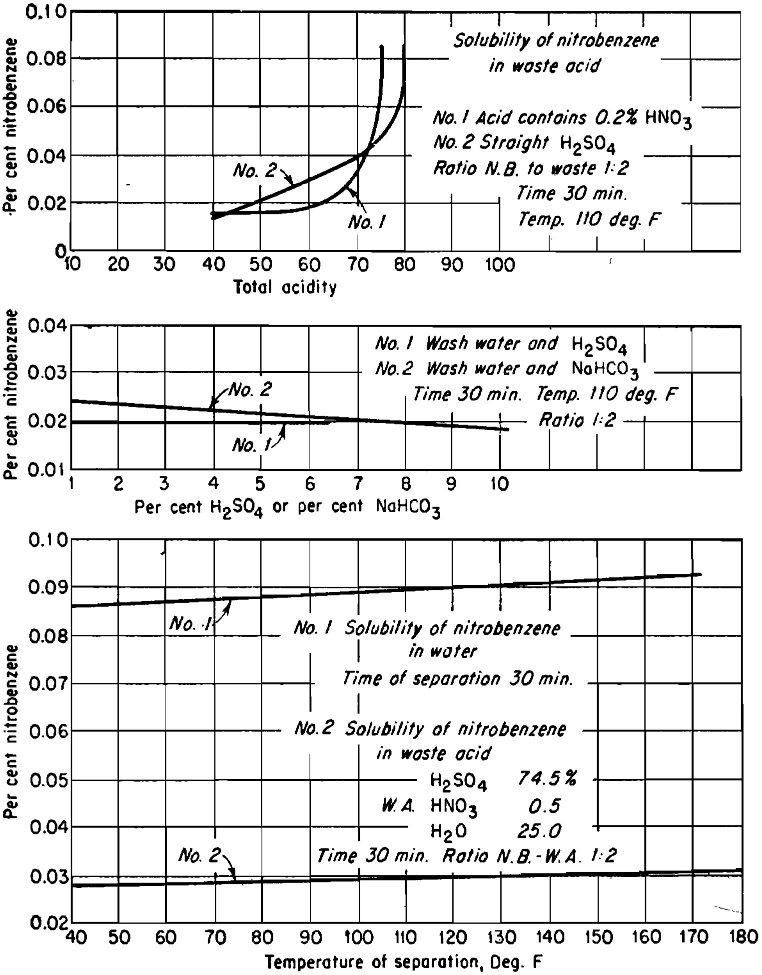

FIG. 4-13. Solubility losses in neutralizing and washing nitrobenzene.

temperature of about 45°C and are agitated with air and steam and then permitted to settle. The wash waters are drawn off at different levels and are delivered to a series of wooden catch boxes, the overflow from the last one going to waste. The quantity of nitrobenzene actually lost at this source is always slightly higher than what might be expected from the curves in Fig. 4-13 showing the solubility of nitrobenzene in wash waters.

At Leverkusen (I. G. Farbenindustrie), a nitration acid of only 2.4 D.V.S. was used, without cycle acid.[1] The nitration temperature was 20–45°C,

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[1] ADAMS and HARRINGTON, *B.I.O.S. Rept.* 1144, Item 22 (British Intelligence Objectives Sub-Committee).

and the operating time was 10 hr compared with 3½ hr for a comparable batch using cycle acid plus high D.V.S. nitrating acid, as recorded below.

NITRATION OF BENZENE: OPERATING DATA

Hough Nitrator

Initial charge of weak acid to represent cycle acid	9,000 lb
Composition of above:	

H_2SO_4	83.0%
HNO_3	2.3%
H_2O	14.7%

Nitric content includes low oxides of nitrogen.

Charge of benzene	10,000 lb
Charge of mixed acid	23,300 lb
Nitric acid ratio	1.04

Composition of mixed acid (99% acidity):

H_2SO_4	62.8%	5.7 D.V.S.
HNO_3	36.1%	
H_2O	1.1%	

Nitric content includes low oxides of nitrogen amounting to about 0.2%.
Yield of nitrobenzene = 156.9 lb nitrobenzene per 100 lb benzene = 99.0% theory.*
Length of time required to introduce benzene into inert (cycle) acid, about ½ hr.
Time required to inject nitrating acid, 1 hr.
Time required to cook at 90°C, 2 hr 5 min.
Total time for run, 3 hr 35 min.

* The yields are based on 100 per cent C_6H_6 as used. No allowance is made for losses in handling. The nitrobenzene dissolved in the waste acid is recovered by washing. with the benzene next to be nitrated either in the nitrator or in a separate vessel.

Nitration with Sleeve-and-Propeller Agitation*

Charge of benzene	6,000 lb
D.V.S. of nitrating acid	3.51
Time of nitration	2.5 hr
Temperature of nitration	50–60°C
Time of digestion or cooking at 50–60°C	2 hr
Yield per 100 lb benzene (98% theory)	154–155 lb
HNO_3 in waste acid	0.3%

* The results are obtained in a closed system of nitration, using cycle acid and top feed. No HNO_3 remains in spent acid when benzene is used in excess.

Continuous Nitration with Fortified Spent Acid. Methods for the continuous nitration of benzene have been proposed by Castner and Mares.[1] Both processes are based on the recognition that a slightly HNO_3-fortified spent acid constitutes a satisfactory nitrating agent for a limited quantity of hydrocarbon. To obtain volume production, it is necessary to circulate

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[1] Castner, U.S. 2,256,999 (1941); Mares, U.S. 2,370,558 (1945).

relatively large quantities of acid of low nitric acid content and high heat capacity and to remove the water of nitration continuously in an integrated evaporator operating under reduced pressures. When the heat of sulfuric acid hydration and the chemical heat of nitration are evolved in separate vessels by adding nitric acid to a prepared mixture of benzene, sulfuric acid, and water, the hazards of nitration are further reduced and it is feasible to operate safely at relatively high temperatures and to utilize the sensible heat in effecting the subsequent removal of water from the spent acid.

As shown in Fig. 4-14 the operation proceeds as follows: Hot sulfuric acid at 90°C is run from the heat-insulated storage tank (*B*) into one of a battery of nitrators (A^1 to A^4). Under vigorous agitation, sufficient 63 per cent nitric acid is added to the nitrator to produce a mixed acid containing 4 per cent HNO_3. Sufficient benzene is then delivered from its storage scale tank to react with all the nitric acid in the nitrator. Upon completion of the reaction, which takes about 10 min, the agitation is stopped and the charge permitted to settle. While the separation of the nitrobenzene and spent acid proceeds, another nitration is started, thus providing a continuity of operations.

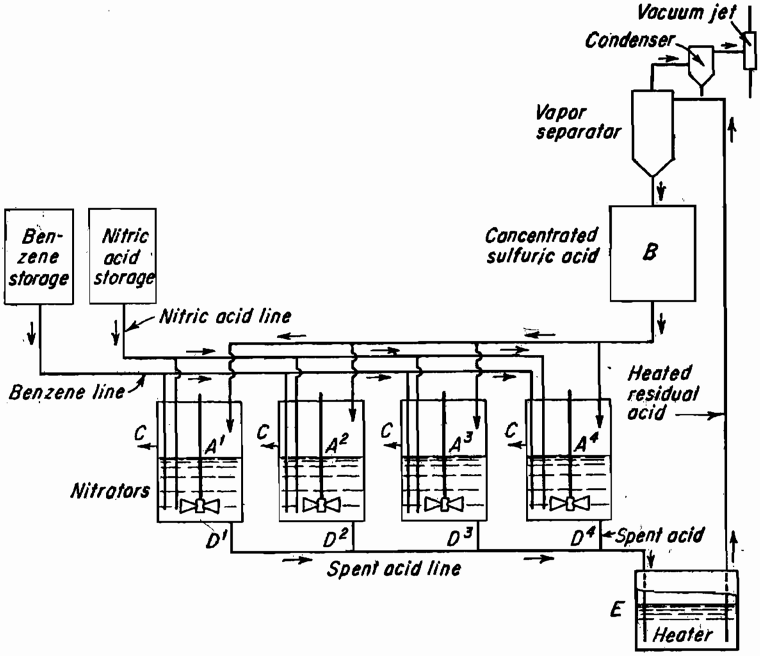
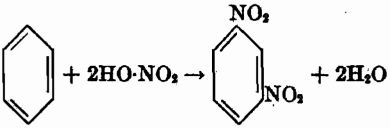


FIG. 4-14. Nitration of benzene with HNO_3-fortified spent acid.

The crude supernatant nitrobenzene is drawn off through side outlets (*C*) on the nitrator and sent to the neutralizer. The spent acid, which is free of nitric acid but contains small amounts of nitrobenzene, is drawn off in operating sequence at the outlets (D^1 to D^4) located at the base of the nitrators. The spent acid is first directed to the acid heater (*E*), which is heated by low pressure steam to maintain the sensible heat of the spent acid (72 per cent H_2SO_4), and then delivered to the vapor separator. The evaporator, operating under a vacuum of 29 in., effectively removes the water of nitration by virtue of the sensible heat of the spent acid and returns the sulfuric acid to the system at its original (75 per cent) strength. The small quantity of nitrobenzene found with the water in the condenser is separated and added to the crude charge.

Preparation of *m*-Dinitrobenzene



The preparation of *m*-dinitrobenzene from benzene is usually accomplished in two stages of nitration. Both may, however, be made to take place in the same vessel.

The first stage is carried out under the conditions previously described for nitrobenzene. At the conclusion of the first nitration, the spent acid is run off from the base of the machine and is replaced by a stronger nitrating acid for the second stage of nitration. The composition of the nitrating acids for the two stages of nitration is closely as follows:

Mixed Acid Compositions

(I) For Mononitration		(II) For Dinitration
60.0%	H_2SO_4	75%
32.0%	HNO_3	20%
8.0%	H_2O	5%
3.52	D.V.S.	7.36
1.01	HNO_3 ratio	1.1

It is readily seen from the above acid compositions that the second nitration requires a more concentrated acid. Moreover, the reaction must be controlled at a higher temperature, i.e., 90–100°C. Although the heat of nitration for the second nitro group is not so great as for the introduction of the first, the operation is nevertheless much slower on account of the lower specific heat and greater integral heat of dilution of the more concentrated acids that are used. Since the rate of feed and time of reaction are determined by the efficiency of agitation and heat exchange, these are matters of special importance in this nitration.

At Leverkusen (I. G. Farbenindustrie), dinitrobenzene was prepared in the same nitrator used for mononitration.[1] In the combined operations, 2,200 kg of spent acid from a dinitration (about 80 per cent H_2SO_4) is retained in a jacketed cast-iron nitrator of 8 cu ft (2,112 gal) capacity that is provided with a lead cooling coil and sleeve in which a stirrer operates at 110 rpm. To this is added 1,900 kg mixed acid analyzing 88 per cent HNO_3, 11 per cent H_2SO_4, and 1 per cent H_2O. Then 2,200 kg of benzene is introduced over a period of 4 hr while controlling the temperature initially at 25° and finally at 40°C. The temperature is then raised to 60°C in 1 hr. The charge is permitted to stratify, and the spent acid is discharged to a lead-lined washer with stirrer, where it is washed with either benzene or nitrobenzene.

To the nitrobenzene retained in the nitrator, there is added over a 3-hr period 5,000–6,000 kg of mixed acid (approximately 33 per cent HNO_3, 67 per cent H_2SO_4), permitting a temperature rise from 25 to 40°C. The temperature is then raised to 90°C and maintained there for 1 hr or until free of nitrobenzene by the steam-distillation test. The charge is settled and the spent acid run into a large washer, where several batches are washed with nitrobenzene. The dinitrobenzene is delivered to a tile-lined or stainless-steel washer, provided with a lead cover and stirrer. Here, it is washed, first with 4,000 liters of hot water, then with caustic soda solution until neutral, and finally with water.

About 4,500 kg of crude molten dinitrobenzene (85 per cent *m*-, 13 per cent *o*-, and 2 per cent *p*-) obtained from each nitrator charge is purified by mixing thoroughly with 3,000 liters water at 80°C in a jacketed cast-iron vessel. The contents are allowed to cool without heat exchange, until about 70°C, when pelleting begins. Then, 650 kg sodium sulfite, which converts the para and ortho derivatives to nitramines, is shoveled in at a rate of 100 kg per ¼ hr. During this period, the temperature rises to 78°C. Stirring is continued for 3 hr, when a solidification point on a washed and filtered sample should not be less than 88.5°C; if lower, 25–50 kg more sodium sulfite is added.

The molten charge is cooled by means of the water jacket to 20–25°C. Then, while water is introduced, the mother liquor is pumped off through a filter basket until the color of the wash waters has changed from dark red to clear yellow. The first wash waters are discarded, and sufficient yellow water is retained for washing the next batch. After as much water as possible has been removed via the basket, the charge is heated to 95°C, settled ½ hr, and the oil run into a cylindrical steel steam-jacketed vacuum drier that is fitted with steam-heated runoff cocks. The residual water is retained for the next batch. The yields are:

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[1] ADAMS and HARRINGTON, *B.I.O.S. Final Rept.* 1144.

	Per cent theory
100 kg crude dinitrobenzene from 48 kg benzene	96.7
100 kg purified dinitrobenzene from 118 kg crude	84.7
Over-all yield on benzene	81.9

The purification of *m*-dinitrobenzene may also be effected by making a paste with the least possible quantity of warm benzene or toluene and then filtering the cooled mass. Another method of purification is based on the greater instability of the ortho and para isomers in dilute caustic. When crude *m*-dinitrobenzene containing 6–10 per cent impurities in the form of isomers is treated with a 5–10 per cent caustic solution at a temperature above the melting point of the product (90–100°C), the ortho and para isomers that are converted to the corresponding nitrophenols are removed as soluble alkali salts with the alkaline solution. The *o*-nitrophenol present in the largest amount in the alkaline wash waters may be recovered by acidifying and distilling with steam. This method of purification has been used extensively in the separation of isomeric compounds, e.g., the removal of *o*- from *p*-nitroaniline. When basic substances are being purified, acids are used as solvents. Under such circumstances, the meta compounds, which are usually the strongest bases, dissociate most and remain in solution, whereas the ortho and para compounds are separated by precipitation.

Preparation of *o*- and *p*-Chloronitrobenzene

In the Leverkusen (I. G. Farbenindustrie) procedure[1] for the nitration of chlorobenzene, 4,500 kg chlorobenzene is added to 2,500 kg spent acid in a cast-iron nitrator of 10 cu m (2,640 gal) capacity, equipped with a jacket and lead coil that provide 24 and 25 sq m, respectively, of cooling surface. The vessel contains a stirrer with two propellers near the bottom, operating at 68 rpm. The stirrer is started, and 7,100 kg of mixed acid (HNO_3 = 35 per cent, H_2SO_4 = 53 per cent, H_2O = 12 per cent) is introduced during a period of 9 hr, meantime permitting a gradual rise in temperature from 20 to 50°C. A washed and dried sample should give a setting point of 53°C.

If the test is satisfactory, the charge is permitted to settle for 3 hr, and the spent acid (H_2SO_4 = 70 per cent, HNO_3 = 0.4 per cent, HNO_2 = 0.2 per cent) is drawn off through a sight glass. It is washed with chlorobenzene, next to be nitrated to recover dissolved or entrained nitro body. After cooling and settling, the washed spent acid is drawn off and pumped to the sulfuric acid plant.

The crude chloronitrobenzene is delivered to a steel washer (5 cu m = 1,320 gal capacity), washed three times with water at 60–70°C, while agi-

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[1] ADAMS and HARRINGTON, *loc. cit.;* CURTIS and FOGLER, *C.I.O.S. Rept.* XXIII-25, Item 22.

tated with air, until neutral to Congo. This is followed by the customary washes with 3,000 liters of dilute alkali and water. The charge is then dried at 90–100°C, under vacuum. The over-all yield of chloronitrobenzene is 98 per cent of theory.

The separation of the chloronitrobenzenes (about 35 per cent ortho and 65 per cent para) is a tedious and difficult matter. The solidifying points of mixtures of *o*- and *p*-chloronitrobenzenes are given in Table 4-13. From this table, it is seen that the eutectic point is 14.65°C, corresponding to a composition of 33.1 per cent of the para and 66.9 per cent of the ortho compound.

TABLE 4-13. SOLIDIFYING POINTS, MIXTURES, *o*- AND *p*-NITROCHLOROBENZENES*

Para, %	Solidifying point, °C	Para, %	Solidifying point, °C
0	32.09	34.09	16.73
12.61	26.10	35.43	18.43
19.22	22.65	48.94	37.65
32.39	15.35	75.48	63.97
33.07	14.77	95.57	79.13
33.10	14.65	100.00	82.15

* According to HOLLEMAN, *Proc. Acad. Sci. Amsterdam*, **11**, 248 (1908).

The separation of the isomers may be accomplished by alternate crystallizations and distillations, taking advantage of the slight differences in their physical constants. From the melting and boiling points of the two compounds given below, along with the information derived from the melting points of the mixtures, it can be predicted that much of the para content will be thrown out upon cooling. Almost half of the para compound is recovered in this way by first cooling the nitration product to 16°C, i.e., a little above the eutectic point (see accompanying chart). The filtrate is then distilled *in vacuo*. The product first coming over is chlorobenzene with traces of *m*-chloronitrobenzene. The second fraction is essentially the para, and that coming over last is essentially the ortho compound. If these fractions are cooled, the isomers may be separated and purified by washing with methanol.

	Melting point, °C	Boiling point, °C	
		760 mm	8 mm
Ortho	32.5	245.7	119
Para	83.5	242.0	113

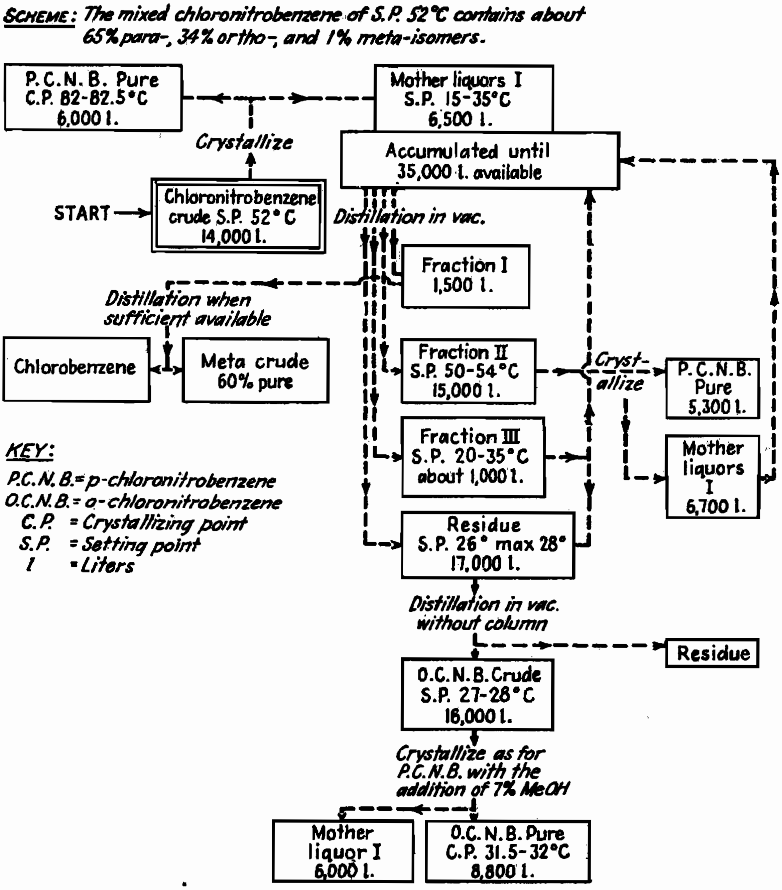
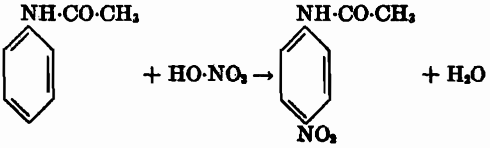


FIG. 4-15. Separation of *o*- and *p*-chloronitrobenzenes.

The separation of the isomers can also be obtained by distilling *in vacuo*, using a tall column filled with rings and maintaining a vapor velocity of 0.5 m per sec. According to this procedure, technically pure compounds are obtained, except in separating part of the para fraction when a liquid mixture containing 35 per cent of *p*-chloronitrobenzene remains. This mixture is incorporated with fresh material to be rectified.

Preparation of *p*-Nitroacetanilide



In the nitration of acetanilide, it is important, in order to prevent hydrolysis, to conduct the nitration at 3–5°C. To ensure a maximum yield of product, use is made of cycle acid, which in this instance is water-white 66°Bé sulfuric acid. Into 4,000 lb of sulfuric acid that is free of nitrous acid 1,000 lb of dry acetanilide (mp, 113°C) is delivered very slowly. During the 3–4 hr that are consumed in this operation, the temperature is maintained at 25°C. The charge is cooled to 2°C, and 1,450 lb of mixed acid of the following composition is then slowly run into the nitrator, the rate of feed being regulated by the capacity of the brine coils to control the temperature at 3–5°C.

Composition of nitrating acid	HNO_3	33%
	H_2SO_4	47%
	H_2O	20%
	HNO_3 ratio	1.015

Agitation is continued for 1 hr longer, the entire operation consuming 10–12 hr. When the temperature rises above 5°C during nitration, there is a distinct tendency toward the formation of the ortho isomeride. To test for complete nitration, a sample is drawn from the nitrator and poured on ice and the *p*-nitroacetanilide washed with cold water. The precipitate is hydrolyzed in a test tube with boiling dilute caustic, and the resulting *p*-nitroaniline should yield a clear yellow solution with hydrochloric acid. If the acetanilide has not been completely nitrated, the odor of aniline may be detected.

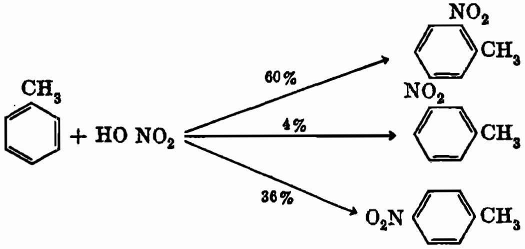
The batch is run from the nitrator onto a suction filter containing 600 gal of water and sufficient ice (or a brine coil) to keep the temperature below 15°C. The filter is a large wooden tub 8 ft in diameter having a false bottom of filtros tile. It is provided with a stirrer that is set in motion just prior to receiving the charge from the nitrator. The temperature should be kept close to 5°C; otherwise, the weak mineral acid present will hydrolyze some of the *p*-nitroacetanilide and the mixture will turn yellow owing to the formation of *p*-nitroaniline sulfate. Part of the amino compound will consequently be lost during the ensuing filtering and washing operations, and a low yield will be the result. The *p*-nitroacetanilide, which is brown as it runs from the nitrator, is changed to a milky-white mass as it comes into contact with the cold water.

When the *p*-nitroacetanilide is to be sold, it is twice washed on the filter with cold water until practically free of acid and then with a minimum of 3 per cent caustic soda or sodium carbonate solution. The neutralized cake is finally washed to remove the excess of alkali and then it is removed and dried.

For the production of *p*-nitroaniline, the filter cake is merely washed and delivered to the hydrolyzing kettle. Any *o*-nitroaniline can be separated on the filter by making the batch slightly alkaline with 20–30 lb of 3.5 per cent sodium hydroxide and heating the charge containing a minimum amount of water up to 80°C. The alkaline liquor containing the soluble salt of the enolized ortho isomeride can then be filtered off. The ortho compound may similarly be removed by continued washing with hot water at 80°C. Separation of the ortho isomeride may also be effected by diluting the nitro charge with cold water so as to obtain a sulfuric acid concentration of 65 per cent. The suspension is then warmed to 70°C, whereby hydrolysis of the acetyl group is effected. Upon cooling to 0°C, the *p*-nitroaniline sulfate separates out and is recovered by filtration.

The yield of *p*-nitroacetanilide is 88–90 per cent of theory, or 160–162 lb per 100 lb acetanilide taken.

Preparation of Mononitrotoluenes



Batch Nitration—"Direct." The process described here is that used in the preparation of mononitrotoluene as the first step in the preparation of dinitrotoluene and TNT. The process is equally useful if the preparation of the mononitrotoluene (MNT) itself is the object. The only difference would arise in the exact composition of the mixed acid. In the over-all TNT process, the mononitration is carried out using mixed acid prepared by fortifying the spent acid from the binitration step (nitration of MNT to dinitrotoluene, DNT) with HNO_3. The binitration acid itself is made up by fortifying the spent acid from the trinitration. One result of this countercurrent flow of acid with fortification by HNO_3 between successive uses is that a considerable amount of nitrososulfuric acid, $HNOSO_4$, is built up in the acid used for the mononitration. Since the $HNOSO_4$ is inert as far as the nitration itself is concerned, the acid composition will look rather different than that which might be used if acid for the mononitration were made up directly and essentially free of $HNOSO_4$. The $HNOSO_4$ arises partly from oxidation reactions with the hydrocarbon, and hence results in a loss in yield of desired nitro compound, and partly from a reaction which takes place in the mixed acid itself under the relatively high temperatures of the binitration and trinitration steps. The former reaction has been written as

$$C_6H_5CH_3 + 18H_2SO_4 + 18HNO_3 \rightarrow 18HNOSO_4 + 7CO_2 + 22H_2O$$

The compositions of acids used in making MNT have been variously listed within the following limits:

% HNO_3	15–30
% H_2SO_4	55–62
% H_2O	12.4–25

Actual examples of mixed-acid compositions in use in the United States are given in the accompanying table.

	MNT as part of TNT process	MNT end product
% HNO_3	14.5	19
% H_2SO_4	50.5	58
% $HNOSO_4$	12.5	
% H_2O	20.0	23
% Nitrobody	2.5	

The reaction of toluene to mononitrotoluene is written

$$\underset{92.06}{C_6H_5CH_3} + \underset{63.02}{HNO_3} \rightarrow \underset{137.06}{C_6H_4CH_3NO_2} + \underset{18.02}{H_2O}$$

Stoichiometrically, therefore, the reaction requires

$$\frac{63.02}{92.06} = 0.685 \text{ lb } HNO_3 \text{ per lb toluene}$$

In practice, in the TNT preparation, the mononitration is carried out in a batch process by nitrating 1,600 lb of toluene with 11,000 lb of the acid listed above. The nitric ratio is then

$$\frac{11{,}000 \times 0.145}{1{,}600} = 0.997 \text{ lb } HNO_3 \text{ per lb toluene}$$

and the D.V.S., assuming complete conversion to MNT, would be

$$\text{D.V.S.} = \frac{50.5}{(0.196 \times 14.5)/0.997 + 20.0} = 2.21$$

The mononitrator in a TNT plant consists of a steel tank 6 ft 6 in. in diameter and 5 ft 5 in. high with a flat covered top and a flat but sloping bottom. An agitator consisting of a 24-in. tribladed propeller is centered in the tank. An exhaust system maintains a 2-in. water vacuum to remove fumes. The cooling surface consists of 1½-in. steel pipe bent into concentric helical coils. There are five banks of coils.

The process is started by introducing the nitrating acid into the nitrator. This acid has been prepared at the binitration operation from spent acid and recovered nitric acid. The temperature of the acid is lowered by circulating water in the cooling coils, with the agitator running, to 105–110°F (40–44°C). Toluene is then added through a feed tube, terminating just below the propeller, at such a rate that the temperature in the nitrator contents rises at a rate of 5°F per min. to a maximum of 135°F. When this temperature has been reached, the toluene feed rate is adjusted to hold the temperature. After all the toluene has been added, the temperature is maintained for a brief (usually 3 to 4 min.) "cooking" period. At the end of the cooking period, the charge is cooled to 125°F, agitation is stopped, and the charge is allowed to settle for 2–3 min. The separated acid is then drawn off to a waste-acid recovery plant, and the MNT (as a liquid) is drained to a tank for further processing. The drain line from the nitrator is equipped with a sight glass which allows the line of separation between spent acid and MNT to be observed readily and permits an accurate separation. A complete cycle of this nitration requires about 40 min.

The nitration of toluene to the mononitrated products follows a definite pattern which is not much influenced by the conditions employed. Thus about 60 per cent of the ortho, 36 per cent of the para, and 4 per cent of the meta isomers are normally produced. Of these products, the meta isomer is undesirable in the TNT process since upon further nitration it yields unsymmetrical isomers which must be removed by some purification process. It is also interesting to note that recent work on the nitration of toluene has indicated that the mononitration step may follow a different mechanism than later steps because the acid compositions employed are such that do not produce nitryl ions in detectable amounts. In addition, it has been demonstrated that the mixed acid effective for nitration is that in which the hydrocarbon dissolves. Little or no nitration takes place from the acid dissolved in the hydrocarbon phase. This would indicate why the older "indirect" nitration procedure by which a supernatant layer of toluene was attacked by fortified cycle acid was a much slower process than the "direct" nitration by which fresh toluene is continuously fed and immediately and thoroughly dispersed into a large volume of more powerful nitrating acid. The "direct" method, as pointed out earlier, requires very thorough agitations and adequate cooling facilities. It has also been shown that the rate of nitration is proportional to the agitation effort up to a maximun rate above which the reaction rate is not increased by increased agitation. This latter comment and its implications are especially important in the design of continuous processes.

Treatment of the mixed mononitrotoluenes depends upon the end use intended for them. When the MNT is to be used in the preparation of DNT or TNT, it is normally not given any treatment but is transferred immediately to the next nitration-process steps after its separation from spent acid. Some European procedures for the manufacture of TNT include washing of the crude MNT followed by a distillation procedure to remove the meta-MNT. It is claimed that TNT produced from MNT containing only ortho and para isomers does not require as extensive purification as if the crude MNT were nitrated as such. In the United States, the distillation to purify crude MNT is not considered economical as part of the TNT process.

When MNT is to be used as such, the separation process from the spent acid is usually prolonged to allow for freeing the product from physically held spent acid as much as possible. Crude product is then washed with water, dilute NaOH solution, and then again with water. Steam distillation is then carried out to strip the crude product of impurities volatile with steam. These consist almost wholly of unreacted toluene. The yield of mixed MNT is about 90–95 per cent of theory.

Aside from toxic properties which nitrotoluenes possess, they are inflammable and require handling as such. Their shipment is controlled along with other inflammable chemicals in most countries, and the containers and methods of handling are subjects of legal regulation.

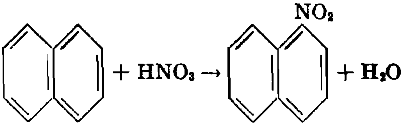
The resolution of the mixed isomers of nitrotoluene is done by a series of distillation and crystallization steps. These are very similar to the processes used in the separation of mixed nitrochlorobenzenes (see Fig. 4-15). The pertinent physical properties of the isomers are given in the accompanying table.

Isomer	Mp, °F	Bp, °F
Ortho α	15.3	431
Ortho β	26.3	431
Meta	61	450.7
Para	124.9–125.8	461.3

An initial fractional distillation under vacuum produces a distillate of nearly pure *o*-nitrotoluene. Its low content of a few per cent of *p*-nitrotoluene may be removed by recrystallization. After the fraction containing the *o*-nitrotoluene has been removed, a higher boiling fraction containing most of the *m*-isomer is recycled to build up its amount for vacuum fractionations to yield finally pure *m*-nitrotoluene. The still residue is cooled and crystallized to obtain pure *p*-nitrotoluene. The vacuum distillation under 12 mm pressure is run at about 96°C for the first fraction and at 97–107°C for the higher fraction.

The nitrotoluenes find uses primarily as intermediates in the dye industry and the toluene diamines derived from dinitrotoluenes are used as intermediates for the production of isocyanates.

Preparation of α-Nitronaphthalene



When naphthalene is nitrated under optimal conditions, the product consists principally of α-nitronaphthalene. The reaction takes place vigorously; and unless precautions are taken, polynitro compounds are formed. If impure naphthalene is used, the nitration product will be unsatisfactory; and inasmuch as it is difficult to isolate α-nitronaphthalene in a pure state, it is advisable to prevent further complications and to use a pure raw material.

When the nitration is made without the use of cycle acid, a mixed acid of the following composition may be used:

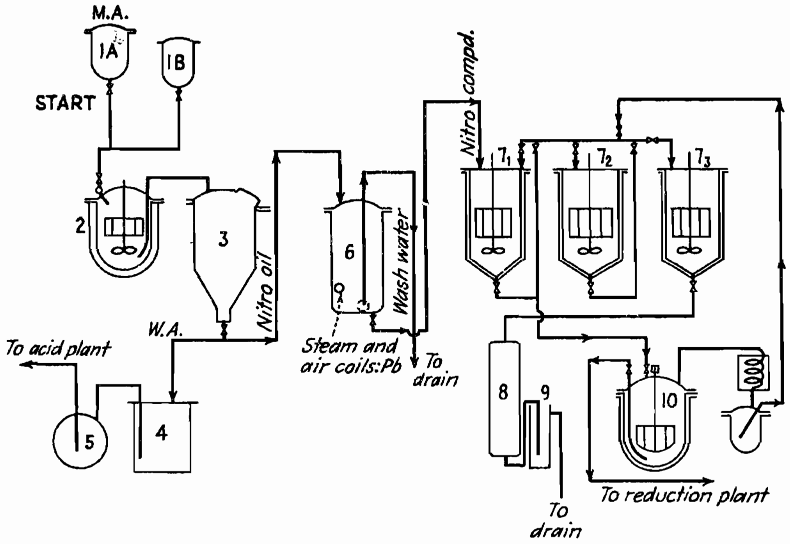
H_2SO_4	59.55%
HNO_3	15.85%
H_2O	24.60%
HNO_3 ratio	1.01
D.V.S.	2.04

This will yield a product consisting of 95 per cent α-nitronaphthalene together with some unchanged naphthalene and very little dinitro derivative.

By using cycle acid to dissolve the naphthalene to be nitrated and then proceeding with the nitration in the usual way, the operating steps are as follows: The naphthalene—1,280 lb—is suspended in 4,500 lb of dilute sulfuric acid or spent acid containing about 65 per cent H_2SO_4. The whole is thoroughly stirred, and 2,350 lb of mixed acid of the following composition is slowly added:

H_2SO_4	56.60%
HNO_3	28.30%
H_2O	15.10%
HNO_3 ratio	1.03

During the addition of the acid, the temperature is kept at 35–50°C; but after the whole of the acid has been run in, the temperature is raised slowly to 65–70°C and maintained at that point for 1 hr. The agitation is then stopped, and the nitronaphthalene which floats on the surface is decanted with part of the spent acid and delivered to a separator (Fig. 4-16), a "heel" of acid being left for the next nitration. After settling for 3 hr, the spent acid is removed and the crude nitronaphthalene is delivered to the washing and granulation kettle. Here it is made free of acid by repeated washings with boiling water and alkali. Any free naphthalene that may be present



1*A*	Mixed-acid supply tank
1*B*	Spent-acid supply tank
2	Nitrators (2), cast iron, steel jacket, 7,000-liter capacity; propeller agitator 65 rpm
3	Settling vessel, cast iron, steel jacket for heating
4	Settling tank for spent acids, lead-lined steel, 10,000-liter capacity; lead siphon-pipe outlet
5	Blow leg for spent acid, cast iron, 12,000-liter capacity
6	Granulation tank, steel, lead-lined; perforated lead coil for air and steam agitation; siphon with lead grating to retain α-nitronaphthalene
7	Washers (3), cast iron, cylindrical with conical bottom; agitator with gate and propeller—40 rpm; steel jacket for heating; capacity 10,000 liters
8	Cylindrical tank, steel, 15,000-liter capacity for alkaline wash liquors
9	Wooden vat, 10,000-liter capacity, with overflow to drain
10	Drier, steel, jacketed vessel with connections to condenser coil and receiver. Charge from still can be discharged by air pressure through standpipe to reduction plant. Condensate receiver has dip-pipe connection to permit condensate to be blown to second washer. Gate-type stirrer rotates at 28 rpm

FIG. 4-16. Flow diagram: α-nitronaphthalene. (*B.I.O.S. Rept.* 1103.)

is removed by steam during the washing process. The crystallizing point must be between 52 and 52.5°C.

The purification of the crude product is accomplished also by recrystallizing it from 10 per cent of its weight of ligroin or solvent naphtha. The success of the purification depends upon certain details of manipulation, which include (1) use of a minimum of solvent and (2) constant agitation while recrystallization takes place in order to assure the formation of small crystals. The nitronaphthalene is dissolved in 10 per cent of its weight of solvent naphtha and heated above the melting point of the crude, i.e., above 50°C, until a homogeneous mixture is formed. The resulting solution is cooled to 25°C with constant agitation, and the thick slurry that is formed is centrifuged. The α-nitronaphthalene obtained in this manner has a solidifying point above 54.4°C. This is not yet pure, as the chemically pure material comes as glistening yellow crystals which melt at 61°C. To obtain the pure product, it is necessary to resort to further purification by recrystallization.

Preparation of Nitroparaffins

The development of the preparation of nitroparaffins from laboratory scale through pilot-plant to full-scale operation covered a 20-year-long effort by Commercial Solvents Corporation. A full-scale plant with a capacity of more than 10,000,000 lb per year went on stream in 1955. By a process of nitration of propane, the main production of nitroparaffins includes nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane. The nitration is done in the vapor phase. A flow diagram illustrating the process is shown in Fig. 4-17. There are five process sections in the nitroparaffin preparation. These involve (1) nitration, (2) products recovery, (3) products purification, (4) products separation, and (5) reactants recovery. A report by Schecter and Kaplan[1] states that conditions for the nitration of propane are 770°F (410°C) at pressures of 115–175 psi. Initially the vapor-phase

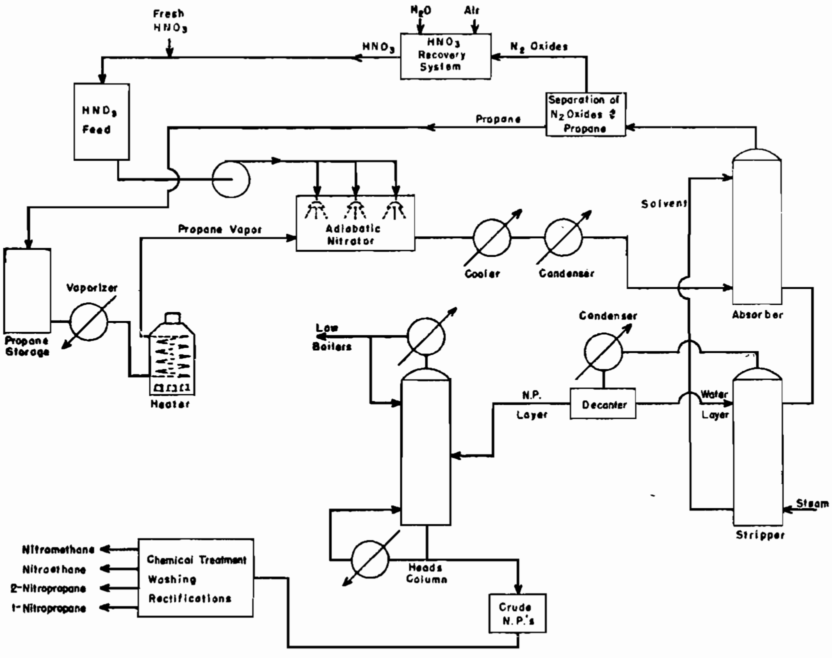


FIG. 4-17. Flow chart for nitration of propane.

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[1] SCHECTER and KAPLAN, Nitroparaffins, in "Encyclopedia of Chemical Technology," vol. 9, p. 428, Interscience Publishers, Inc., New York, 1952.

nitration was carried out in heated tubes through which a mixture of HNO_3 vapor and hydrocarbon was passed. The present plant nitrator combines the two steps, using the heat of reaction to vaporize the nitric acid. Since, under perfectly balanced conditions, no heat would have to be added to, or removed from, the nitrator, it is called an adiabatic nitrator. In the form adopted, the nitric acid is introduced into a stream of heated hydrocarbon by a number of spray nozzles. Because of the high temperatures of 750–850°F, short reaction times of 0.1–5.0 sec, and the corrosive properties of nitric acid, serious problems of design arose which have now been solved.

The conditions of nitration can be varied widely, but these have been worked out to the optimum values of temperature, pressure, reaction time, ratio of reactants, and the like. The proportion of the four nitroparaffins from propane is said by Bachman and Pollack[1] to be about as follows:

Nitromethane	25%
Nitroethane	10%
1-Nitropropane	25%
2-Nitropropane	40%

Nitrations in the vapor phase such as these are always accompanied by competing oxidative and decomposition reactions which may produce such organic materials as aldehydes, ketones, alcohols, carboxylic acids, olefins, nitrolefins, and polymers. Such simple compounds as CO_2 and CO, NO, and H_2O are also end products of the nitration reaction. The nitrator is operated to minimize production of nitrogen, and little excess nitric acid appears in the effluent stream.

After leaving the nitrator, the product is cooled to condense the nitroparaffins and the pressure is reduced to atmospheric. The total effluent is then passed through an absorber, where it is scrubbed with a suitable solvent such as hydroxylamine hydrochloride which removes from the vapor phase the ketones, aldehydes, etc. This is done so that these will not be recycled to the nitrator with recovered propane. The gases from the absorber contain oxides of nitrogen and propane and are delivered to the reactants recovery process. The recycling of propane and recovered HNO_3 leads to high yields of nitroparaffin based on HNO_3. It is reported that over 90 moles of nitroparaffin may be obtained per 100 moles of HNO_3 consumed. The liquid phase from the absorber is transferred to the top of a steam-heated column called the stripper in which the crude nitroparaffins and water are stripped out of the solvent The regenerated solvent is recycled to the absorber. The stripped nitroparaffins along with water and the oxidation products are condensed and form a two-layer mixture which is separated in a decanter. From the decanter the nitroparaffin layer is fed to the first rectification operation called the heads column. Here the low-boiling aldehydes, ketones, etc., are removed, and a cutoff is made for the

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[1] BACHMAN and POLLACK, *Ind. Eng. Chem.*, **46**, 713 (1954).

initial boiling point of the hydrocarbons. The crude nitroparaffins are taken from the bottom of the column, condensed, and subjected to a purification process. The purification process is designed to remove trace impurities in the nitroparaffins which lead to instability, corrosiveness, and color development in the final products. This purification is a chemical treatment carried out in agitated pots. After the chemical treatment, a decanting separation, water washing, and another decanting separation, the wet nitroparaffins are sent to the separation process. The water is first removed in a drying column, and then the separation is accomplished in four successive atmospheric-pressure rectifying columns which strip out in order nitromethane, nitroethane, 2-nitropropane, and 1-nitropropane. The finished nitroparaffins are water white, stable in storage, and noncorrosive in steel storage or shipping containers.

This continuous process is operated from a centralized control panel which contains more than one hundred recorders and controllers. In addition, a data-reduction system continuously scans 70 key temperatures and at intervals types them out on the plant log. If, in the scanning process, a deviation from control is noted, the operator is notified by an alarm and the deviating data are recorded automatically. The control panel also contains start-stop switches for all motors. Included in the instrumentations are an infrared analyzer on the nitric oxide stream, a hydrogen analyzer on the derivative autoclaves, and a mass spectrometer for nitroparaffin analysis.

Some of the physical properties of the nitroparaffins mentioned here are shown in Table 4-14.

TABLE 4-14. PHYSICAL PROPERTIES OF NITROPARAFFINS*

Property	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane
Boiling point, 760 mm, °C	101.2	114.0	131.6	120.3
Vapor pressure 20°C, min	27.8	15.6	7.5	12.9
Surface tension at 20°C, dynes/cm	37	31.3	30	30
Flash point, °F (Tag open cup)	112	106	120	103
Solubility of water in NP at 20°C, % by vol.	2.2	0.9	0.5	0.6

* Tabulation from a paper by W. C. Ashley, given at a Nitroparaffin Symposium. New York, Oct. 25, 1955.

Nitroparaffins, themselves, are useful solvents, additives, and fuels for piston engines and rockets. At least 2,000 derivatives of nitroparaffins have been produced by research. Numerous nitrohydroxy compounds may be formed by condensing nitroparaffins with aldehydes. These find use as heat sensitizers for latex and as hardening agents for proteins. Aminohydroxy compounds such as aminomethylpropanol are useful emulsifiers. Another similar derivative, *tris* (hydroxymethyl) aminomethane is an interesting polyfunctional raw material for the alkyd resin and synthetic drying oil and similar polymer fields. Hydroxylamine salts which are useful as reducing agents and in the synthesis of oximes are also interesting and important derivatives.

CHAPTER 5

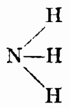
AMINATION BY REDUCTION

By Jesse Werner and P. H. Groggins

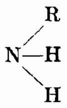
I. INTRODUCTION AND DEFINITIONS

Amination by reduction involves the synthesis of amines by reductive methods. Amines may be defined as derivatives of ammonia, where one or more of the hydrogens are replaced by alkyl, aryl, hydroaryl (cycloalkyl), aralkyl, or heterocyclic groups. Amines can be produced by reducing nitro, nitroso, hydroxylamino, azoxy, azo, and hydrazo compounds, as well as oximes, amides, nitriles, and azides. In each case, a carbon-to-nitrogen bond already exists. Amines may also be formed by reacting compounds containing certain labile groups (e.g., halogens, hydroxyl and sulfonic) with ammonia.

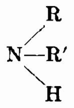
Amines are divided into three classes—primary, secondary, and tertiary—depending upon the number of replaced hydrogens in the parent substance *ammonia*. Primary amines contain two remaining hydrogen atoms attached to the ammonia nitrogen, secondary amines contain one, and tertiary amines have none remaining.



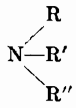
Ammonia



Primary Amine



Secondary Amine

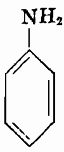


Tertiary Amine

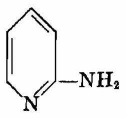
Examples of Primary Amines

$CH_3—NH_2$

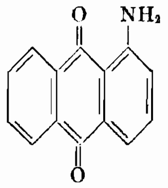
Methylamine



Aniline



2-Aminopyridine

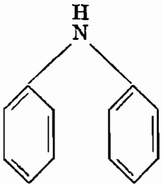


1-Aminoanthraquinone

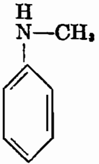
Examples of Secondary Amines

$(CH_3)_2NH$

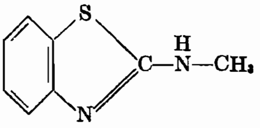
Dimethylamine



Diphenylamine



N-Methylaniline

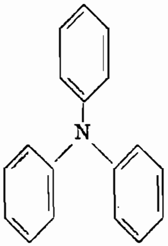


N-Methyl-2-aminobenzothiazole

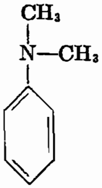
Examples of Tertiary Amines

$(CH_3)_3N$

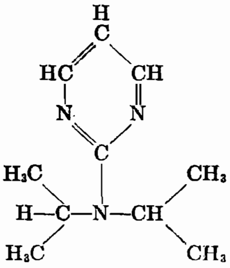
Trimethylamine



Triphenylamine



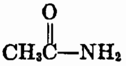
Dimethylaniline



N,N-Diisopropyl-2-aminopyrimidine

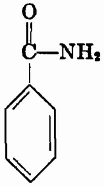
Amides, in contrast to amines, are derivatives of ammonia, where one of the hydrogens has been replaced by an organic acid-derived group, such as acyl, aroyl, heteroyl, sulfonyl, etc. An imide is one in which two hydrogens of the parent ammonia have been so replaced.

EXAMPLES OF AMIDES

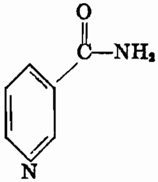


$CH_3\overset{\overset{O}{\|}}{C}{-}NH_2$

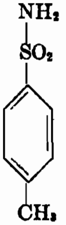
Acetamide



Benzamide



Nicotinamide



p-Toluenesulfonamide

Amides are generally prepared by ammonolysis reactions and not by reductive methods.

The methods generally used for the preparation of primary amines are the following:

1. The reduction of nitro, nitroso, hydroxylamino, azoxy, azo, and hydrazo compounds.
2. The reduction of nitriles, amides, oximes, and azides.
3. The replacement of labile groups, such as nitro, halogen, hydroxyl, and sulfonic acid by reaction with ammonia or ammonia progenitors, such as urea.
4. Intramolecular rearrangement of (*a*) hydrazobenzenes and hydroxylamines, (*b*) amides, and (*c*) secondary and tertiary amines.
5. The hydrolysis of N-substituted amides.
6. Direct amination by means of hydroxylamine and sulfuric acid.

The most important of these methods, from a chemical engineering point of view, are the first four given above. This chapter will deal with methods 1, 2, and (to a lesser extent) 4*a*. Method 3 is covered in Chap. 8.

Amines occur as gases (methylamine: bp, −6.7°C), liquids (aniline: bp, 184°C), and solids (1-naphthylamine: mp, 50°C). Their basic characteristics are best illustrated by the list of basic dissociation constants (K_b), given in Table 5-1.

where

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

in the equation

$$RNH_2 + HOH \rightarrow [RNH_3]OH \rightleftharpoons [RNH_3]^+ + OH^-$$

As can be seen in Table 5-1, the aromatic amines are relatively weak bases as contrasted with aliphatic amines.

Amines are of very great importance as intermediates in the chemical-process industries. They are used in the production of dyes, rubber chemicals, nylon, pharmaceuticals, gasoline additives, surfactants, textile

TABLE 5-1. BASIC DISSOCIATION CONSTANTS OF PRIMARY AMINES

Name	Formula	K_b
Methylamine	CH_3NH_2	5.0×10^{-4}
Ethylamine	$C_2H_5NH_2$	5.6×10^{-4}
Isobutylamine	$C_4H_9NH_2$	5.3×10^{-4}
sec-Butylamine	$C_4H_9NH_2$	3.1×10^{-4}
Trimethylenediamine	$H_2NCH_2CH_2CH_2NH_2$	5.0×10^{-4}
Tetramethylenediamine	$H_2NCH_2CH_2CH_2CH_2NH_2$	3.5×10^{-4}
Ammonia	NH_3	5.1×10^{-4}
Aniline	$C_6H_5NH_2$	4.6×10^{-10}
o-Toluidine	$CH_3C_6H_4NH_2$	3.3×10^{-10}
p-Toluidine	$CH_3C_6H_4NH_2$	2.0×10^{-9}
m-Chloroaniline	$ClC_6H_4NH_2$	4.0×10^{-11}
p-Bromoaniline	$BrC_6H_4NH_2$	1.0×10^{-10}
o-Nitroaniline	$O_2NC_6H_4NH_2$	1.5×10^{-12}
o-Anisidine	$H_3COC_6H_4NH_2$	2.0×10^{-10}
o-Aminobenzoic acid	$HOOCC_6H_4NH_2$	1.4×10^{-12}
o-Phenylenediamine	$H_2NC_6H_4NH_2$	3.3×10^{-10}
Benzidine	$H_2NC_6H_4—C_6H_4NH_2$	7.4×10^{-13}
α-Naphthylamine	$C_{10}H_7NH_2$	9.9×10^{-11}
β-Naphthylamine	$C_{10}H_7NH_2$	2.0×10^{-10}

auxiliaries, photographic chemicals, chelating agents, sweetening agents, agricultural chemicals, polyurethanes, inks, plastics, etc. Several are made in fairly large volume, as is shown in Table 5-2, which gives the annual production in the United States of a few amines during the decade following World War II, as reported to the U.S. Tariff Commission by the manufacturers.

TABLE 5-2. PRODUCTION OF AMINES*
(In Thousands of Pounds)

Amine	1946	1948	1950	1952	1954	1955
Aniline	88,366	92,083	98,010	95,852	97,349	131,761
1-Naphthylamine	4,297	5,737	n.a.	n.a.	n.a.	n.a.
2-Naphthylamine	n.a.	n.a.	1,344	n.a.	1,086	1,284
Phenylenediamines	1,156	2,688	1,807	524	1,423	1,252
2,4-Toluylenediamine	1,475	1,349	1,099	989	1,627	1,903
Xylidines	n.a.	n.a.	n.a.	433	485	537

* From Tariff Commission Reports.
n.a. = not available.

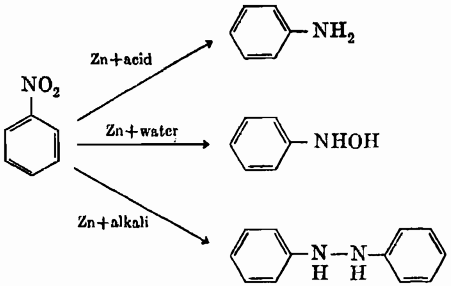
In recent years, the production of diamines by reductive methods has become increasingly important. Hexamethylenediamine is a prime intermediate, together with adipic acid, in the production of nylon 66. It is made in very large, but undisclosed, volume by catalytic reduction of adiponitrile, NC—$(CH_2)_4$—CN. *m*-Phenylenediamine is used as a cross-linking agent in epoxy resins. Toluylenediamines are intermediates in the production of toluene diisocyanates, from which are made polyurethane foams, rubbers, coatings, and adhesives.

II. METHODS OF REDUCTION

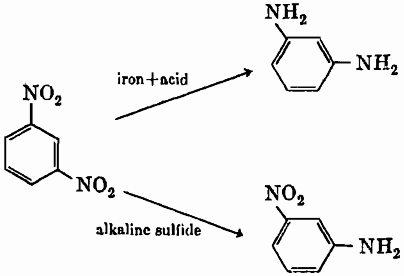
A great variety of reduction methods have been used for the preparation of amines. Among these are:

1. Metal and acid. Iron and acid (Béchamp method) is the major example in this category, but other metals (tin, zinc) have also been employed. Generally, hydrochloric acid is preferred, but sulfuric, acetic, and formic acids have also been used.
2. Catalytic. This method involves the use of hydrogen (or hydrogen-containing gases) and a catalyst such as nickel, copper, platinum, palladium, or molybdenum sulfide.
3. Sulfide. This is used mainly for the partial reduction of polynitro aromatic compounds to nitroamines and for the reduction of nitroanthraquinones to aminoanthraquinones.
4. Electrolytic.
5. Metal and alkali. This method is used mainly for the production of azoxy, azo, and hydrazo compounds. The latter are important in the manufacture of the benzidine series.
6. Sodium hydrosulfite (hyposulfite).
7. Sulfite (Piria method). The reaction of sodium sulfite and bisulfite on an aromatic nitro compound leads to a mixture of amine and aminoarylsulfonic acid.
8. Metal hydrides.
9. Sodium and sodium alcoholate.
10. Strong caustic oxidation reduction.
11. Hydrogenated quinolines and naphthalenes.

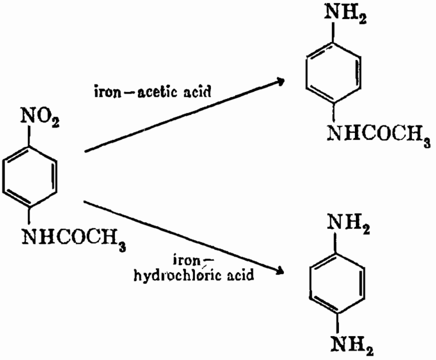
By a proper selection of reducing agent and careful regulation of the process, reductions may often be stopped at intermediate stages and valuable products other than amines obtained. Metal and acid reductions are most vigorous and usually yield amines as end products. When nitrobenzene is treated with zinc and a mineral acid, the resultant product is aniline. When an alkaline solution is employed, hydrazobenzene is generally obtained, but very vigorous conditions sometimes result in the formation of aniline. When zinc dust and water are used, the reaction product is phenylhydroxylamine. The following formulas represent the three possibilities:



When the compound to be treated contains more than one nitro group, the products of reduction depend upon the agents used. Thus, *m*-phenylenediamine is obtained by the iron and acid reduction of *m*-dinitrobenzene, while the alkaline sulfide reduction yields *m*-nitroaniline:



With certain compounds containing acid- or alkali-sensitive groups (e.g., esters or amides), it is necessary to adjust the pH carefully to avoid decomposition and side reactions. In such reductions on the acid side, it is generally advisable to replace the normally used mineral acids with organic acids like acetic acid. An example of the latter is the reduction of nitroanilides, for here the presence of mineral acids would tend to hydrolyze the anilide to an amine.



The method to be used will, therefore, depend upon the degree of reduction desired, the sensitivity to the process of both starting material and final product, the need for avoiding contaminants, and the over-all economics.

The reduction of nitro compounds involves the progressive removal and replacement by hydrogen of the oxygen in the —NO_2 group. The intermediate products in the reduction of nitrobenzene, whose interrelationships are shown in Fig. 5-1, are obtained by control of the reduction potential of the system.

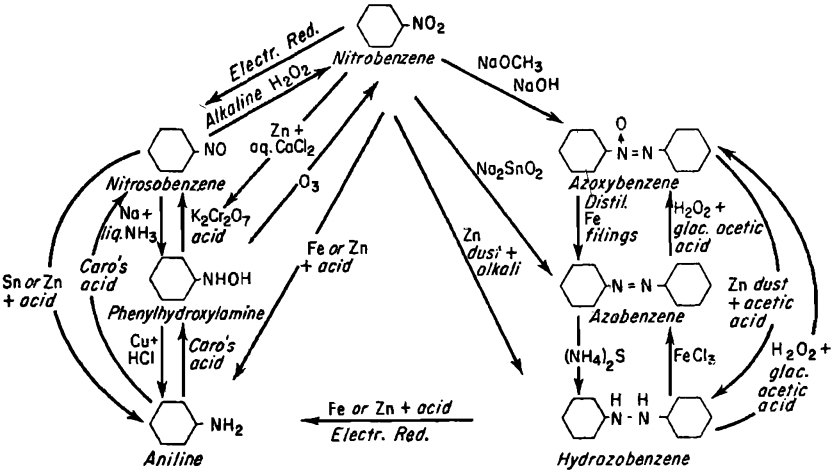


FIG. 5-1. Reduction products of nitrobenzene.

III. IRON AND ACID (BECHAMP) REDUCTION

Historical Introduction

Béchamp's discovery in 1854 that nitro compounds could be reduced in the presence of iron and acetic acid and Perkin's subsequent application in 1857 of the reaction in the commercial production of aniline were events of great significance in the development of the dye industry, and thus in the birth of industrial synthetic organic chemistry. Technical progress in the application of this reaction was first made by substituting hydrochloric acid for the acetic acid originally employed. Subsequently, it was discovered that the ferrous salt functions in such a way that reduction can be carried out with far less than the theoretical quantity of acid.

Considerable discussion has taken place in attempting to explain the consumption of less acid than that theoretically required by the following equation:

$$C_6H_5NO_2 + 2Fe + 6HCl \rightarrow C_6H_5NH_2 + 2H_2O + 2FeCl_3$$

Formula wt 123 2(55.84) 6(36.45)

In industrial practice, less than 2 per cent of the amount indicated above is actually used. Operating experience has shown that 3.0 lb of hydrochloric acid (10 lb of 30 per cent solution) is sufficient to bring about a satisfactory reduction of 100 lb of nitrobenzene to aniline.

The presence of free acid, which was long considered essential to the reduction process, has been shown to be unnecessary. Wohl, in 1894. demonstrated that nitrobenzene could be reduced with iron powder in alcoholic or aqueous solution, in the presence of magnesium or calcium chloride, and stated that the absence of free acid is advantageous. In 1914, von Girsewald showed that ferrous chloride could be used as the catalytic agent in reductions. Moore, in 1920, found that even sodium chloride could be employed in the iron reduction of azo compounds to amines. It has been demonstrated that aniline hydrochloride, aluminum chloride, sodium bisulfate, or other salts derived from strong acids can be successfully employed. All that is required is a salt that acts like an acid in water solution, liberating hydrogen ions.

Explanations of the mechanism of iron and acid (Bechamp) reductions can be made on the basis of observed chemical phenomena as well as electronic theory. Both explanations are useful in providing a better understanding of the reduction process and in providing guides for efficient industrial operations.

Reaction Mechanism

Chemical Mechanism. The arylamines, in contrast to the alkylamines, dissociate on solvation only to a slight extent, forming weak bases, as shown in Table 5-1. In the case of aniline, this can be represented as

$$C_6H_5NH_2 + HOH \rightarrow [C_6H_5NH_3]\,OH \rightleftharpoons [C_6H_5NH_3]^+ + OH^- \qquad (1)$$

The salts of aromatic amines (e.g., aniline hydrochloride) are thus quite acidic and easily hydrolyzed. It is this hydrolysis of the amine salt that gives the acidic medium in which the Béchamp reduction takes place. The degree to which this hydrolysis occurs determines the treatment given the final reducer charge prior to isolation of the amine.

It is also known that hydrogen is evolved when iron powder and water are intimately mixed. This reaction is greatly accelerated by heating in the presence of salts derived from strong acids.

$$3Fe + 6H_2O \xrightarrow{FeCl_3\text{ (also }NaHSO_4,\ AlCl_3\text{, etc.)}} 3Fe(OH)_2 + 3H_2 \qquad (2)$$

When a nitro compound is introduced into such a system, the hydrogen (possibly as hydrogen ions) and ferrous hydroxide participate in the reduction process. Although a stepwise reduction is unquestionably involved, the basic reactions may be represented as follows:

$$2RNO_2 + FeCl_2 + 6Fe + 10H_2O \rightarrow 2RNH_3Cl + 7Fe(OH)_2 \qquad (3)$$

$$RNO_2 + 6Fe(OH)_2 + 4H_2O \rightarrow RNH_2 + 6Fe(OH)_3 \qquad (4)$$

When the reduction of nitrobenzene is carried out in a glass vessel, the early formation of a greenish precipitate, characteristic of ferrous hydroxide [Eq. (3)], is observed. This turns to a brown [Eq. (4)] and finally to a black color, which suggests that the formation of the known end product—magnetic iron oxide, Fe_3O_4—is a secondary effect resulting from the interaction of ferrous and ferric hydroxides.

$$Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 + 4H_2O \qquad (5)$$

The amine hydrochloride produced in Eq. (3) may be presumed to react further with iron and nitrobenzene in one or two steps:

$$6RNH_3Cl + 3Fe + RNO_2 \rightarrow 7RNH_2 + 3FeCl_2 + 2H_2O \qquad (6)$$

The step which is implicit in Eq. (3) and which permits the replacement of acids by acidic salts is shown in Eq. (7).

$$2RNH_3^+ + 2OH^- + Fe^{++} + 2Cl^- \rightarrow 2RNH_3Cl + \underset{\text{Limited Solubility}}{Fe(OH)_2} \qquad (7)$$

The reactions indicated by Eqs. (1) and (7) show that weak bases such as aniline behave similarly to ammonia. They unite with water to form weakly dissociated bases, e.g., arylammonium hydroxides. These, like ammonium hydroxide, precipitate the hydroxides of the heavy metals from solutions of their salts. The last step [Eq. (6)] shows the completion of the "catalytic" cycle and emphasizes the role of iron in the regeneration of the "catalyst," ferrous chloride, and the amine. This reaction is in accord with practical observations that aqueous solutions of aniline hydrochloride, or other salts that are hydrolyzed in the presence of metals with the formation of hydrogen ions, are useful "catalysts." The over-all reaction can be represented as

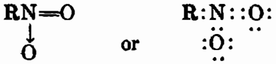
$$4RNO_2 + 9Fe + 4H_2O \xrightarrow{FeCl_2} 4RNH_2 + 3Fe_3O_4 \qquad (8)$$

This is an idealized equation, since in practice it has been found that the iron oxide sludge (after dehydration) often contains some FeO. The $FeCl_2$ is not a true catalyst in that it is continually consumed and new $FeCl_2$ formed from fresh iron.

It is interesting to note that the ferrous ion which is essential to the reduction process is hardly present in the products of Eqs. (3) and (7). In this connection, it has been observed that only a faint test for soluble iron can be obtained by spotting on filter paper with sodium sulfide solution directly after feeding considerable nitro compound to the reducer. When, however, reduction is complete, qualitative or spot tests show very distinctly the presence of soluble iron. From Eq. (7), it may reasonably be inferred that the quantity of ferrous chloride catalyst should be proportional to the amount of amine that is dissociated, a slight excess being necessary in order to ensure an acid reaction. This is a matter of considerable practical importance in order that maximum yields and purity of product may be obtained. It has previously been shown that nitrobenzene may yield directly hydrazobenzene, phenylhydroxylamine, or aniline, depending on the hydrogen-ion concentration of the solution. A slight but definite acidity is required for the production of primary amines in this type of reduction.

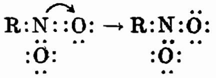
Electronic Mechanism. According to Luder and Zuffanti,[1] the use of iron and acids to reduce nitrobenzene to aniline can be explained as follows: Any acid (using the word in the Lewis sense) will increase the concentration of hydrogen ions (hydrated, of course) in water solution.[2] The salts ($FeCl_2$ and RNH_3Cl) and cations that have appeared in the equations above are acids in this general sense, and in the presence of iron and water a plentiful supply of both electrons and protons is available.

According to the electronic theory, the nitro group is electrophilic and accepts electrons from the iron. The usual method of writing the formula of nitrobenzene fails to indicate the electrophilic nature of the nitrogen atom:



$$\begin{array}{l}\mathrm{RN{=}O}\\ \ \downarrow\\ \ \mathrm{O}\end{array}\qquad \text{or}\qquad \begin{array}{l}\mathrm{R{:}\underset{\cdot\cdot}{N}{::}\underset{\cdot\cdot}{O}{:}}\\ \quad {:}\underset{\cdot\cdot}{\mathrm{O}}{:}\end{array}$$

The nitrogen atom in this arrangement is bound to be electrophilic because of the pull on its electrons by the phenyl group and the two oxygen atoms. If this is indicated by the following device, we can picture the reduction of nitrobenzene to aniline a little more clearly:



$$\begin{array}{l}\mathrm{R{:}\overset{\frown}{\underset{\cdot\cdot}{N}{::}}\underset{\cdot\cdot}{O}{:}}\\ \quad {:}\underset{\cdot\cdot}{\mathrm{O}}{:}\end{array} \rightarrow \begin{array}{l}\mathrm{R{:}\underset{\cdot\cdot}{N}{:}\underset{\cdot\cdot}{\ddot{O}}{:}}\\ \quad {:}\underset{\cdot\cdot}{\mathrm{O}}{:}\end{array}$$

The second formula emphasizes the electrophilic nature of the nitrogen atom by showing only six electrons. In the presence of iron and H^+, we picture the first step in the reduction as an almost simultaneous addition of two electrons (from the iron shown as $^{\circ\circ}$) and two protons to the nitro group:

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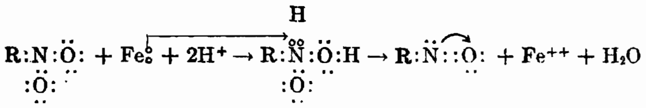
[1] Private communication.

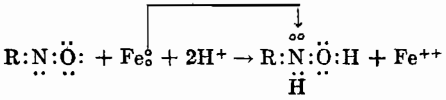
[2] Luder and Zuffanti, Catalysis from the Viewpoint of the Electronic Theory of Acids and Bases, *Chem. Revs.*, **34,** 346 (1944).



$$\mathrm{R{:}\underset{:\ddot{O}:}{\ddot{N}}{:}\ddot{O}{:} + Fe\overset{\cdot\cdot}{\circ} + 2H^+ \rightarrow R{:}\underset{:\ddot{O}:}{\overset{H}{\ddot{N}}}{:}\ddot{O}{:}H \rightarrow R{:}\ddot{N}{::}\ddot{O}{:} + Fe^{++} + H_2O}$$

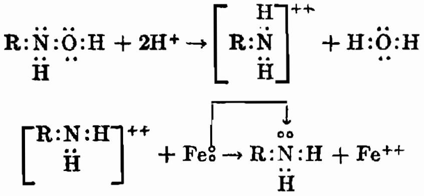
According to this picture, the evolution of hydrogen during the reduction is merely the result of a side reaction between the iron and hydrogen ions. The older chemical interpretation assumed that the hydrogen formed in contact with metals is responsible for the reduction. But breaking down a hydrogen molecule requires a large amount of energy. According to the electron theory, such a roundabout hypothesis is unnecessary, since electrons and protons are readily available from the iron and the acid solution.

The second step is the formation of phenylhydroxylamine by the same process as assumed in the first step:



$$\mathrm{R{:}\ddot{N}{:}\ddot{O}{:} + Fe\overset{\cdot\cdot}{\circ} + 2H^+ \rightarrow R{:}\underset{H}{\ddot{N}}{:}\ddot{O}{:}H + Fe^{++}}$$

The third step is essentially the same but is shown in two parts to aid in picturing the details:



$$\mathrm{R{:}\underset{H}{\ddot{N}}{:}\ddot{O}{:}H + 2H^+ \rightarrow \left[R{:}\underset{H}{\overset{H}{N}}\right]^{++} + H{:}\ddot{O}{:}H}$$

$$\mathrm{\left[R{:}\underset{H}{N}{:}H\right]^{++} + Fe\overset{\cdot\cdot}{\circ} \rightarrow R{:}\underset{H}{N}{:}H + Fe^{++}}$$

Discussion of Mechanisms. The reduction of 1 mole of nitrobenzene requires either six protons or 3 moles of hydrogen.

$$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O$$

The reduction of 1 lb of nitrobenzene would require 6 ÷ 123 = 0.049 lb of hydrogen. Using 0.0053 lb per cu ft (188.8 cu ft per lb) as a factor, we have 0.049 ÷ 0.0053 = 9.25 cu ft of hydrogen as a requirement.

In practice, hydrogen is liberated regularly during the reaction and, in efficient operations, amounts to slightly more than 0.1 cu ft per lb of nitrobenzene reduced. To what extent this hydrogen is generated by the action of water on finely ground cast iron in the presence of iron salts [Eq. (2)] (see chemical mechanism) is not known. Hydrogen may also be formed in the following side reaction:

$$2(RNH_3)^+ + 2Cl^- + Fe \xrightarrow{H_2O} 2RNH_2 + FeCl_2 + H_2\uparrow$$

According to the proponents of the electron theory, such a small amount (about 1 per cent of total requirements) can be attributed to the difficulty in maintaining a practically homogeneous reaction mass. Thus, the liberated hydrogen may be due to the reaction in Eq. (2) above, because the total iron surface is not in contact with molecules of nitrobenzene. It is rather remarkable, however, that such a high efficiency in proton or hydrogen-ion utilization is obtained in the iron and acid reduction.

Chemical and Physical Factors

Amount of Iron Used. In plant practice, it is customary to use slightly over 2 moles Fe per mole of nitro compound to carry out the reduction process. Under such circumstances, not all the iron is converted to the ferrosoferric oxide, some reducto-active ferrous hydroxide also being present. Iron sludge obtained from the reduction of nitrobenzene gives the analysis shown in Table 5-3. Since magnetic iron oxide consists of 1 part FeO + 1 part Fe_2O_3, the ferric content would be about 66 per cent Fe^{III} if all the iron were converted to the ferrosoferric oxide.

The iron oxide sludge analyses given in Table 5-3 show that slight fluctuations in the ratio of iron to nitrobenzene will produce magnified differences in the composition of the final sludge. The quality of the iron will also affect the sludge similarly. It is important to employ a good grade of cast iron, generally in the form of turnings or borings, free of other metals and foreign impurities. Iron containing excess grease or oil should be avoided, as it will react more slowly and be a source of contamination for the resulting amine. New lots of iron should always be checked in the laboratory for activity before they are used in the plant, in order to avoid difficulties. Adjustments of quantities of different lots required can thus be made as necessary. It is not always possible to translate exactly from the laboratory to the plant, and the first commercial run with a lot of iron from a new source should be controlled very carefully.

TABLE 5-3. ANALYSIS OF IRON OXIDE SLUDGES

Expt.	Sludge analysis, %			Iron:nitrobenzene	
	Metallic iron	Ferrous iron	Ferric iron	Weight ratio	Molar ratio
1	None	11.05	50.16	1:1	2.24:1
2	None	8.44	54.47	1:1	2.24:1
3	1	46.81	13.50	1.1:1	2.45:1

Nitrobenzene, 4,000 lb; $FeCl_2$ (58 per cent), 139 lb.

Undue economy in the use of iron is a faulty practice, as it may lead to side reactions, with consequent lowering of the yield. In plant practice, it has been found that when insufficient iron is present the addition of heat or acid is not effective in carrying the reduction to completion, and a poorly filtering iron oxide sludge is obtained. The introduction of some finely divided iron under such circumstances brings about a vigorous reaction which results in the complete reduction of the nitro compound. The range of iron generally used is about 2.5–5.0 moles per mole of nitro compound. This has been found satisfactory for a wide variety of aromatic amines.

Some operators prefer to use very finely divided iron to finish a reduction, and this practice is particularly advisable when the bulk of the iron turnings is not of good quality.

Physical Condition of Iron. From a study of the equations outlining the reduction process, it is obvious that the iron fed into the reducer not only supplies the metal absorption surface but enters into the reactions by providing the iron for the regeneration of the ferrous chloride upon the hydrolysis of the phenylammonium chloride (aniline hydrochloride) and also acts as an oxygen carrier. An analysis of the residual sludge reveals that the bulk of the iron is converted to iron oxides, the degree of oxidation depending on the quantity of iron employed. Experiments have shown that a clean, finely divided, soft, gray cast iron yields the best results. The rate of reduction depends in part on the fineness and porosity of the iron particles, the homogeneity of the charge in the reducer, and the degree of etching imparted to the iron by the preliminary acid treatment. To ensure a thoroughly etched iron, it is customary to boil the iron and acid suspension before adding any nitro compound. When this precaution is observed, the reaction proceeds very readily, with no danger of a violent deferred reaction. Iron borings, turnings, or shavings are generally used. With coarse particles, the oxidation of the iron is retarded and an excess of it must be provided. Furthermore, an accumulation of partially oxidized iron, as ferrous and ferric hydroxide, often throws such a load on the stirring mechanism as to bring it to a stop. Since the reaction velocity for nitro compound reduction is a function of the rate of iron oxidation, it is clear that the use of finely divided iron shortens the time of reaction.

Amount of Water Used. Theoretical considerations involving the progressive oxidation of the iron indicate the desirability of using 4–5 moles of water per mole of nitro compound treated. This approximation is based on the assumption that the iron employed is converted first to ferrous and then to ferric hydroxide as intermediate products during its oxidation to the oxide, thus:

$$4RNO_2 + 9Fe + 16H_2O \rightarrow 4RNH_2 + 3Fe(OH)_2 + 6Fe(OH)_3 \rightarrow$$
$$4RNH_2 + 3Fe_3O_4 + 12H_2O$$

Owing to the fact that part of the iron hydroxides formed loses water to form the ferrosoferric oxide during the course of the reaction, it is entirely possible that the reduction may be made with less than 4 moles of water, provided, however, that a uniform reaction mass can be maintained by effective agitation. Practical problems relating to (1) the agitation of the reaction mass, (2) the promotion of a smooth active reaction, and (3) the conservation of the heat of reduction frequently make it advisable to employ a slight excess over this proportionality. Where the nitro compound contains a solubilizing group, such as sulfonic or carboxylic residue, and the resulting amine is filtered from the alkalinized iron oxide sludge, much more water is generally used (50–100 moles). The solubilities of the nitro and amino compounds determine the amount of water used in the reduction. Unnecessary dilution, however, not only places undesirable restrictions on the productivity of each reducer but also reduces the concentration of the catalyst so that it is less effective.

Amount of Acid Used. This reaction requires the presence of small amounts of ferrous ion to act as a catalyst. Generally about 0.05–0.2 of an equivalent of acid is used. The acids usually employed in the reduction process are hydrochloric and sulfuric. It should be borne in mind that hydrochloric acid sometimes causes the formation of small amounts of chlorinated amines whereas sulfuric acid may rearrange the intermediate arylhydroxylamines to hydroxyarylamines and cause the formation of darker amines in lower yields, particularly in the case of solid amines. Where the danger of hydrolysis or contamination by such products exists, acetic or formic acid is employed instead. The disadvantages in the use of sulfuric acid appear to be minimized when the sulfuric acid is introduced as sodium acid sulfate (niter cake). When used alone or preferably in conjunction with a calculated quantity of sodium chloride, a very economical and satisfactory promoter is obtained. For example, 2.4 lb of sodium chloride with 6 lb of niter cake per 100 lb of nitro compound gives satisfactory results. The niter cake is first ground and is added, along with the sodium chloride, to the water and finely divided iron in the reducer.

Effect of Agitation. Since the reduction process under consideration is a multiphase reaction, it is clear that the best results are obtainable only when the nitro compound, iron, and water-soluble catalyst are in intimate contact. A stirrer that merely pushes the iron around the bottom of the vessel and permits the charge to separate out into layers does not function efficiently. It is apparent, therefore, that a sturdy sleeve-and-propeller or double-impeller type of stirrer will in some cases be superior to the slow-moving plow type, speeding up the reaction considerably.

Furthermore, most aromatic nitro compounds (not containing basic groups) are practically insoluble in faintly acid solution, and thorough mixing is consequently a factor of major importance. When the rate of reduction is limited by the quality of the iron used, an increased agitation will not show a corresponding improvement in operations. A rate of agitation beyond that necessary throws an extra burden on the driving mechanism.

Mow[1] has developed the use of rotary mills using freely moving ponderous agitators, such as iron balls, for the reduction of nitro, nitroso, and azo compounds to amines with iron in aqueous emulsion in order to effect grinding action during the reduction. Such mills are also useful in the distillation of aromatic amines from the iron oxide sludges in vacuum.

Reaction Temperature. It has been found that the use of a high catalyst concentration (3 per cent or more compared to nitrobenzene taken) during reduction results in a finely divided iron sludge which, although it is generally a poorly filtering sludge, is of possible commercial value (for removing sulfur compounds from illuminating gas). This result can be obtained by limiting the quantity of water introduced into the jacketed reducer and utilizing the heat of reaction to carry on the reaction. An obvious advantage arising from operating with such concentrated solutions is the fact that the charge is easily maintained at the boiling temperature. The vigorous reflux that characterizes such a reduction ensures against the formation of intermediate products of reaction. The reaction is not only rapid but is economical on account of the lower consumption of steam.

A study of the thermal factors relating to the reduction of nitrobenzene shows that the reaction is distinctly exothermic. It is necessary, therefore, to remove the surplus heat generated while maintaining the reduction at the optimum reaction temperature. When nonvolatile materials are treated, as in the conversion of *p*-nitroaniline to *p*-phenylenediamine, flumes of suitable diameter and height are sufficient. When volatile nitro compounds are used, an efficient tubular condenser (vapors pass on *outside* of water-cooled pipes) gives eminently satisfactory results.

The data in the accompanying table show the heat in Btu generated during the "feed" and reduction of a 1,200-lb charge of nitrobenzene.

Operation	*Heat Generated, Btu*
Feed	1,805,000
Reduction	488,000
Total heat liberated	2,293,000
Heat of conversion per pound nitrobenzene	1,911
Heat of conversion per pound mole nitrobenzene	235,053

In the catalytic hydrogenation of nitroxylene to xylidine, it was found that the heat of reduction is about 210,000 Btu per lb mole at 200°C and 215 atm pressure and 238,000 Btu per lb mole at 20°C and 1 atm.[2] These figures are in reasonable agreement with those shown above for the iron

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[1] U.S. 2,163,617 (1939); 2,174,008 (1939).

[2] VOORHIES, SMITH, and MASON, *Ind. Eng. Chem.*, **40**, 1543 (1948).

and acid reduction of nitrobenzene, which is generally carried out at 100°C without pressure.

Additions of Solvents. Where a very insoluble and difficultly reducible nitro compound is to be reduced, the addition of a solvent miscible with water, such as ethyl alcohol, methanol, or pyridine, is often of considerable help. This makes for a smoother and more rapid reduction. In carrying out the reduction, the alkalinized iron oxide sludge is filtered off hot and washed with hot solvent. The resulting amine is then isolated from the filtrate. This method is used where reduction in water alone is extremely slow or where the final amine can be isolated only by solvent extraction.

Testing for Completion. Reduction will not take place in the absence of ferrous ions, which can be demonstrated by the lack of a black precipitate on spot testing with sodium sulfide solution. The reaction is considered complete when an aliquot no longer increases its take-up of sodium nitrite on further reduction with a stronger reducing agent, such as zinc and hydrochloric acid.

Work-Up of Reaction Mixture. Soluble iron is generally precipitated with alkali, using caustic soda, soda ash, lime, or magnesia. Where the amine is volatile, it may be isolated by steam distillation or by vacuum distillation from the iron oxide cake after distilling off the water. In the latter case, an efficient scraper agitator must be used to keep the iron oxide from lumping and occluding the product. Where the final amine is soluble in alkaline solution, as is the case with sulfonic acids, carboxylic acids, or sulfonamides, the iron oxide cake is filtered off and the amine isolated from the filtrate.

Where neither of these two methods may be applied, a third and technically undesirable process is sometimes used. This involves solvent extraction of the iron oxide cake, which brings with it filtration problems and costly solvent recovery. Where a cheap solvent, such as naphtha, can be used, these difficulties are somewhat mitigated. Where a water-miscible solvent can be used, it is usually added to the reduction mixture initially, as discussed above.

When the final amine is volatile but sensitive to alkali, as is the case with some polychloroamines, the amine may be steam distilled from the slightly acid mixture.

Continuous Processing. Although the Béchamp reduction is generally carried out on a batch basis, it has been run continuously. This involves passing an acidified solution or emulsion of the nitro compound through a suitable tower packed with iron shavings or scrap iron and kept at the required temperature.[1]

Recovery of By-Products. In the technical preparation of amines by catalytic reduction with iron and a soluble salt, it is not customary to recover and utilize the dissolved catalyst. This step is not always feasible,

[1] Vikman and Mukhanova, Rus. 52,006 (1937).

particularly when the amino compound is also soluble in aqueous solutions. In many instances, however, such a step can be made part of the chemical-engineering operations employed in separating the amine from the aqueous suspension of iron compounds. Utilization of the aqueous portion in subsequent reductions appears to be an excellent method of introducing the catalyst in an active form. In this connection, it is known that the impure mother liquors from the aniline hydrochloride crystallizing pans can be used advantageously.

In the United States, the iron oxide sludge is often discarded. In Germany, however, considerable effort has been expended toward the development of processes whereby the sludge can be converted into useful pigments. The reductions may be carried out so that black, yellow, and red pigments are obtained as an integral part of the process. Addition of salts such as aluminum chloride influences the shade toward yellow.[1]

Yields of Amine. In plant practice, yields in the range of 85–98 per cent of theory are obtained with the Béchamp reduction. Depending upon the solubility and stability of the starting nitro and final amine, many variations of this process can be used to obtain the highest yield in the most economical fashion. Method and rate of addition of the nitro compound, temperature, agitation, addition of a solvent or an emulsifying agent may all influence the yield. Careful study in the laboratory is often required before a satisfactory plant process can be developed even for such an old method as the Béchamp reduction.

Equipment

Materials of Construction. Béchamp reductions are usually carried out in cast-iron vessels and alkali reductions in carbon-steel vessels of desired sizes. The larger ones (1,600-gal capacity) are favored by plant engineers because of the possibilities of more economical operation. The standard machines made by a number of equipment manufacturers resemble one another quite closely. Each manufacturer has, however, introduced one or more accessories or refinements calculated to appeal to the experienced chemical engineer.

The reducers for iron and acid reductions are sometimes equipped with side and bottom cast-iron lining plates, which may be reversed or replaced, in order to protect the vessel against the continuous erosive action of the iron borings. Alternatively, the reducers may be lined partially or entirely with acid-resisting brick or tile.[2] Such a protective coating lasts almost indefinitely and performs satisfactorily in service.

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[1] See *B.I.O.S., Final Rep.* 1144 and 1272 (British Intelligence Objectives Sub-committee); Haberland, U.S. 2,273,101 (1942); Riskin, *J. Appl. Chem.* (*U.S.S.R.*), **19**, 148, 262, 569 (1946).

[2] Adams and Harrington, *B.I.O.S. Final Rept.* 1144, Item 22. I. G. Farbenindustrie, Ürdingen.

The vessel is equipped with a nozzle at the base so that the iron oxide sludge or entire charge may be run out upon completion of the reaction. A wooden plug faced with iron discs and operated by a screw device fills the nozzle so that it is flush with the inside of the machine and makes an effective seal. Alternatively, the completed reaction mixture may be sucked out or blown out through a wide blowleg. Addition of water may be required to thin out the batch for such a discharge.

Wooden equipment is also used, particularly for the reduction of solid nitro compounds such as *p*-nitroaniline. These vessels are made of staves 2–3 in. in thickness, and the base is constructed of a double layer of 2-in. boards. Such tubs may range from 6–12 ft in diameter and up to a height of 12 ft. They are equipped with wooden exhaust stacks to vent the vapors and gases liberated during the reaction. The top of such a reducer contains a large opening through which the solid nitro body, iron, and acid are delivered, and it is provided with a removable cover. Bronze pipes are employed for the introduction of steam to such reducers.

Agitation. In some reducers a vertical shaft carries a set of cast-iron plows which can be removed through the side door to the reactor (Fig. 5-2). These plows travel at the rate of 30–50 rpm and serve to keep the iron particles in suspension in the lower part of the vessel. It will be recalled that the iron and acid reduction process is a four-component system, e.g., reducible organic compound, water, acid or metal salts, and metal. Obviously, the best results in such a catalytic process can be obtained only when all of the components are in intimate contact. If, in the reduction of nitrobenzene or similar compounds, the agitation is poor, most of the iron will be at the bottom, whereas the aqueous portion containing the acid or soluble metal salt will be at the top. It appears that a gate-and-propeller agitator of the type shown in Fig. 5-3 is more satisfactory, since it will be instrumental in bringing the iron particles to the upper portion of the reactor and providing more thorough mixing throughout the reaction mass. It is recognized that such an agitator needs to be made of material that will resist both the corrosion and erosion incidental to such reactions. It is to be expected that some of the deficiencies in mechanical agitation are balanced by the mixing provided by the evolution of molecular hydrogen which is generated in the reducer.

Jacketing of Reducers. Practically all the iron reducers employed for the Béchamp reduction of liquid nitro compounds are equipped with jackets. Although the reduction process is distinctly exothermic, the reaction proceeds best at slightly elevated temperatures. It is customary, therefore, to warm the reactants at the start. Sometimes it is found necessary to add heat to maintain an active reaction, and it is generally necessary to do so to complete the reduction.

When jacketed reducers are employed, the heat is applied indirectly and

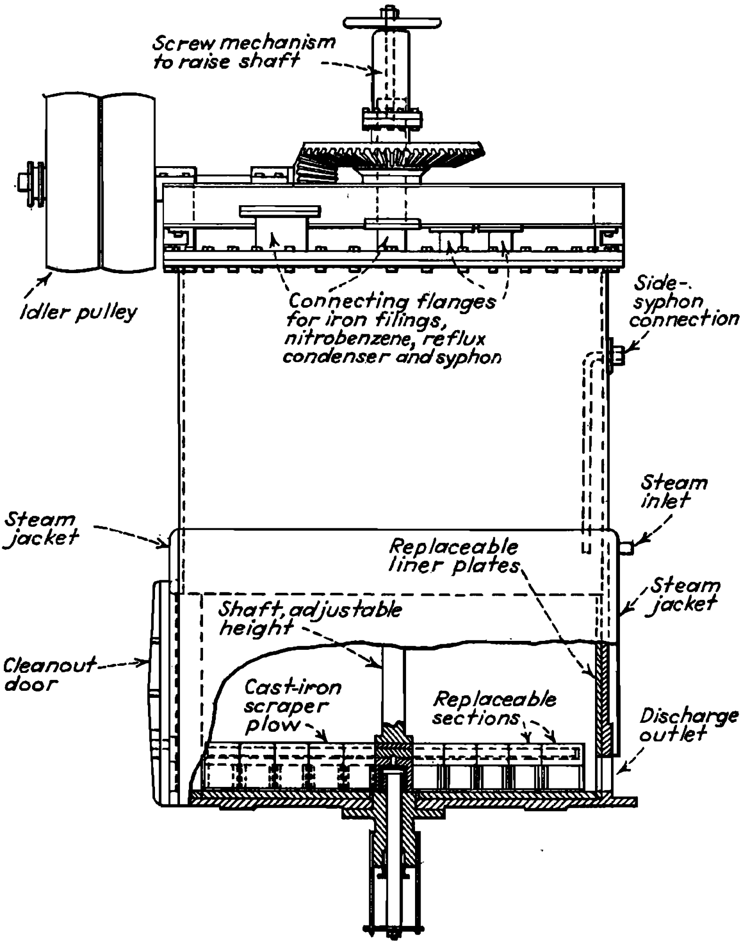
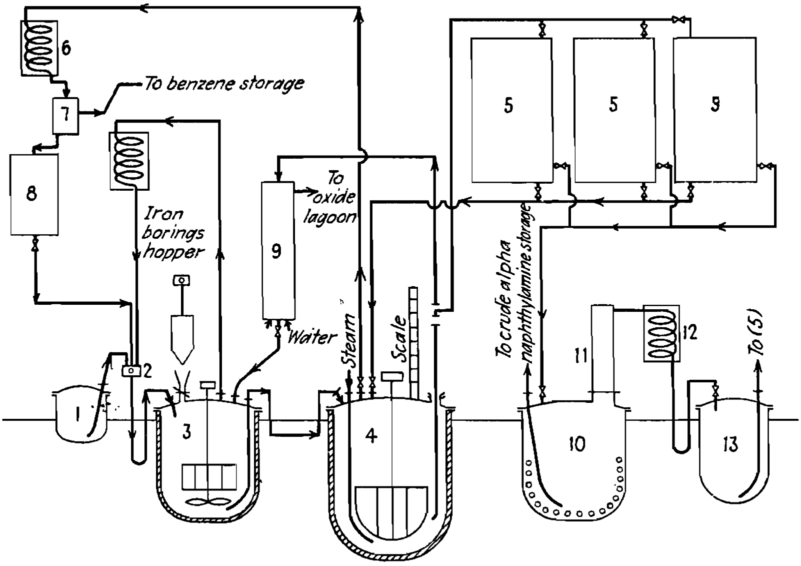


FIG. 5-2. Jacketed reducer.

no dilution of the charge occurs. Under such circumstances, the optimum quantity of water can be delivered during the "feeding" stage, and the reaction is kept active by regulating the introduction of the reactants. When the reaction vessels are not jacketed, as is the case with brick- or tile-lined kettles, live steam is introduced to start and maintain the reaction. Care must be taken that the charge does not become unduly diluted. Otherwise, the concentration of acid is lowered and the reaction rate decreased. Yields may also suffer.

It is apparent that the introduction of excessive water also entails an

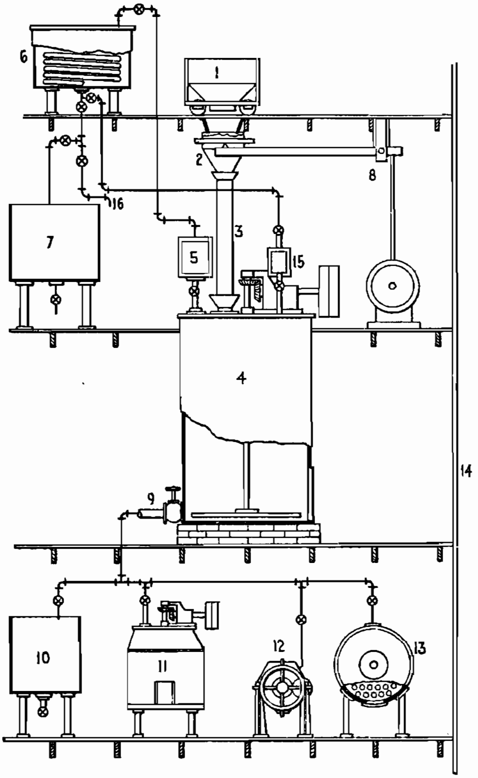


1 Nitronaphthalene in calibrated measuring tank
2 Mixing box connected with nitronaphthalene feed pipe and reflux condenser on reducer
3 Reducer, steel, tile-lined, with gate and propeller agitator and blow leg to extractor
4 Extractor, steel, tile-lined, gate agitator, adjustable dip pipe for removing solvent benzene; nitrogen and air connections
5 Benzene storage tanks with bottom outlet for sludge leading back to extractors; nitrogen connection for blowing
6 Coil condenser, steel, for use in steam distillation of extractor residues
7 Continuous separator, benzene-aqueous distillate during recovery of benzene from iron oxide sludge
8 Storage vessel for aqueous condensate, used in reducer
9 Iron oxide separator to reducer or lagoon
10 Solvent recovery still with plate column 11, condenser 12, receiver 13

FIG. 5-3. Reduction of α-nitronaphthalene in the presence of a solvent. (*B.I.O.S. Final Rept.* 1143, *Item* 22.)

increased cost in subsequent operations. It is immaterial whether the amine is a liquid or a solid or is recovered by fractional distillation or removal of water in a vacuum drier; any excess of water introduced during the reduction proper later requires a proportional amount of heat to effect its removal.

Reducer Accessories. The reducer (Fig. 5-2) is, of course, equipped with a suitable feeding device, which will deliver the iron borings as required. The borings bin is frequently attached to a scale so that the charge entering the reducer is being weighed continuously and accurately (Fig. 5-4). Suitable flanged or screwed openings are provided for the introduction of the liquid nitro compound and catalyst solution. Steam connections are made in accordance with specific requirements, depending on whether or not the vessel is jacketed and whether or not the resulting amine is to be distilled with steam. A sight box, which is placed in the reflux line from



1 Delivery car for iron borings
2 Hopper and automatic feeder
3 Iron-borings delivery line
4 Reducer
5 Baffle box
6 Condenser (note connections at base for refluxing or for distilling into 7)
7 Crude receivers
8 Weighing apparatus for iron borings
9 Outlet valve to reducer leading to 10, 11, 12, or 13
10 Ordinary receiver used in siphon system
11 Vacuum distilling kettle
12 Filter press
13 Horizontal vacuum still
14 Elevator shaft
15 Sight box on reflux line
16 Safety drip which is kept open during reflux period to prevent contamination of system with nitrobenzene

FIG. 5-4. Plant assembly: reducer house.

the condenser to the reducer, is located over the reducer to enable the operator to watch the progress of the reduction. By means of a valve or gooseneck under the sight box, a heel of condensate is retained to prevent the escape of fumes from the reducer.

A very efficient and compact heat exchanger for condensing the vapors from the reducer consists of a closed tank completely filled with concentric layers of lead coils. Water at a high velocity circulates through the coils, entering at the base and discharging at the top. The vapors rising from the reducer through the baffle box to the top of the condenser are distributed by a cylinder in the center of the condenser. The advantages of this heat exchanger are that it offers a maximum of surface to the vapors, no deposit or bubbles cover the outside of the coils to cut down the heat transfer, and the flow of cooling liquid is countercurrent to the descending vapors. The condensed liquid collects in a lower cast-iron sleeve from which it flows back to either the reducer or the distilling tanks (aniline receivers) in the event that the reaction is completed and the amine is to be distilled with steam.

Where the amine is recovered by vacuum distillation directly from the iron oxide, steel or cast-iron stills with heavy plow agitators are used. They may be heated by means of hot oil or Dowtherm. A column equipped with baffie plates is employed to prevent entrainment of iron oxide dust.

Manufacture of Aniline

Charging the Reducer and Carrying Out the Reaction. An accurately weighed charge of nitrobenzene (Table 5-4) is delivered to the reducer from a lower floor level to avoid the danger of contamination, which is inherent in gravity-flow systems. About 10–20 per cent of the total iron, water, and catalyst is added, and the charge is warmed to the reflux temperature, maintaining a constant effective agitation. The rate of reflux as observed in the sight glass must be quite vigorous and the condensate fairly hot. If the reaction temperature is too low, intermediate compounds are formed, and these are later reduced to aniline only with great difficulty.

TABLE 5-4. OPERATING DATA. REDUCTION OF NITROBENZENE; EFFECT OF SIZE OF IRON PARTICLES

	Fine	Coarse	Through mesh No.	Fine, %	Coarse, %
Charge of nitrobenzene, lb.	4,000	4,000	10	98.7	76.0
Initial feed completed, min.	30	30	20	70.0	40.5
Iron all in, hr.	8.5	10	40	27.8	17.5
Reduction complete, hr.	4	4.2	60	19.1	11.5
Total time to feed and reduce, hr.	12.5	14.2	80	11.4	7.0
Iron used, lb.	4,030	4,462			
Molar ratio, iron:nitrobenzene	2.2	2.46			
Ferrous chloride, 58% crystals, lb.	240	240			
$FeCl_2$ used, % theory	1.2	1.2			

From an operating viewpoint, the process of feeding the reducer is a comparatively simple matter. A smooth reaction devoid of pressure peaks is obtained when the iron is uniform in quality, free of oil, and of a good physical character. It should preferably be delivered in small quantities to the boiling charge. The frequent delivery of small batches of iron minimizes the possibility of "sticking" the stirrers, because of the presence of an abnormal amount of iron hydroxides. When a solid catalyst, such as ferrous chloride or sodium acid sulfate, is used, it is customary to feed it along with the iron, although theoretical considerations would suggest its complete introduction at the start. Such a practice, although simplifying the operation, may lead to excessive pressures. The water required for the hydrolytic reactions may be introduced in a number of ways. It may consist of (1) aniline waters recovered from certain steps in the operation, (2) dilute aniline-salt mother liquors when such a catalyst is available, (3) the aqueous solution containing the soluble active catalyst from a previous reduction, or (4), finally, it may be tap water that is used to wash down each addition of iron borings.

During the addition of iron, no external heat is required to carry on the reaction, as the reduction process is distinctly exothermic, about 1900 Btu being liberated per pound of nitro compound that is converted. It is necessary, therefore, to provide an efficient condenser in order to maintain a rapid rate of reduction and to avoid excessive operating pressures.

Obviously, the preceding outline relating to the feeding of materials to the reducer is susceptible to many modifications. It is entirely feasible to add all the water, iron, and soluble catalyst at the start. This mass is then thoroughly heated and agitated to etch the iron. The aromatic nitro compounds can thereupon be introduced at definite time intervals, the precaution being taken that each portion is completely reduced before continuing with further addition. This technique gives satisfactory results in the reduction of many nitro compounds.

After all the reactants have been introduced, external heat is required to maintain a lively reflux. Steam may be introduced directly into the reducer charge, or it may be circulated through the jacket of the reducer. The condenser water is throttled down to avoid overcooling of the condensate, as this should be only slightly below the boiling point. As the reduction nears completion, the color of the distillate changes from orange to yellow and finally becomes colorless.

From an inspection of the equations representing the reduction process, the presence of combined aniline ($C_6H_5NH_3Cl$) in appreciable quantities would not be expected at the close of the reduction. The use of chalk to neutralize the charge (as practiced at Ürdingen),[1] when small proportions of a chloride salt are used as catalyst, is then largely a precautionary measure, for it can be shown that the base has been set free almost in entirety by hydrolytic action. The more highly dissociated ferrous chloride is, of course, concomitantly regenerated at the close of the reduction, and the test for soluble iron with sodium sulfide solution is very distinct. It is clear that the reaction represented below proceeds to the right most readily in the presence of metallic iron. In its absence, the weak base would be almost completely converted to the salt of the amine by the strong acid.

$$2(RNH_3)^+ + 2Cl^+ + Fe \xrightarrow{H_2O} 2RNH_2 + FeCl_2 + H_2\uparrow$$

[1] *B.I.O.S. Final Rept.* 1144, Item 22.

The introduction of alkali does, however, break up soluble iron aromatic compounds, such as hydroxylamine derivatives. Furthermore, it makes possible a more rapid distillation of the amine, as the introduction of the common ion OH^- reduces the solubility of aniline in water. In the preparation of water-soluble amines, neutralization of the charge is desirable only when the crude product is to be dehydrated and purified by distillation. The preparation of *p*-phenylenediamine is such an example. When the soluble amine is recovered by partial dehydration and crystallization, the faintly acid mother liquors, containing the active catalyst, can be used in subsequent reductions.

Recovery of Aniline. The most important problem in the preparation of aniline concerns its separation from the reducer charge. The problem is essentially one of chemical engineering. The engineer's goal is to provide for the continuous mechanical separation of the aniline and water from the iron oxide sludge and to recover the latter as a finely divided dry powder of commercial value, where a market exists. The aniline should then be separated from the water in a reasonably pure state, the amine going to the storage for final distillation (Fig. 5-5), while the aqueous solution containing dissolved catalyst and some amine is returned to the reducer. Groggins, in a survey of the processes for the manufacture of aniline, showed that considerable economic advantage accompanies the choice of an efficient separating scheme.[1] In this work, the following criteria were suggested as a guide in the selection of equipment:

1. *Simplicity.* Minimum handling of material.
2. *Yields.* Reduction to a minimum of the known sources of loss.
3. *Productivity.* Discharging the batch immediately after reduction is complete.
4. *Water balance.* Elimination of methods that cause an accumulation of aniline water, as this involves a great loss in yield and an increase in power costs.
5. *Power load.* The consumption of steam, water, and electricity is an important factor in determining the cost.
6. *By-product sludge.* In some localities, a market can be obtained for a dry, clean, finely divided aniline-free iron oxide.

These criteria will be better appreciated by reviewing four methods used for separating the aniline from the reducer charge. These will be presented very briefly, giving due attention to the underlying economic factors.

The first method entails *steam distillation* of the product aniline from the charge. This is one of the first and most costly systems. After reduction is complete, the reflux from the reducer condensers is directed to a receiving tank, and live steam is introduced to carry on the distillation. Approxi-

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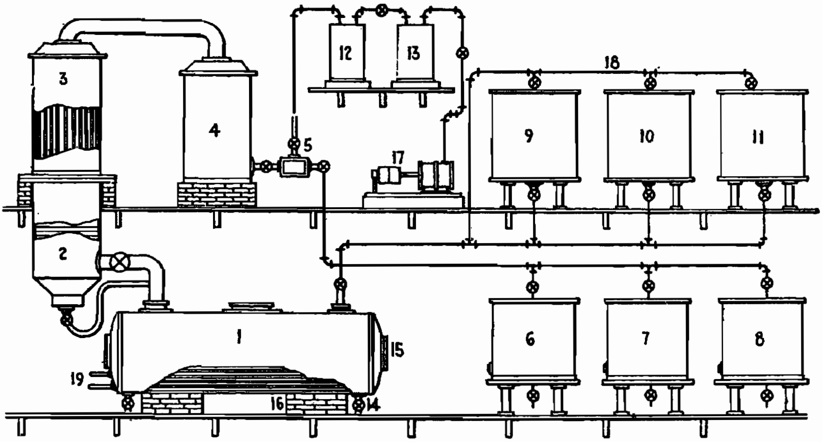
[1] GROGGINS, "Aniline and Its Derivatives," D. Van Nostrand Company, Inc., New York, 1924.

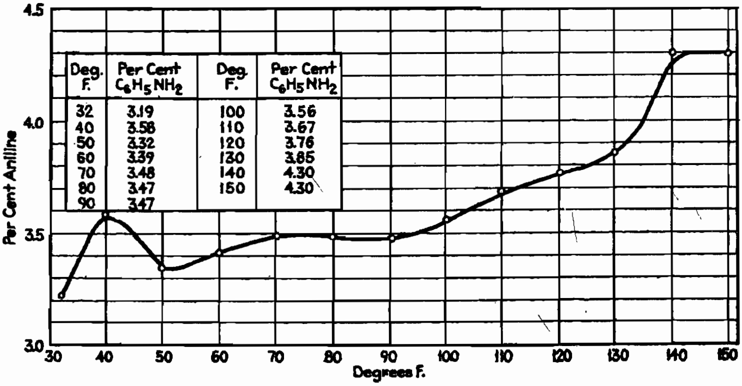


1 Horizontal still, completely lagged
2 Dephlegmator
3 Dephlegmator condenser
4 Condenser
5 Sight box with connection leading to 6, 7, 8
6, 7, 8 Receivers for pure aniline
9, 10, 11 Crude-aniline reservoirs
12, 13 Catch-all tanks for aniline vapors
14 Bottom outlet to still
15 Clean-out hole
16 Horizontal steam coils in still
17 Vacuum pump
18 Vacuum feed line from crude-aniline reservoirs to still
19 Outside steam connections to still

FIG. 5-5. Aniline distillation: plant assembly.

mately 5.9 lb water per pound aniline is thus introduced into the system. The distillate in the receiving tank is permitted to cool, and the heavier oil is drawn off and delivered to the rectifier. The aniline water, containing 3.5–5.0 per cent amine (Figs. 5-6 and 5-7), is drawn from an upper valve and pumped to storage tanks.

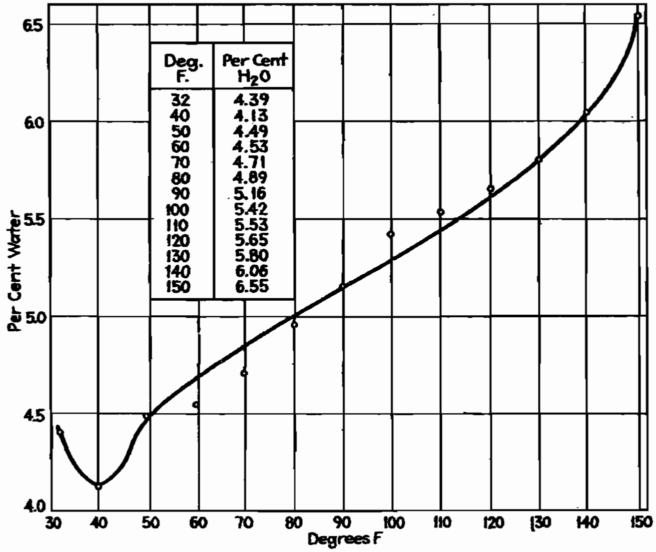
This aniline water may be treated in various ways for recovery of the aniline. If it is to be distilled, it is usually made slightly alkaline prior to



Deg. F.	Per Cent $C_6H_5NH_2$	Deg. F.	Per Cent $C_6H_5NH_2$
32	3.19	100	3.56
40	3.58	110	3.67
50	3.32	120	3.76
60	3.39	130	3.85
70	3.48	140	4.30
80	3.47	150	4.30
90	3.47		

FIG. 5-6. Solubility of aniline in water.

its being delivered to the aniline-water stills. The latter are usually long horizontal tanks provided with steam coils. When half the charge is distilled, the residual liquor shows only a trace of aniline. The distillate is cooled and settled, and the aniline that separates out owing to its increased concentration is removed. The aniline water is again returned to the system and treated again. It is evident in this steam-distillation process, requiring about 9 lb steam per pound aniline recovered, that large volumes of material must be handled. The method is, furthermore, objectionable, as it curtails production because the reducer is used as a still.



Deg. F.	Per Cent H_2O
32	4.39
40	4.13
50	4.49
60	4.53
70	4.71
80	4.89
90	5.16
100	5.42
110	5.53
120	5.65
130	5.80
140	6.06
150	6.55

FIG. 5-7. Solubility of water in aniline.

When the reduction takes place in a jacketed reducer, a significant improvement is realized. This is due to the fact that the jacket cuts down the dilution during the reduction period. Furthermore, some of the ensuing distillate is fortunately consumed in the reduction of the next charge. Finally, less steam is required during the distillation period, owing to the increased aniline concentration in the reducer charge.

Another system, used by I. G. Farbenindustrie,[1] is identical with the preceding up to the point where the aniline oil is drawn off from the settling tanks. The supernatant water is now treated with nitrobenzene intended for the reducer house. Two extractions are made on each batch of aniline, according to the flow sheet shown in Fig. 5-8, after which the water is practically free of both aniline and nitrobenzene.

[1] *B.I.O.S. Final Rept.* 1144, Item 22.

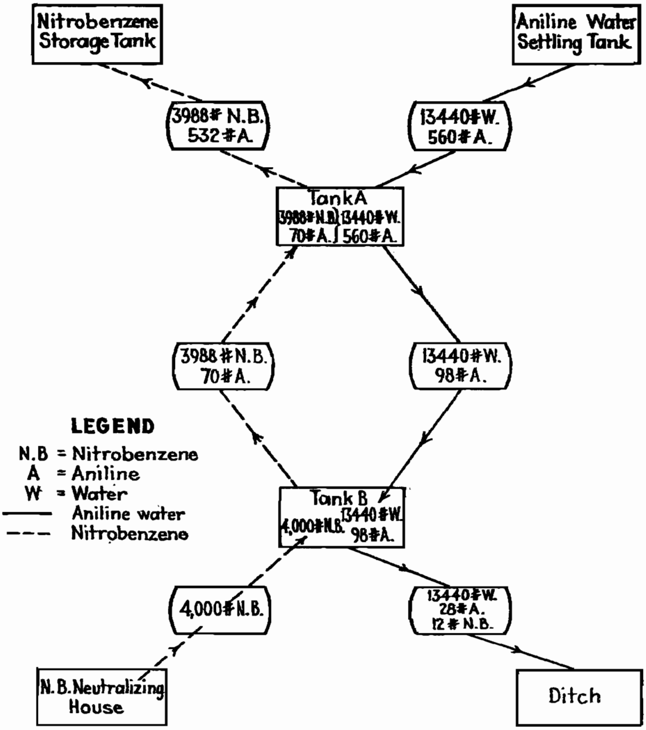


FIG. 5-8. Flow sheet: nitrobenzene extraction of aniline.

The practice of using the surplus aniline water in a boiler to generate steam for use in the reducers is one that formerly found considerable favor in Europe. The operation calls for a large aniline-water reservoir to which all the water from the settling tanks is delivered. From a side valve considerably above the base of the tank, the water is drawn off and delivered under pressure to the boiler. The steam line from the boiler is led to the reducers and is connected separately, so that "pure" steam can be used to complete the reduction and distillation. It is apparent that this is a fairly economical method of treating distillation waters. Precautions must be taken to neutralize the aniline waters in order to diminish boiler-tube trouble, which is one of the disturbing features of this system.

The second method of separation (see Fig. 5-4) involves *direct vacuum distillation* from the iron oxide cake. This system generally employs large cast-iron vacuum stills into which the reducer charge runs by gravity, vacuum, or pressure. As soon as delivery is complete, the reducer is prepared for the next run and the distillation of the finished charge started. Inasmuch as the distillation is carried on *in vacuo*, the aniline water comes over first, and then a mixture containing increasing proportions of aniline, until all the water is removed. The aniline content is about half distilled by the time water-free aniline is obtained. This fraction continues only for a short time, when the distillate is darkened by contamination with the residual sludge. The installation of an auxiliary dephlegmator makes possible a better separation, but, of course, entails additional cost.

The system works fairly satisfactorily, the greatest difficulty being the reduction of the aniline content of the iron oxide sludge. When the residual amine content is about 10 per cent, the charge becomes gummy, and a tremendous load is put on the stirring mechanism. This condition prevails until the oxide granulates and falls over the plows. Approximately half the operating time is consumed in recovering the last 10 per cent of the yield. When the distillate is reduced to negligible proportions, the dry sludge is discharged into industrial cars.

An analysis of the hot residue, which is very fine and dusty, shows that it is practically all magnetic iron oxide. As it is hot, the surface material sets up an oxidation, with the formation of the red Fe_2O_3. Analytical tests show that considerable aniline remains behind unless long drying periods are provided.

A modification of the preceding method is carried out as follows. The reducer charge is dropped into a large horizontal vacuum tank that is fitted with a large number of welded, seamless extra-heavy steam pipes. Heat is applied as before, and the distillation proceeds even more rapidly on account of the greater heating surface. At the close of the distillation, the manhead to the vacuum tank is removed and the dry iron oxide flushed out at the base by means of a powerful stream of water.

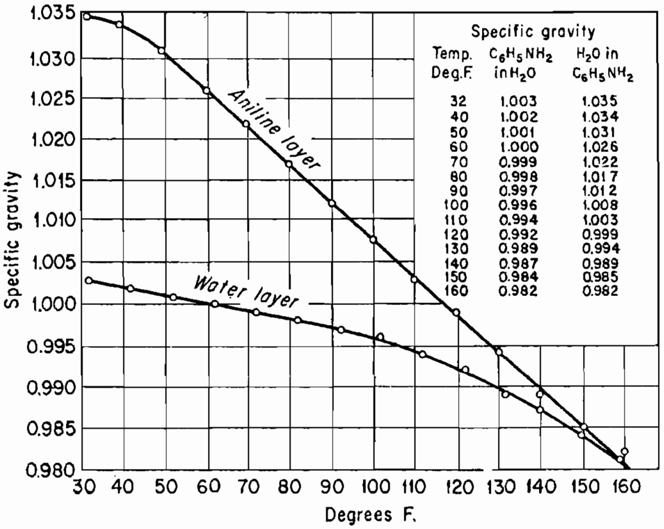
The vacuum-distillation system is improved by distilling with live steam the final 10 per cent of aniline. Such a practice does not introduce a large quantity of water into the system and saves considerable time. The vacuum-distillation system apparently doubles the productivity of the reducers; but since the cost of the stills is considerable, the saving is more apparent than real.

The third method encompasses *filtration of the reducer charge.* In this system, the entire charge from the reducer is delivered to a large filter box containing three parallel rows of coarse to fine sieves that can be turned for dumping. Since the sludge retains considerable aniline, the cake is first washed with a stock solution of aniline water and then with fresh boiling water and then blown with hot air or steam. This procedure leaves about 8 per cent aniline water of 5 per cent aniline content with the sludge and constitutes a loss of less than 1 per cent of the total yield. Some of the advantages of filtration separation are simplicity of operation, low operating cost, increase in productive capacity of reducers, elimination of cooling water, and lowering of steam and power costs.

The success of this procedure depends on the solution of the unit operation—filtration. The reducer charge contains iron hydroxides and filters very poorly. It is necessary, therefore, to effect the filtration in stages through metal screens, preferably after the introduction of an electrolyte to expedite the precipitation of colloidal iron compounds. Centrifuges have also been used. The filtrate can be settled for the separation and decantation of aniline.

The fourth method includes a *siphon separation.* The introduction of a siphon into the reducer at the completion of the reduction stage to draw off the supernatant oil from the lower aqueous layer is a convenient and inexpensive method of effecting the separation. A glance at the temperature—specific gravity curves (Fig. 5-9) reveals that the two curves cross at 71°C (160°F). The separation is accelerated and made sharper by the addition of salt, which increases the density of the aqueous layer and decreases the solubility of aniline therein.

Jacketed reducers are used in this system, and reduction is effected by the use of external heat. Owing to the fact that there is a slight loss of water during the reduction process, it is necessary to provide sufficient at the start to ensure fluidity. An excessive water content, however, may slow



Temp. Deg.F.	Specific gravity $C_6H_5NH_2$ in H_2O	Specific gravity H_2O in $C_6H_5NH_2$
32	1.003	1.035
40	1.002	1.034
50	1.001	1.031
60	1.000	1.026
70	0.999	1.022
80	0.998	1.017
90	0.997	1.012
100	0.996	1.008
110	0.994	1.003
120	0.992	0.999
130	0.989	0.994
140	0.987	0.989
150	0.984	0.985
160	0.982	0.982

FIG. 5-9. Temperature—specific gravity curves: aniline-water system.

up the reduction on account of the lower concentration of soluble catalyst.

The siphon is usually an inverted funnel operated by a worm drive and enters the vessel through a tight stuffing box. During the operation, it is worked up toward the top of the reducer so as to clear the paddles or other type of stirring mechanism. An alternate scheme utilizes a bent tube for withdrawing the aniline. A 2-in. pipe penetrates the side of the reducer through a stuffing box above the jacket line, and an improvised gauge on the outside of the reducer indicates the position of the bend on the inside. By this means, it is possible to lower the siphon end accurately to the desired level and later raise it out of the sphere of agitation. This scheme avoids almost completely any stoppage and breaks in the draw-off line, difficulties that are encountered when the siphon is suspended from the top cover of the reducer.

After reduction is completed, 5–10 per cent by weight of salt (compared with nitrobenzene used) is added and the agitation continued until the sodium chloride is completely dissolved. Agitation is then stopped, the plows are raised above the sludge, and the charge is allowed to settle. Steam is kept on the jacket to maintain a temperature of 85–90°C in the reducer. The introduction of a demulsifying agent along with the salt has been suggested for expediting the separation of the layers.

After settling about 1 hr, a slight vacuum is put on the receiving tank and the siphon mechanism lowered to the desired level. A sight glass on the delivery line indicates the rate of delivery and the quality of the aniline. If too great a vacuum is used, considerable turbidity results. The tube is lowered slowly until the sight glass indicates that the aniline is being contaminated with considerable water.

The remainder of the charge consists of aniline water and iron oxides. Live steam is admitted, with continued stirring, until the batch is free of aniline. The final distillation may be made in a separate still when production requirements justify such an installation. In view of the fact that only a small quantity of aniline remains after the separation, very little time and steam are consumed in the final operation. In fact, the aqueous layer may be returned to the reducer for the next charge and thus save the bulk of the soluble catalyst. Still another use for the aqueous layer is its utilization in washing the nitrobenzene intended for the reducer house. These alternative methods save some of the expense of steam distillation and, incidentally, serve a useful purpose in the scheme of operations.

The siphon system is indeed attractive, as it is easily adapted to existing plants. It is compact, economical, and devoid of aniline water problems. The cost of salt, the use of which may be dispensed with, is quite insignificant when compared with the cost of steam necessary to distill the aniline from the reducer charge. A filter box can be used to advantage in order to eliminate the fine iron oxide that is drawn over with the aniline. These boxes are constructed so that they can be opened and cleaned in a few minutes, and if necessary, a new filter plate may be installed. In all cases, it is advisable to clarify the aniline by some method before submitting it to final distillation.

In the siphon system of aniline-oil separation, the cost of installation and maintenance is very low, less machinery being used than in any of the other systems. There is also a minimum of handling of the amine, which is reflected in better operating yields.

Owing to the fact that the sludge has to settle out to effect a satisfactory separation, a mechanical problem is presented in providing a proper type of transmission to permit resumption of agitation after the amino compound is drawn off. When fine iron borings are used and are fed in small portions, the resultant sludge should not cause any transmission trouble. In fact, in some reductions (*p*-nitroaniline to *p*-phenylenediamine), it is customary to permit the reduced charges to stand overnight. When, however, the transmission apparatus is designed to permit the raising of the stirrer (see Fig. 5-2), no difficulty is experienced in restarting.

Distillation of Aniline. The purification of the crude aniline derived from any of the previously described processes is generally carried out in a batch still provided with a rectifying column and a condenser (Fig. 5-5). A reflux of about 30–40 per cent is usually employed. The distillation involves three stages as follows:

20–125°C, 760 mm	Water + some aniline
125–113°C, 760–785 mm	Aniline water
113°C, 85 mm	Aniline

The amount of steam required is given in Table 5-5. In some plants the

TABLE 5-5. STEAM REQUIRED TO DISTILL ANILINE

Average temperature of crude oil delivered to rectifier	80°F (27°C)
Boiling point maintained at 28 in. vacuum	230°F (110°C)
Difference in temperature—sensible heat	150°F
Specific heat of aniline	×0.52
	78.0 Btu
Latent heat of vaporization	180.0 Btu
Reflux in dephlegmator ⅓ latent heat (est.)	60 Btu
Total Btu required per lb aniline	318.0 Btu
Latent heat of steam supplied at 140 lb pressure	860 Btu

$\frac{860}{318}$ = 2.70 lb aniline distilled per lb steam used

$\frac{31{,}800}{860}$ = 37 lb steam required per 100 lb aniline*

* In actual practice, because of the presence of water and radiation, about 52 lb steam is used per 100 lb refined aniline produced from a charge comprising 25,350 lb aniline and 1,950 lb water.

residue from the primary still is transferred to a second still, where it is mixed with absorbent clay and then distilled with steam.

Economic Summary. It would be misleading to draw conclusions solely from the known sources of loss and energy consumption in the various methods of separating the aniline from the charge. A number of other factors enter into the preparation of the cost sheet besides the tabulation of comparative losses and power charges. The figures do present, however,

TABLE 5-6. MANUFACTURE OF ANILINE: ECONOMIC SURVEY

Type of separation	*Approx. cost per 1,000 lb aniline*
Steam distillation of aniline in nonjacketed reducer	$12.75
Steam distillation of aniline in jacketed reducer	10.25
Steam distillation of aniline: nitrobenzene extraction of aniline water:	
Nonjacketed reducers	8.25
Steam distillation of aniline: nitrobenzene extraction of aniline water:	
Jacketed reducer	6.25
Use of aniline boiler to generate steam from aniline water	4.00
Jacket reduction, accompanied by vacuum distillation	3.00
Filtration of reducer charges	1.25
Siphon separation, according to modifications	1.00–4.25

TABLE 5-7. COST FACTORS IN PRODUCTION OF ANILINE BY BÉCHAMP REDUCTION

Reduction of nitrobenzene to aniline:	
Molecular weight benzene (C_6H_6)	78
Molecular weight nitrobenzene ($C_6H_5NO_2$)	123
Molecular weight aniline ($C_6H_5NH_2$)	93
Theoretical yield of aniline per 100 lb benzene	119.2 lb
Standard yield of aniline per 100 lb benzene	109.8 lb
Theoretical yield of aniline per 100 lb nitrobenzene	75.6 lb
Standard yield of aniline per 100 lb nitrobenzene (98%)	74.0 lb
Materials to produce 100 lb aniline from nitrobenzene:	
135 lb nitrobenzene, at $0.08 (captive manufacture)	$10.80
140 lb iron borings, at $0.025	3.50
15 lb HCl (or equivalent), at $0.015	0.23
Total material costs	$14.53
Operating costs: labor operating, repairs, supplies, direct supervision	$ 1.68
Power costs: electricity, steam, air, water	0.44
Overhead: administration, depreciation, insurance, fixed charges	0.46
Plant cost per 100 lb aniline	$17.11

Aniline Cost Data Analysis

$$\text{Percentage cost of raw materials} = \frac{14.53}{17.11} = 84.9\%$$

$$\text{Percentage cost of operation} = \frac{1.68}{17.11} = 9.8\%$$

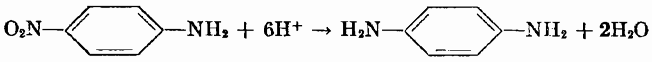
$$\text{Percentage cost of power} = \frac{0.44}{17.11} = 2.6\%$$

$$\text{Percentage cost of overhead} = \frac{0.46}{17.11} = 2.7\%$$

the known possible efficiencies that may be expected from the several modifications of this unit process. If the variables of operating efficiencies are disregarded for a moment, the approximate comparative charges for separating the crude aniline from the reducer charge are as shown in Table 5-6.

Some of the theoretical considerations and economic factors entering into the cost of producing aniline by the Béchamp reduction are presented in Table 5-7.

Manufacture of *p*-Phenylenediamine



p-Phenylenediamine is manufactured commercially by the reduction of *p*-nitroaniline. This reduction is quite similar to that of aniline, and its technique is subject to some of the same numerous modifications.

The process may be conveniently divided into four steps:

1. Reduction of the *p*-nitroaniline to *p*-phenylenediamine.
2. Filtration of the reduction batch to remove iron oxide sludge.
3. Dehydration of filtered liquor.
4. Vacuum distillation of crude *p*-phenylenediamine.

Reduction. A large wooden vat is used to carry on this operation (Fig. 5-10). The batch is stirred by means of a steel shaft which carries two or more sets of plows. A heavy-duty motor is provided to take care of the heavy initial reduction load and also when starting up tubs that have been left quiescent overnight. Two tubs are required for plant operations. One is used for preparing a new batch while the other is delivering the reduced charge to the filter.

The operation is started by pumping up sufficient wash water from previous charges to cover the paddles of the agitator. The stirrers operating at 40 rpm are then started, and 1,000 lb of iron borings is slowly put into the tub. Then 100 lb of 20°Bé hydrochloric acid is added and the mixture agitated and heated until the iron is etched and a good paste of ferrous chloride is made. It should react immediately and distinctly when spotted with a weak sodium sulfide solution. Either dry or moist *p*-nitro-

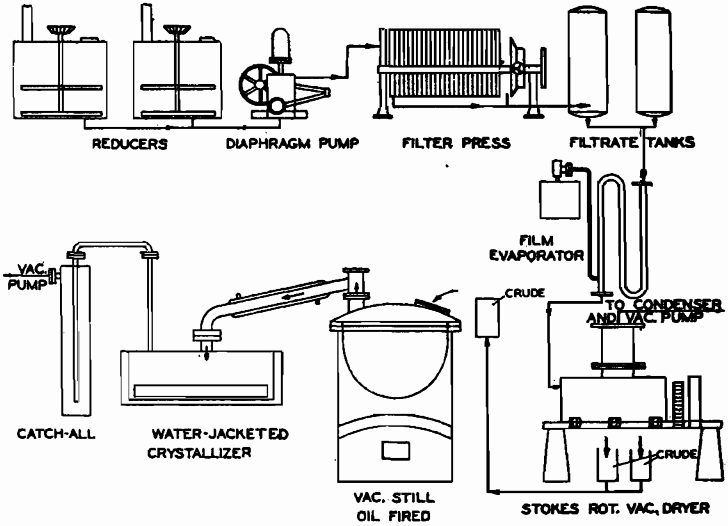


FIG. 5-10. *p*-Phenylenediamine plant.

aniline is then introduced, about 50 lb at a time. After each addition, sufficient time must elapse to ensure the presence of ferrous chloride, for it will be noticed that the spot test for soluble iron fails immediately after the addition of nitro compound. The charge must be kept sufficiently warm so that a foaming reaction prevails. It has been found that a ratio of 1.20 lb of iron to 1 lb of *p*-nitroaniline (molar ratio 3:1) gives the best results, although it is possible, as in the production of aniline, to lower this ratio slightly. Toward the close of the feeding operation, the balance of iron necessary for reduction is introduced. Thus, when 750 lb out of a total of 1,200 lb of nitro compound has been fed into the vat, the balance of approximately 500 lb of fine iron is added. The total time of charging of *p*-nitroaniline is about 12 hr.

Toward the end of the run, the reaction slows down, and it is necessary to introduce steam to carry on and complete the reduction. The test for soluble iron also becomes less distinct. As long as there is any *p*-nitroaniline present, a yellow spot test will be obtained on filter paper. *p*-Phenylenediamine yields a purple spot with a perfectly clear ring around the sludge spot. It is always advisable to test for soluble iron with sodium sulfide to ensure completeness of reduction. If the reduction is not carried on at the boiling temperature, intermediate azo and hydrazo products are sure to be formed. These are not so easily reduced and cause a lowering of the yield.

To prevent any oxidation of the *p*-phenylenediamine liquor prior to filtration, it is advisable not to neutralize the charge until this phase of the process begins. An excess of soda ash is used, and a test for alkalinity with phenolphthalein is required. Then 2 lb of sodium bisulfite and 3 lb of sodium sulfide (30 per cent crystals) are added to precipitate soluble iron salts and to prevent subsequent oxidation.

Filtration of Reduction Batch. A large plate-and-frame filter is customarily used to separate the residual iron sludge from the *p*-phenylenediamine liquor. Preceding the press is a pump for delivering the charge from the tubs. Air and water lines and an ejector for delivering hot water during the washing period complete its accessories. The press is first warmed by passing in live steam, and the delivery pump is started. The filtrate is tested for completeness of reduction and for clarity. A spot on filter paper should be very light purple with no traces of yellow. The presence of a blue tint indicates the formation of indulines.

As soon as the batch is on the filter, it is washed with wash water from previous batches. This liquid follows the rest of the batch into one of two storage tanks that are placed below the press level, so that the filtrate flows into them by gravity. Hot water is then introduced into the press, and this filtrate runs into a large tank. Just enough hot water is used to maintain a water balance, i.e., to have sufficient to provide a heel for the reducer tub and to replace the original mother liquor on the filter. The filter is then blown with air until the cake is dry. The cake is dropped into a pan underneath the press and removed. It is analyzed regularly for amino content.

Dehydration of Diamine Liquor. The filtrate from the press is a dilute solution of *p*-phenylenediamine containing a small amount of iron oxide in suspension. Since only 940 lb of *p*-phenylenediamine can be theoretically obtained from 1,200 lb of *p*-nitroaniline and about 9,000–10,000 lb of water is used during the reduction, it is apparent that a 10 per cent solution of phenylenediamine is delivered to the liquor-storage tank. Although it is feasible and practicable to deliver a solution of such strength directly to the drier, it is more economical from the standpoint of both yield and steam consumption first to concentrate this liquor. Two-stage vertical evaporators and film evaporators have been used successfully for this purpose. A steam-jacketed vacuum drier of suitable dimensions can be used for effecting the final dehydration. On top of the drier is an upright steel shell 2 ft in diameter and 4 ft high, packed with suitable material to prevent entrainment, that leads to a tubular condenser. A sight box at the base of the condenser permits the operator to inspect the condensate. This should not contain more than a trace of color; otherwise, a loss of *p*-phenylenediamine is indicated. When the sight box indicates that most of the water has been distilled off, the jacket steam pressure is reduced from 15 to 5 lb and after 1 hr turned off completely. If the batch in the drier is now further agitated for 1 hr, it will be ready for dumping. A sample must always be first taken to ensure absolute dryness. The crude product must be black, with a purplish tinge. A gray tinge indicates moisture. The presence of 1 per cent water in the crude product is detrimental to the production of a good *p*-phenylenediamine.

The material in the drier is discharged into large steel cans and weighed. From this weight, the yield of crude *p*-phenylenediamine is obtained, and the charges for the vacuum still are made up. It is advisable to analyze the crude *p*-phenylenediamine for salt and iron at regular intervals, as these figures give valuable information regarding the operations. About 82 lb of crude product is obtained for every 100 lb of *p*-nitroaniline reduced.

Vacuum Distillation of Crude *p*-Phenylenediamine. A cast-iron still (Fig. 5-11) capable of holding 1,000 lb of crude *p*-phenylenediamine is placed on a masonry setting, and a solid arch is built underneath it so that it runs back within 10 in. of the rear wall. In this way, the heat furnished either by gas or by fuel oil reaches the still mainly by radiation. A stirred kettle, heated by oil or Dowtherm, may also be used as the still. When optimum conditions prevail, the temperature of the batch in the still will be 230–250°C, and the temperature of the vapors in the line leaving the still will be 180–190°C. An efficient vacuum pump is needed to obtain a very attractive crystalline product. The crystallizing pans that receive the molten product from the still are placed in water-cooled castings. At the close of each run, the pans are allowed to stand and cool for several hours and then pulled out. It is necessary to cool the distilled product about 36 hr before breaking it up, as it remains molten on the inside for a long time. If the fused cake is broken prematurely, the color deteriorates.

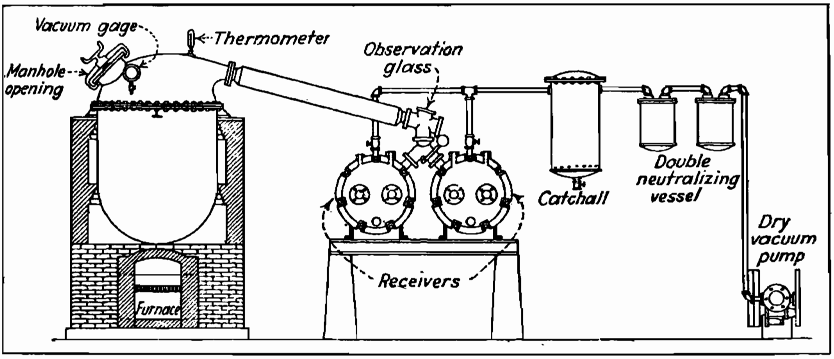


FIG. 5-11. Vacuum-distillation plant for *p*-phenylenediamine.

If the crude is moist, the final product will be very poor and sometimes sloppy. A distinct red coloration of the finished product indicates either moisture or acidity in the crude product.

Yields. The yields obtained by the process outlined above should be about 90 per cent of theory, or slightly over 70 lb of finished *p*-phenylenediamine per 100 lb of *p*-nitroaniline used. The sources of loss in the system are

Reduction	3%
Filtration	1½%
Dehydration	1½%
Distillation	3%
Total	9%

COST OF MATERIALS USED IN REDUCTION

Reduction	*p*-Nitroaniline	1,200 lb at	\$0.445 =	\$534.00
	Iron borings	1,460 lb at	0.025 =	36.50
	Hydrochloric acid	115 lb at	0.015 =	1.73
Neutralization	Sodium carbonate	60 lb at	0.015 =	0.90
	Sodium sulfide	4 lb at	0.02 =	0.08
	Sodium bisulfite	2 lb at	0.05 =	0.10
Cost of raw materials:				\$573.31
Cost of raw materials per 100 lb *p*-phenylenediamine based on yield of 70.1 lb per 100 lb *p*-nitroaniline used				\$68.15

Based on a monthly production of approximately 20,000 lb of *p*-phenylenediamine, the factory cost data per 100 lb of product will be close to the following:

Raw materials	\$68.15
Operating charges	4.73
Power charges	4.20
Plant overhead	3.54
Plant cost per 100 lb *p*-phenylenediamine, exclusive of package, storing, and sales expense	\$80.62

An analysis of the cost elements again reveals the importance of obtaining high operating efficiencies:

$$\text{Percentage cost of raw materials} = \frac{68.15}{80.62} = 84.5\%$$

$$\text{Percentage cost of operation} = \frac{4.73}{80.62} = 5.9\%$$

$$\text{Percentage cost of power} = \frac{4.20}{80.62} = 5.2\%$$

$$\text{Percentage cost of plant overhead} = \frac{3.54}{80.62} = 4.4\%$$

IV. OTHER METAL AND ACID REDUCTIONS

Zinc and Acid. A method which, although quite expensive, is often very useful in reducing certain insoluble and difficultly reducible nitro compounds, such as sulfones and highly ring-substituted derivatives of nitrobenzene, is that involving zinc dust and acid. The reaction may be represented as follows:

$$RNO_2 + 3Zn + 3H_2SO_4 \rightarrow RNH_2 + 3ZnSO_4 + 2H_2O$$

Usually sulfuric or hydrochloric acid is used but, where a milder acid is required because of sensitivity of the nitro compound or amine, acetic acid may be substituted. Generally, 3.5–7.5 moles of zinc dust is used per mole of nitro compound and excess acid of about 20–50 per cent concentration.

Normally the nitro compound is slurried in acid and zinc dust added gradually, with stirring, at whatever the optimum temperature may be, usually somewhere between 50 and 100°C. (The use of hot concentrated sulfuric acid results in *p*-aminophenol rather than aniline.) A variation of this method is to slurry the nitro compound in water together with zinc dust and (at times) an emulsifying agent and to add strong acid slowly.

This process is technically most feasible for the preparation of those amines which are insoluble at a pH lower than 5.0, so that the amine may be separated from dissolved zinc salts without resorting to a very elaborate isolation scheme such as extraction with organic solvents.

Tin and Acid. Owing to the comparatively high cost of tin, this method of effecting reductions can hardly be considered of commercial importance. In place of tin and hydrochloric acid, a solution of stannous chloride in hydrochloric acid can be employed; but there is little advantage, in general, in this procedure, as double the amount of tin must be used to effect the reduction.

There are, however, occasional uses for stannous chloride reductions on account of the mildness of the reaction. It can be employed in the reduction of 4,4′-dinitrodiphenylamine, which accompanies *p*-nitroaniline as an impurity when the latter is prepared by the ammonolysis of *p*-nitrochlorobenzene. Stannous chloride is also employed when it is desired to reduce one nitro group of two originally present. In alcoholic solution, this reduction proceeds very smoothly, yielding excellent products.

Ogata and Sugiyama[1] calculated the reaction constants given in Table 5-8 for reduction with stannous chloride solution (at 90°C) for a bimolecular reaction.

In general, with para-substituted compounds they found that the speed

TABLE 5-8. REACTION CONSTANTS FOR STANNOUS CHLORIDE REDUCTIONS OF NITRO COMPOUNDS

o-Nitroaniline	0.390×10^{-3}	Nitrobenzene	4.14×10^{-3}
p-Nitrophenol	0.707×10^{-3}	*o*-Dinitrobenzene	4.45×10^{-3}
p-Nitroaniline	0.814×10^{-3}	*p*-Nitrobenzyl chloride	6.56×10^{-3}
p-Nitroanisole	1.147×10^{-3}	*o*-Nitrobenzoic acid	8.22×10^{-3}
p-Nitrophenetole	1.235×10^{-3}	*m*-Nitrobenzoic acid	10.3×10^{-3}
p-Nitrotoluene	3.01×10^{-3}	*p*-Chloronitrobenzene	11.8×10^{-3}
m-Nitrotoluene	3.81×10^{-3}	*p*-Nitrobenzoic acid	19.7×10^{-3}
o-Nitrotoluene	4.13×10^{-3}		

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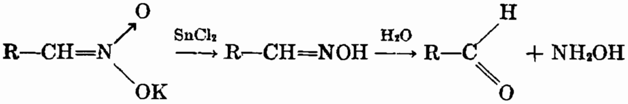
[1] *Science (Japan)*, **19**, 232 (1949).

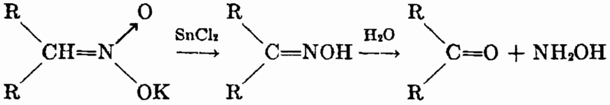
of reaction was $COOH > Cl > CH_2Cl > H > CH_3 > C_2H_5 > OCH_3 > NH_2 > OH$.

Stannous chloride in hydrochloric acid can also be employed for the reduction of the nitroparaffins. Ordinarily, however, this procedure results in the formation of the related hydroxylamine in addition to the primary alkylamine:

$$RCH_2NO_2 \xrightarrow{2H_2} RCH_2NHOH \xrightarrow{H_2} RCH_2NH_2$$

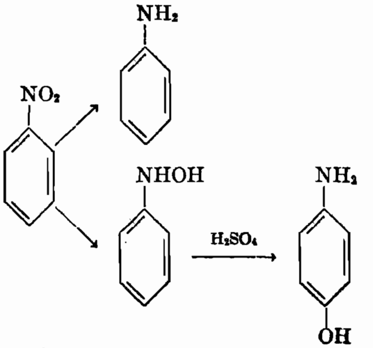
When, however, a large excess of stannous chloride and fuming hydrochloric acid is used, primary and secondary nitro compounds are reduced to the corresponding oximes. Thus, by adding an aqueous solution of the alkali salt of the isonitro compound to about 2.5 times the theoretical quantity of stannous chloride and hydrochloric acid, as required by the equations below, the oxime is formed:





If the charge is neutralized and live steam introduced, the oxime will be distilled over. By passing steam into the acid charge, however, hydrolysis occurs, with the formation of a ketone or aldehyde and hydroxylamine. The carbonyl compound will distill over while the hydroxylamine hydrochloride remains in solution.

Aluminum and Sulfuric Acid. Treatment of aromatic nitro compounds, containing a free para position, with aluminum in 15–50 per cent mineral acid, particularly sulfuric acid, results in the formation of *p*-aminophenols along with amines.[1] The reactions taking place may be represented as follows:



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[1] Bean, U.S. 2,446,519 (1948).

V. CATALYTIC HYDROGENATION

Historical Introduction

The first recorded catalytic hydrogenation of an organic compound was a reduction of a nitrile to an amine. In 1863, Debus passed hydrogen cyanide with hydrogen over platinum black and obtained methylamine. Saytzeff, in 1871, hydrogenated nitrobenzene in the vapor phase over palladium black and obtained aniline. The classical researches of Sabatier in collaboration with Senderens and others in this field, based on the discovery of the catalytic activity of nickel in all types of hydrogenations, started in 1897. Senderens obtained a German patent in 1901 on the production of aniline by passing nitrobenzene vapor over heated nickel, copper, cobalt, iron, or palladium in the presence of hydrogen or water gas. In the same year, Sabatier and Senderens described a vapor-phase reduction of nitrobenzene to aniline over a copper catalyst, using hydrogen or water gas, in a yield of 98 per cent of theory. One year later, the same workers found that nitroethane could be reduced to ethylamine at 200°C over a nickel catalyst. Mailhe carried out considerable work in 1905 and 1906 on the vapor-phase reduction of oximes and amides to amines. Gerum reported in 1908 that the same reaction can be carried out in the liquid phase, using palladium black and ethyl alcohol as a solvent. The early history of catalytic reduction is recorded by Ellis.[1] From these early beginnings, this method of amination by reduction has been developed to the stage of feasible, economical commercial processes. Chemists and chemical engineers in many countries have contributed to our knowledge of catalysts, reaction conditions, and materials of construction. In recent years, at least as many publications and patents have been devoted to this method of reduction as to all the other methods of amination by reduction, combined.

Production of Hydrogen

Hydrogen is manufactured in large quantities for a variety of uses in addition to amination. It is used for hardening of oils and fats in the food industry, for the production of ammonia and methanol, for improving the octane number of gasoline, for the production of alcohols by the Oxo process and by reduction of fats and fatty acids, for the production of synthetic gasoline and lubricating oils, for the desulfurization of hydrocarbon materials, for providing reducing atmospheres in the metalworking industry, and for many other purposes in industrial synthetic organic chemistry.

Hydrogen can be manufactured electrolytically, by the water gas process, by the steam-iron process, by the hydrocarbon-steam process, and by the

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[1] "Hydrogenation of Organic Substances," 3d ed., pp. 73, 261, 264, 265, 276, 277, D. Van Nostrand Company, Inc., New York, 1930.

methanol-steam process. A brief review of these processes is presented here; a more detailed discussion is found in Chap. 10.

In the *electrolytic process*, the reaction may be represented as

$$2H_2O \rightarrow 2H_2 + O_2$$

or as

$$2H_2O + 2NaCl \longrightarrow Cl_2 + 2NaOH + H_2$$

These reactions have been widely used to produce hydrogen either as a major product or as a by-product. In the case of the first reaction, direct current is made to flow between electrodes suspended in water containing an electrolyte such as sodium or potassium hydroxide. The electrolyte is not consumed, but is present to speed up the reaction. Hydrogen is evolved at the cathode and oxygen at the anode. By suitable diaphragms (such as asbestos) and collecting chambers, the two gases are kept separate. In the second reaction, concentrated sodium chloride or potassium chloride solution is treated similarly in a variety of cells to produce chlorine, hydrogen, and sodium hydroxide or potassium hydroxide. In this case, hydrogen is generally considered a by-product, although its utilization improves the over-all economics considerably.

In the *water gas process*, a mixture of hydrogen and carbon monoxide is first produced by intermittently passing air and then steam through a bed of coke. The air raises the temperature of the coke to incandescence, and the steam then reacts with it according to the following equation:

$$C + H_2O \rightarrow H_2 + CO$$

Pure hydrogen can be obtained from this mixture by passing the water gas over a catalyst (such as Cu-Zn-Cr) at about 370°C, whereby the following reaction takes place:

$$CO + H_2O \rightarrow H_2 + CO_2$$

The carbon dioxide may then be removed by scrubbing with caustic solutions or, preferably, with amines such as ethanolamines.

The *steam-iron process* involves essentially the following reaction:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

Steam is passed over hot iron ore which has been previously reduced by a gas such as water gas. The process is intermittent, with alternate cycles of ore reduction and hydrogen production. The crude hydrogen obtained contains some carbon monoxide as an impurity, but this can be removed as described in the water gas process.

The *hydrocarbon-steam process* involves the reaction of hydrocarbons, such as natural gas, refinery gases, or propane, with steam over a catalyst (such as nickel on magnesia) at about 800°C, to produce a mixture of hydrogen, carbon monoxide, and carbon dioxide. Starting with methane, the following reactions take place:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

The mixture of gases can then be treated with steam again, as described under the water gas process, to give a mixture of hydrogen and carbon dioxide. The latter is removed by scrubbing. On a large scale, this process operates very well and is very economical. Single furnaces have been built for hydrogen production rates varying from 25,000–5,000,000 cu ft per day.[1]

The *methanol-steam process* utilizes the following reaction:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

This process lends itself to portable units. The reaction takes place at about 260°C and can be carried out in ordinary steel. The carbon dioxide can be scrubbed out with monoethanolamine solution.

Which of the above processes should be used for any given operation depends upon many factors. Among these are location of plant, volume of hydrogen required, possibility of integration with other processes, and purity requirements.

If hydrogen containing small amounts of carbon monoxide is available, the carbon monoxide may be removed by passing the heated gas over a catalyst to reduce the carbon monoxide to methane. This process is called methanation. Carbon monoxide may also be removed by scrubbing with ammoniacal cuprous salt solutions at low temperatures and under high pressure. The carbon monoxide may then be recovered by heating the absorbent.

Types of Reductions

Very extensive laboratory work on all phases of the use of catalytic reduction to produce both aliphatic and aromatic amines has been reported in the literature. Studies have been carried out on many types of catalysts, catalyst supports, promoters and poisons, solvents, temperatures, pressures, and equipment. Considerable pilot-plant work and engineering studies have been undertaken and a number of commercial installations built for batch catalytic reduction and for continuous catalytic reduction. Commercial installations are now in operation for the catalytic reduction of nitro compounds and nitriles.

Among the reactions which can be carried out using suitable catalysts and conditions are the following:

$$RNO_2 + 3H_2 \longrightarrow RNH_2 + 2H_2O$$
$$RCN + 2H_2 \longrightarrow RCH_2NH_2$$
$$RCONH_2 + 2H_2 \longrightarrow RCH_2NH_2 + H_2O$$
$$2RR'C{=}NOH + 5H_2 \longrightarrow 2(RR'CH_2NH_2) + 2H_2O$$
$$RCSNH_2 + 2H_2 \longrightarrow RCH_2NH_2 + H_2S$$
$$C_6H_5NO_2 + 2H_2 \xrightarrow{H_2SO_4} 1,4\text{-}HOC_6H_4NH_2 + H_2O$$

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[1] "Hydrogen," The Girdler Company, Louisville, Ky., 1946.

In addition to *nitro* compounds, *nitroso*, *hydroxylamino*, *azoxy*, *azo*, and *hydrazo* compounds can also be reduced to amines. *Nitriles*, *amides*, *thioamides*, and *oximes* of both aldehydes and ketones can be hydrogenated to amines.

As shown in the last equation, aromatic compounds, which are unsubstistituted in the para position, can be converted to *p*-aminophenols by reduction in the presence of sulfuric acid.[1] Sulfides of cobalt, tungsten, molybdenum, or platinum are used as catalysts. Presumably, this reaction proceeds by way of rearrangement of the intermediate hydroxylamines, as is the case when aluminum is used in the presence of sulfuric acid. The reduction is carried out at about 150°C and 400–500 lb pressure. The degree of aminophenol production depends upon the catalyst, as can be seen from Table 5-9.

TABLE 5-9. HYDROGENATION OF NITROBENZENE IN H_2SO_4 SOLUTION

Materials	Parts by weight			
Nitrobenzene	369	369	369	369
Sulfuric acid	300	600	300	300
Water	450	900	450	450
Catalyst	10 MoS_3	10 MoS_3	10 CrS_3	10 CoS
Aniline*	100	225	76	189
p-Aminophenol	175	10	181	30
Total amines	275	235	257	219

* Theoretical yield of aniline, 279 parts.

Amino derivatives having enolizable groups have a tendency to react with themselves and may also be attacked at the enol grouping unless mild reducing conditions are employed. The reduction of nitro compounds such as *m*-nitroacetanilide, which contains an enolizable group, can be satisfactorily carried out by first dissolving the compound in dilute aqueous alkali and subsequently treating it with hydrogen at 35 lb pressure in the presence of a platinum oxide catalyst. A concentration of aqueous alkali of about one-fifth normal (0.8 per cent) and a reaction temperature of 20°C give satisfactory results.[2]

A number of patents have been issued on the catalytic reduction of nitro compounds in the presence of alkali to give hydrazo compounds.[3] These are useful intermediates for the benzidine series by acid rearrangement.

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[1] Henke and Vaughen, U.S. 2,198,249 (1940).

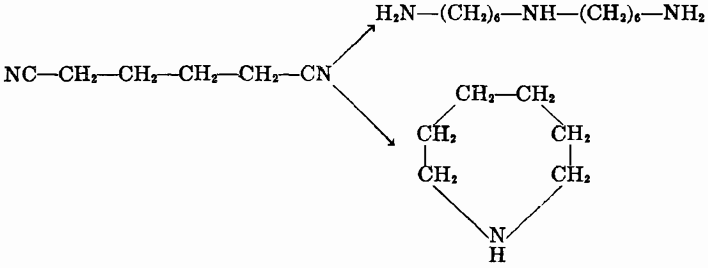
[2] Kenyon and Lowe, U.S. 2,311,054 (1943).

[3] Henke and Benner, U.S. 2,194,938 (1940); 2,233,129 (1941). Henke, Benner, and Jones, U.S. 2,233,128 (1941). Freed and Signaigo, U.S. 2,344,244 (1944).

The production of diamines, both aliphatic and aromatic, has become of increasing importance during recent years. Hexamethylenediamine, produced by catalytic hydrogenation of adiponitrile, is an essential component in the manufacture of nylon 66. This step in the synthesis of hexamethylenediamine may be represented as follows:

$$NC{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CN \rightarrow H_2N{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}NH_2$$

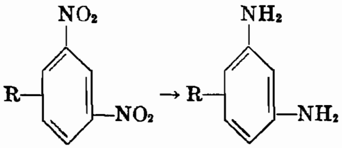
Unless conditions are carefully controlled, the following types of side reactions will take place:



The formation of polyimines and of cyclic compounds proceeds by the loss of ammonia. These reactions can be suppressed by reducing in the presence of ammonia under high pressures (see Hydroammonolysis, Chap. 8).

The reduction can be carried out in batches or continuously at about 9,000 psig and 125°C in an ammonia atmosphere, over a cobalt-copper catalyst, in yields of over 90 per cent of theory.[1] A number of other catalysts have been described for this reaction, including Raney nickel, cobalt on silica, and cobalt-silver-magnesium. The starting nitrile must be quite pure to avoid poisoning the catalyst. It is claimed that the presence of carbon monoxide, in addition to hydrogen and ammonia, extends the life of the cobalt catalysts normally used.[2]

Aromatic diamines are essential for the manufacture of diisocyanates, intermediates for polyurethane foams, elastomers, coatings, and adhesives. The expanding usage of epoxy resins also requires increasing quantities of aromatic diamines as cross-linking agents, or hardeners. Reductions of aromatic dinitro compounds must be carried out under mild conditions to avoid explosive decompositions[3] and loss of nitrogen by hydrogenolysis. The normal course of the reaction is



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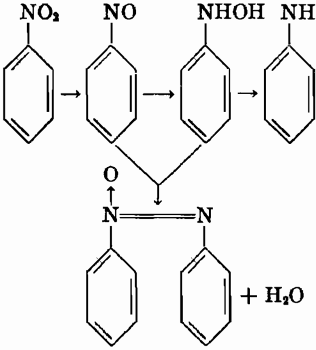
[1] Larchar and Young, U.S. 2,284,525 (1942).

[2] Du Pont, Brit. 728,599 (1955).

[3] Gage, U.S. 2,430,421 (1947).

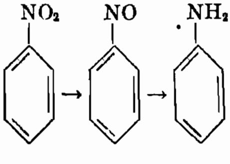
Since the dinitro compounds are rather insoluble in water and the diamines are quite soluble, Benner and Stevenson[1] have developed a method involving reduction of a dispersion of dinitro compound in water, effected by very rapid agitation, using noble-metal catalysts. This process can be run continuously by using a series of vessels to carry out the reduction. Similar reductions of *m*-dinitrobenzene, in water dispersion, using nickel and copper catalysts were also carried out in the laboratories of I. G. Farbenindustrie.[2]

Considerable study has been directed toward the *reaction mechanism* of catalytic reduction under different conditions. Nord[3] has shown that the reduction of nitrobenzene by hydrogen gas in the presence of colloidal platinum gives rise to the same intermediate compounds that are obtained by metal and acid or electrolytic reductions. The following shows the course of the reaction:



When Raney nickel catalysts were used, it was found that the intermediate products of reduction absorbed hydrogen at lower rates than did nitrobenzene.[4] The relative rates of hydrogenation were found to be as shown in Table 5-10. It would therefore appear that nitrosobenzene is not one of the intermediate steps in going from nitrobenzene to aniline.

Sokol'skiĭ and Shmonina[5] studied the rate of hydrogenation of nitro benzene in 0.1 N sodium hydroxide and in neutral alcohol in the presence of a nickel catalyst and in the presence of a nickel catalyst plus rhodium. They conclude that in alkali the reaction is



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[1] U.S. 2,619,503 (1952).

[2] *O.P.B. Rept.* 30049 (Office of Publication Board, U.S. Department of Commerce).

[3] NORD, *Ber. deut. Chem. Ges.*, **52**, 1705 (1919).

[4] SCHOLNIK, REASENBERG, LIEBER, and SMITH, *J. Am. Chem. Soc.*, **63**, 1192 (1941).

[5] *Doklady Akad. Nauk SSSR*, **78**, 721 (1951).

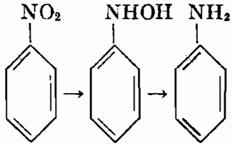
TABLE 5-10. RATES OF HYDROGENATION IN THE PRESENCE OF RANEY NICKEL AND THE EFFECTS OF PLATINUM AND OF ALKALI

Compound reduced	Rates* of hydrogenation with catalysts			
	a	*b*	*c*	*d*
Nitrobenzene	195	344	20.5†	127
Nitrosobenzene	0	0	0	0
Azobenzene	42.1	135	95.2	199
Hydrazobenzene	31.2	227	1.08	228
Azoxybenzene	22.4	165	218	325
N-Phenylhydroxylamine	120	270	197	26

* The rates are expressed as milliliters of hydrogen absorbed per 100 sec.

† The average rate is probably less than that recorded. Catalyst *a*, Raney nickel; *b*, Raney nickel and platinum; *c*, Raney nickel and alkali; *d*, Raney nickel, platinum, and alkali.

and in neutral alcohol the reaction is;



Albert and Ritchie[1] studied the reduction of various nitro compounds in the presence of Raney nickel at atmospheric pressure and room temperature and concluded that the reaction proceeds in steps by way of the nitroso, hydroxylamino, and amino derivatives, just as did Nord, as mentioned above.

There is abundant evidence, including the above data, that slight modifications in the composition of catalyst, the source of materials used, the method of preparation, the nature of the carrier, the impurities, and the pH have a marked influence on the course of the reaction, the hydrogenation rates, the formation of by-products, and the life of the catalyst.

Linstead and coworkers[2] have found that partially hydrogenated aromatic compounds can be used as hydrogen donors in the place of gaseous hydrogen in the catalytic reduction of nitro compounds. For example, nitrobenzene and *p*-nitrotoluene can be reduced to aniline and *p*-toluidine, respectively, by refluxing with cyclohexene, with or without solvent, over palladium black. The presence of aldehyde, amine, or halogen groups inhibits the reaction, which does not appear to involve separate donor-dehydrogenation and acceptor-hydrogenation steps, but rather specific donor-acceptor relations.

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[1] *J. Proc. Roy. Soc. N.S. Wales*, **74** (1940).

[2] *J. Chem. Soc.*, **1954**, 3586; Brit. 705,919 (1954).

Kametani and Nomura[1] have described another very interesting catalytic reduction without the use of gaseous hydrogen. They have found that various nitriles can be reduced to amines by utilizing the hydrogen formed *in situ* by reacting Raney nickel-aluminum alloy with aqueous alkali. In this manner, they have prepared various benzylamines and phenylethylamines.

Reaction Conditions

Catalytic reductions can be carried out in batches or in continuous processes, in the liquid phase or in the vapor phase. This method has many advantages over other methods of reduction, particularly for large-volume production. With low-cost hydrogen, as is the case when by-product hydrogen is available from other installations or when large hydrocarbon-steam units are installed, this process cannot be matched by other methods of reduction in so far as economics and quality of product are concerned.

Catalytic reductions have been carried out under an extremely wide range of reaction conditions. Temperatures of 20°C to over 300°C have been described. Pressures from atmospheric to several thousand pounds have been used. Catalysts have included nickel, copper, cobalt, chromium, iron, tin, silver, platinum, palladium, rhodium, molybdenum, tungsten, titanium and many others. They have been used as free metals, in finely divided form for enhanced activity, or as compounds (such as oxides or sulfides). Catalysts have been used singly and in combination, also on carriers, such as alumina, magnesia, carbon, silica, pumice, clays, earths, barium sulfate, etc., or in unsupported form. Reactions have been carried out with organic solvents, without solvents, and in water dispersion. Finally, various additives, such as sodium acetate, sodium hydroxide, sulfuric acid, ammonia, carbon monoxide, and others, have been used for special purposes. It is obvious that conditions must be varied from case to case to obtain optimum economics, yield, and quality.

A large number of patents have been issued covering the *vapor-phase reduction* of nitrobenzene, nitroxylene, and other relatively low-boiling mononitro compounds by hydrogen and hydrogen-containing gases in the presence of metal catalysts. Such a process has many attractive features. Some of these are (1) continuous conversion of reactants to finished amine, (2) minimum operating labor requirements, (3) low steam and power costs as a result of utilizing the heat in vapors leaving the catalytic chamber, and (4) absence of industrial-waste problems, e.g., disposal of iron oxide sludge.

Vapor-phase reductions are sometimes fraught with a number of technological problems: (1) limited per-pass conversion, thus necessitating separation of aniline from nitrobenzene (unless the heat of reaction is gainfully employed, this will constitute a significant item of expense), and (2) sensitivity of catalytic operations which may result in overreduction and

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[1] *J. Pharm. Soc. Japan*, **74**, 889 (1954).

relatively low yields of amine compared with competitive processes, particularly Béchamp reductions.

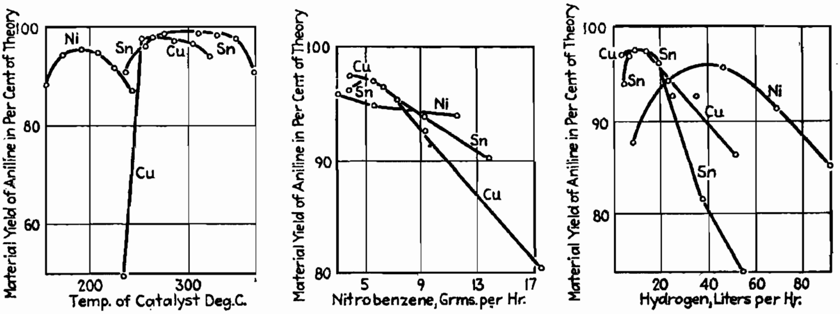
No specific conclusions can be drawn regarding the groups of metals that are most effective. Although nickel and copper are considered the most active catalysts for a large number of hydrogenation processes, it is not always advisable in the reduction of nitro compounds to employ the most active catalysts. Other factors such as stability, wide plateaus of temperature effectiveness, and high throughput per catalyst volume and life are important. It has been found that the metals both preceding and following hydrogen in the electrochemical series can be used as catalysts. Thus, nickel, iron, tin, copper, silver, platinum, nickel-copper and cobalt, molybdenum, and tungsten as sulfides are all mentioned in the literature on this subject.

Working under favorable conditions with a nickel catalyst, Brown and Henke[1] obtained a 95 per cent yield of aniline from nitrobenzene. With a constant rate of flow of nitrobenzene, the yields drop off with too much or too little hydrogen. This fluctuation has been ascribed to over- or underreduction. Since nickel is such an active catalyst for this purpose, reduction of the aniline to cyclohexane and ammonia is known to take place.

When a catalyst prepared from precipitated copper oxide is used, the reaction is more moderate, and the yields under optimum conditions are uniformly good.

When tin is employed as a catalyst, good results are obtained in the reduction of nitrobenzene to aniline. The catalyst made from the hydroxide prepared by precipitation with sodium carbonate from a stannous chloride solution is the best.

The relative activity of some of the metal catalysts employed by Brown and Henke is shown in Figs. 5-12 to 5-14. In Fig. 5-13, showing the effects



FIGS. 5-12 to 5-14. Vapor-phase reduction of nitrobenzene.

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[1] BROWN and HENKE, *J. Phys. Chem.*, **26**, 161, 273, 715 (1922); **27**, 739 (1923).

of "rate of feed" for nitrobenzene, it can be seen that at only one point is the curve for tin below that of copper; in most places, the values for tin are above those for copper. Tin is likewise superior to nickel at all but the highest rates of feed.

The effect of "flow of hydrogen" in the presence of the same catalysts is shown in Fig. 5-14. It will be noted that the curve for tin has a shape different from that of the other two curves. Thus, the decrease in yield with too much or too little hydrogen is more rapid for tin than for nickel or copper. However, the region within which high yields are secured is as wide or wider with tin than with other catalysts.

Since active catalysts, such as nickel and the noble metals, are often poisoned by traces of sulfur-containing compounds, it is necessary to purify the feedstock rather rigorously to remove such poisons. It is for this reason that sulfides (e.g., nickel sulfide, molybdenum sulfide) are sometimes found advantageous as catalysts for such systems, since they do not suffer from the same disadvantages as do more active catalysts. A mixture of alumina and nickel sulfide has been claimed to have particularly long life in the reduction of nitrobenzene to aniline at 300°C.[1]

Condit and Haynor[2] have studied the explosive decomposition of nitrobenzene and nitroxylene. They found that the minimum temperature for nitrobenzene is about 356°C and for nitroxylene, about 308°C. The temperatures are relatively independent of the pressure of the surrounding gas, are the same in hydrogen as in methane, and are unaffected by the presence of various steels or activated carbon. Amine concentrations of 25 per cent prevent explosive decomposition, giving resinous masses instead.

The American Cyanamid Company has developed a process for the continuous catalytic vapor-phase hydrogenation of nitrobenzene to aniline, using a fluid-bed system. The nitrobenzene is vaporized into a purified hydrogen stream, and the combined streams, containing excess hydrogen, flow to a fluidized catalytic bed reactor which operates at 225–325°C under pressure. The reduction occurs almost instantaneously, producing few by-products. Since the reaction is exothermic, the heat of reduction is utilized for the generation of steam which is used in other parts of the process. The vapors from the reactor are condensed and sent to purification, where the aniline is continuously fractionally distilled. A copper catalyst with long life is used. Unreacted hydrogen is recycled to the reaction after being mixed with fresh hydrogen. The flow used is given in Fig. 5-15.

In the case of high-boiling mono- and polynitro compounds, nitro compounds which decompose at high temperatures, or where undesirable side

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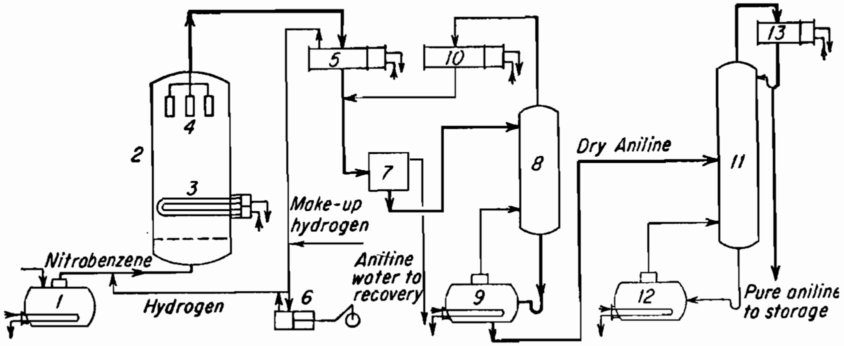
[1] Allied Chemical & Dye Corporation, Brit. 718,615 (1954); Winstrom, U.S. 2,716,135 (1955).

[2] *Ind. Eng. Chem.*, **41**, 1700 (1949).



1 Nitrobenzene vaporizer
2 Reactor with fluidized catalyst bed
3 Cooling tubes
4 Catalyst filters
5 Product condenser
6 Hydrogen recycle compressor
7 Aniline-water settler
8 Aniline dehydrating column
9 Reboiler for dehydrating column
10 Condenser for dehydrating column
11 Aniline purifying column
12 Reboiler for aniline purifying column
13 Condenser for aniline purifying column

FIG. 5-15. Continuous fluid-bed vapor-phase reduction of nitrobenzene.

reactions occur at high temperatures, *liquid-phase reduction* is used. This method is generally used for 1-nitronaphthalene, *m*-dinitrobenzene, dinitrotoluene, and aliphatic nitriles and dinitriles. A wide variety of catalysts are employed, and water-soluble or water-insoluble solvents are often added. Where possible, water emulsions or dispersions are preferable, in order to avoid added cost due to recovery of solvents. The pH may also be adjusted as necessary.

Henke and Benner[1] have described a process for the reduction of 1-nitronaphthalene to α-naphthylamine in a purity of 99–100 per cent. The conditions used are 80–100°C, 400–500 psig, 5 per cent water, 0.5 per cent nickel catalyst, and 0.12 per cent sodium acetate. The yields are over 90 per cent of theory.

Kise[2] was granted a patent on the catalytic hydrogenation of nitrobenzene or other nitro, nitroso, nitrosoamine, azoxy, or N-hydroxylamino compounds of the benzene or napthalene series, whereby the compound to be reduced is dissolved in the resulting amine carrying a suspended catalyst of nickel, cobalt, or copper on an inert carrier. Hydrogen is passed in at approximately 100°C at a rate sufficient to agitate and remove the formed water as vapor; the gas is cooled to condense water from it and recirculated together with added hydrogen, and the product is withdrawn from the reaction zone as it is formed.

A large number of patents and publications have appeared with reference

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[1] U.S. 2,105,321 (1938).

[2] U.S. 2,292,879 (1942).

to the catalytic hydrogenation of nitroparaffins, including aliphatic and alicyclic hydrocarbons, alcohols, glycols, ketones, and various other derivatives.[1] In most of these cases, the reduction is carried out in the liquid phase at low temperatures and high pressures, using nickel catalysts generally. Catalytic reduction of aliphatic nitriles, amides, lactams, and carboxylic acids (in the presence of ammonia) to amines is generally carried out at moderate temperatures (50–200°C) and high pressures using a cobalt or nickel catalyst. Fatty amines are produced by treating fatty nitriles with hydrogen over a Raney nickel catalyst at 150°C and 200 psig in yields of about 85 per cent of theory.[2] The production of diamines by the liquid-phase reduction of dinitriles has already been discussed under Types of Reactions.

The sulfide method of reduction and catalytic hydrogenation in the liquid phase can be combined in the presence of iron as a catalyst.[3] In this method, sulfur or sulfides are used in small amounts and the hydrogen serves to reduce their oxidation products back to sulfides for further reduction.

Equipment

Catalytic reduction can be carried out in batches in steel or, preferably, in stainless-steel kettles equipped with agitators or in towers packed with a catalyst and equipped for recycling operation. Gas-liquid and liquid-liquid separators are required, as well as filters or centrifuges to remove the catalyst, which may be used as such or deposited on inert carriers. Where necessary, purification is carried out, as by fractionation in columns.

In the case of continuous operation, a series of kettles may be employed. A more preferable method of operation is the use of packed towers or columns constructed of steel or stainless steel. The thickness of the wall will depend on the pressures required for the particular reduction conditions being used. The size will depend upon the production volumes required. The towers may be packed with catalyst, generally on a support for ease of handling and greater surface, in random fashion, on trays, in wire-mesh baskets, or alternately with wire-mesh entrainment packing. Fluid-bed systems have also been employed.

The feed of hydrogen and nitro compound may be countercurrent or cocurrent. Cocurrent feeding is generally employed, although a counter-

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[1] See WERNER, *Ind. Eng. Chem.*, **40**, 1579 (1948), and subsequent annual reviews of this unit process in *Industrial and Engineering Chemistry*.

[2] See KENYON, STINGLEY, and YOUNG, *Ind. Eng. Chem.*, **42**, 208 (1950), for a description of the Armour and Company plant at McCook, Ill.

[3] See KIRK and OTHMER (eds.), "Encyclopedia of Chemical Technology," vol. I, p. 687, Interscience Publishers, Inc., New York, 1947.

current system is sometimes preferred to allow a greater relative concentration of hydrogen for the small amounts of unreacted nitro compound at the outlet of the tower to make for higher conversions. An additional clean-up hydrogenation is sometimes carried out in another tower, for the same purpose.

Cooling of the highly exothermic reaction may be provided in a variety of ways. Outside circulation of water or other cooling media can be used. Recirculation of large volumes of hydrogen may be employed, with the addition of an outside heat exchanger. In such cases, the heat is generally used to bring the nitro compound feed to initial reaction temperature. Injection of water at suitable spots in the tower has also been found advantageous to control the reaction.

Suitable screens or entrainment packing must be provided to remove catalyst fines which are carried along by the liquid or gas streams. This can be done in external "knockout" pots for ease of cleaning and for removal of the fines from the system to avoid plugging.

Condensers and coolers are used to bring the products down closer to normal temperatures, and the remaining excess hydrogen is removed in gas-liquid separators. The hydrogen can be recycled after compression in a recycle compressor. The amine is separated from the water in a liquid-liquid separator. If significant amounts of amine are present in the water phase, the latter may be subjected to extraction by fresh nitro compound before it is fed to the reduction tower.

The amine is then generally purified by fractionation through columns under vacuum. Where a low-boiling solvent is used as a diluent during the reduction, it must be stripped off first, using a short column. When reduction is incomplete, care must be taken to prevent a high build-up of nitro and particularly dinitro compounds in the heavy ends to avoid explosions at high temperatures.

Manufacture of Aniline

The continuous manufacture of aniline by the reduction of nitrobenzene with hydrogen, as carried out by I. G. Farbenindustrie, at Ludwigshafen, is as follows.[1] The reaction is carried out at very slight pressure (about 5 psig) over a reduced copper carbonate catalyst at temperatures ranging from about 200°C at the entrance to the catalytic reactor to 350°C at the exit. (The operation can be carried out in facilities shown in Fig. 5–16.) The process starts by vaporizing a descending film of nitrobenzene in the tubes of an evaporator by an ascending stream of preheated hydrogen.

From 500–600 kg per hr of nitrobenzene is vaporized into a circulating

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[1] I. G. Farbenindustrie, operations at Ludwigshafen, *F.I.A.T.* (Field Information Agency Technical) *Final Repts.* 1313 (vol. 1) and 649; *O.P.B. Rept.* 1777.

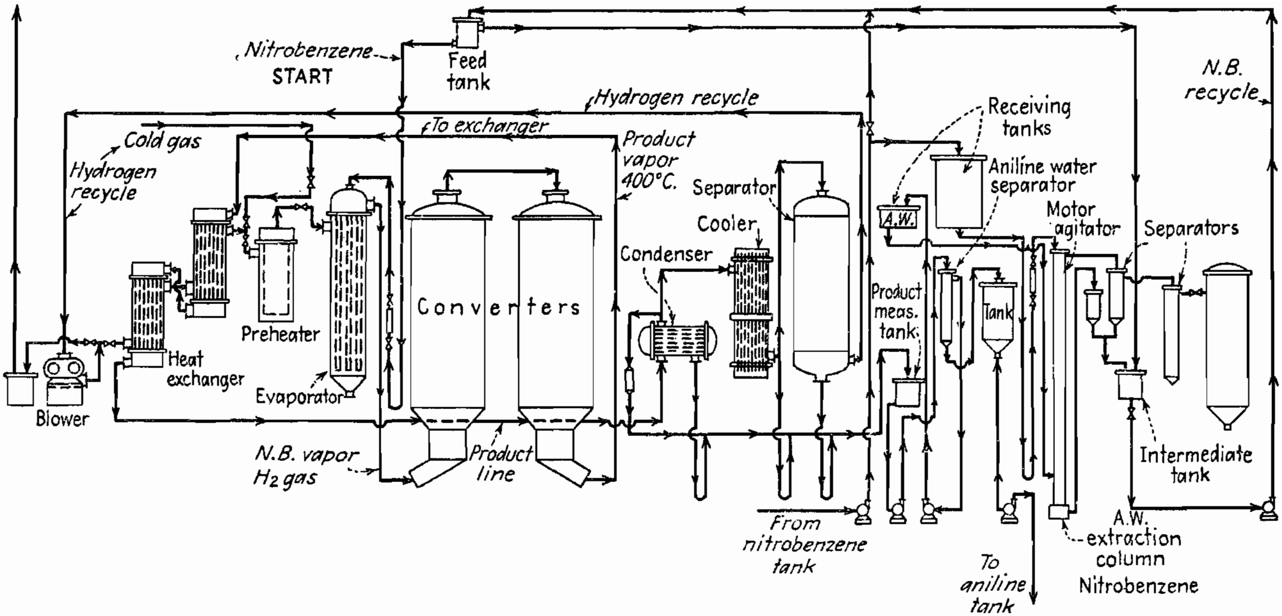

FIG. 5-16. Catalytic vapor-phase reduction of nitrobenzene.

gas stream of 6,000 cu m per hr, which has been preheated in a heat exchanger. Hydrogen (free of CO) and nitrobenzene vapor are passed over a catalyst contained in two chambers in series, each of 50 cu m volume. The catalyst is made by impregnating lumps of pumice stone with a slurry of 3,500 kg of basic copper carbonate contained in water and 2,500 kg of 50 per cent sodium silicate solution. The impregnation is accomplished by spraying this solution onto the pumice stone in a concrete mixer. The catalyst is first reduced in a circulating hydrogen gas stream at 190–200°C. This temperature is obtained by passing the hydrogen over a heater containing superheated water under high pressure. With fresh catalyst, the reaction temperature is 170°C on entering the first chamber. Gases leaving the second chamber will have a temperature of 350–370°C under the above condition.

The reaction is strongly exothermic, and temperature control is accomplished by a stream of relatively cool hydrogen which is diverted from the circulating stream ahead of the heat exchanger and regulated by a valve. The entering temperature to the first catalyst chamber must be increased as the catalyst deteriorates. It is necessary to reactivate the catalyst after 1,200 tons of nitrobenzene has been passed through the system, at which time the entrance temperature to the first catalyst chamber will be 280°C. Reactivating is accomplished by roasting (carefully controlled oxidation with air) followed by reduction with hydrogen. This process can be repeated four to five times. After a total of 2,600 tons of nitrobenzene has passed through the system, it is possible to increase the service life further by having an ammoniacal copper carbonate solution percolate through the catalyst, which will serve to reduce another 1,400 tons of nitrobenzene. One filling of the contact chambers will, therefore, serve in the reduction of about 4,000 tons of nitrobenzene, which is equivalent to a usage of 0.07 kg copper per 100 kg aniline. The normal production capacity of the plant is 300 tons of aniline per month.

After passing through a heat exchanger, the reaction products are separated from the circulating gas stream by two water-cooled tubular condensers followed by a separate cooler with impingement plates. Aniline and water are separated in a separator. The former flows to storage tanks and from there to distillation in a 24-plate bubble-cap column. The latter is passed to a continuous extraction column in which dissolved aniline is extracted by a descending stream of nitrobenzene that is to be used as feedstock (see Fig. 5-8). The yield is 98 per cent of theory based on distilled aniline. About 0.34 per cent *o*-aminophenol can be obtained from the still residues.[1]

Some of the factors entering into the cost of producing aniline by this method of catalytic reduction are presented in Table 5-11.

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[1] *O.P.B.* (Office of Publications Board, U.S. Department of Commerce) *Rept.* 30,099.

TABLE 5-11. COST FACTORS IN PRODUCTION OF ANILINE BY CATALYTIC REDUCTION

Materials to produce 100 lb aniline from nitrobenzene:	
135 lb nitrobenzene, at $0.08 (captive manufacture)	$10.80
1,250 cu ft hydrogen, at $1.00 per 1,000 cu ft	1.25
0.07 lb catalyst (as copper), at $1.50	0.11
Total material costs	$12.16
Operating costs: labor operating, repairs, supplies, direct supervision	$ 1.20
Power costs: electricity, steam, air, water	0.35
Overhead: administration, depreciation, insurance, fixed charges	0.90
Plant cost per 100 lb aniline	$14.61

ANILINE COST DATA ANALYSIS

$$\text{Percentage cost of raw materials} = \frac{12.16}{14.61} = 83.2\%$$

$$\text{Percentage cost of operation} = \frac{1.20}{14.61} = 8.2\%$$

$$\text{Percentage cost of power} = \frac{0.35}{14.61} = 2.4\%$$

$$\text{Percentage cost of overhead} = \frac{0.90}{14.61} = 6.2\%$$

Manufacture of Xylidines

During World War II, xylidines were produced on an enormous scale (over 1 million lb per day) by the hydrogenation of a mixture of 3-nitro- and 4-nitro-*o*-xylenes.

Aromatic amines have long been used for their antiknock properties as blending agents for automotive fuels. Of these, xylidine has outstanding characteristics in providing increased power output under conditions of rich-mixture operation in aircraft engines required for take-off and combat operations. The preeminence of xylidine is attributable to its antiknock performance, stability, low freezing point, adaptability to production by continuous hydrogenation, and the important consideration that the raw material, xylene, is readily available as a co-product in the production of synthetic toluene from petroleum by a re-forming (platforming or hydroforming) process.

In 1943, Shell Chemical Corporation undertook to convert an ammonia plant located at Cactus Ordnance Works to the production of xylidines by continuous catalytic reduction. The nominal design capacity of the plant was 960,000 lb per day.[1]

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[1] DE LARGEY, OKIE, and ROBERTS, *Chem. Eng.*, **55** (10), 124 (1948); and NELSON, WILSON, and RAYMOND, *Chem. Eng. Progr.*, **45** (12), (1949). See also Souders, U.S. 2,458,214 (1949). The similar production by Esso Standard Oil of Louisiana has been reported by VOORHIES, SMITH, and MASON, *Ind. Eng. Chem.*, **40**, 1543 (1948); and BROWN, SMITH and SCHARMANN, *ibid.*, **40**, 1538 (1948).

Preparation of Reactants. Crude nitroxylene was treated with hot 20 per cent soda ash solution to remove nitrophenolic impurities and then washed and fractionated to remove unnitrated material and lower the dinitroxylene content. The hydrogen was obtained by mixing steam with natural gas and cracking the mixture over a supported nickel catalyst at 700°C. The synthesis gas was then passed over an iron oxide shift catalyst, and the resultant gases were scrubbed with water at 240 psig (CO_2 removal) and copper ammonium formate at 1,700 psig (CO removal) to complete the purification. Gas used for reaction analyzed about 96.5 per cent hydrogen. The hydrogenation catalyst was nickel (or Ni-Cu) on an inert carrier in the form of $\frac{1}{4}$–$\frac{3}{8}$ in. pellets. Useful life of the catalyst was in the order of 70 volumes of xylidine per volume of catalyst. The ultimate failure of the catalyst was probably due to accumulation thereon of 5–7 per cent carbon, which accretion was accompanied by a loss of activity. Reactivation was accomplished *in situ* by passing hot steam (up to 450°C) with gradually increased oxygen content through reactor beds.

Operation of Plant. The reduction process, shown in greatly simplified form (Fig. 5-17), was operated substantially as follows. The hydrogenation was carried out in a 10-bed carbon-steel catalytic reactor, 8 ft in diameter and 72 ft high. Each bed was preceded by a conventional bubble tray. Between the tray and catalyst bed, there was a set of vapor-mixing baffles to promote uniform distribution of nitroxylene vapors and hence catalyst-bed temperatures. On the first (bottom) tray, about one-tenth of the liquid nitroxylene was fed. A large circulating stream of hydrogen (mole ratio H_2 to nitroxylene about 3), preheated to 200°C, vaporized the nitroxylene from this tray and carried it upward through the mixing baffles to the first catalyst bed. The hydrogenation reaction (1370 Btu per lb) heated the whole stream from 180 to 225°C. The combined stream, now containing some xylidine, entered the next upper bubble tray to which was delivered more nitroxylene along with enough recycle water to adjust the vapor temperature to 180°C. The nitroxylene increment was hydrogenated in the second catalyst bed, and so on, up the reactor through 10 sets of trays and catalyst beds.

The temperature of vapors entering each catalyst bed was the most important single variable. Too low a temperature permitted liquid nitroxylene to deposit on the catalyst, making it prematurely ineffective. Low temperatures also reduced the over-all catalyst life. Too high a vapor temperature resulted in lower yields because of by-product formation.

A major problem was the distribution of liquid on the tray and the obtaining of uniform vapor composition in the catalyst beds as the mixture was carried upward through the beds. This was solved successfully by installing the disc-and-doughnut type of vapor-mixing baffles between the trays and the catalyst beds. The overlapping part of the disc and dough-

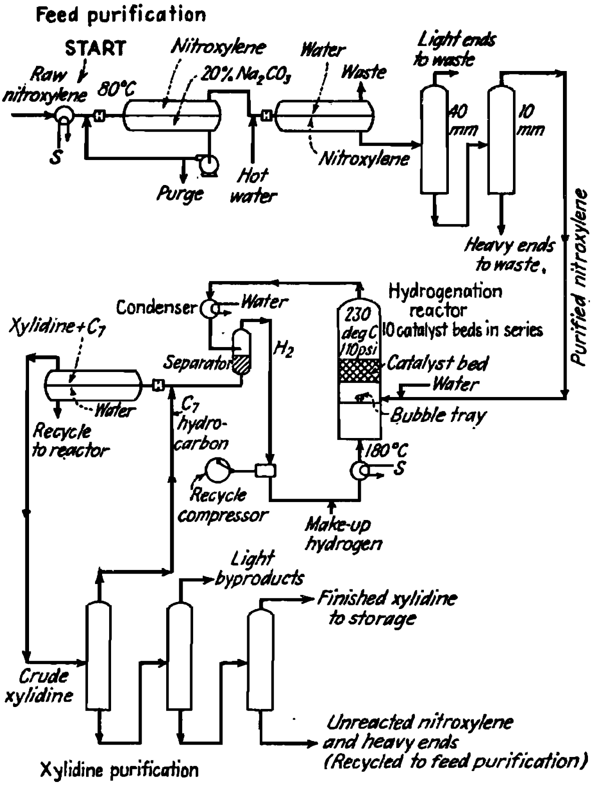

FIG. 5-17. Reduction of nitroxylene to xylidine by hydrogen in the presence of a catalyst.

nut was provided with vanes placed at an angle to impart a swirling motion to the gas. The doughnut was above the disc in the reactor and was secured to the wall by angle supports. These baffles had a beneficial effect on the temperature distribution in the catalyst and, as a result, greatly enhanced ease of control and increased the reactor capacity more than 50 per cent.

The reactor exit stream, rich in xylidine, was condensed in conventional water-cooled tube bundles, totaling 30,000 sq ft. The large excess of hydrogen emerging from the separator (see Fig. 5-17) was recycled. The system pressure and temperature were only about 110 psig and 230°C compared with 3,000 psig and 200°C for the process using molybdenum sulfide on activated charcoal as catalyst.[1]

The condensed reactor product contained the expected isomers of xylidine, unreacted nitroxylene, by-products, and a large amount of water

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[1] BROWN, SMITH, and SCHARMANN, *op. cit.*

(process and reaction); the average mole ratio of water to nitroxylenes was 5.9:1. After separating the hydrogen, some heptane was added to the liquid phase to facilitate the ensuing separation of two liquid phases. The aqueous phase containing appreciable dissolved ammonia was largely recycled to the bubble trays in the reactors. The composition of the organic phase (excluding diluent heptane) was approximately as shown in the accompanying table, which indicates a per-pass conversion of about 92 per cent.

	Per cent by weight
Xylidines	84
Nitroxylenes	2
By-products	4–8
Water (dissolved)	Balance

Crude xylidine was *refined* in a series of three distilling columns. The first operated at about 350 mm Hg top pressure and a 0.37R/F ratio (quantity of reflux to unit quantity of distillate removed as product). Here the diluent heptane was removed as a top cut and recycled to the separator. The second column, which operated at about 400 mm Hg pressure and an internal R/F of approximately 1, served for the removal of light by-products, principally dimethycyclohexylamine, which boils fairly close to xylidine. In the third column, operating at 200 mm Hg top pressure and an R/F of 1 to 2, xylidine was removed overhead, while the heavy ends were recycled to the nitroxylene purification column for recovery of unconverted nitro compound. Because of the rather close separations required for both light and heavy impurities, the operation of the finishing column was necessarily a balancing of capacity against output of the specification material. The product obtainable by this procedure contained over 99 per cent xylidines, with 0.5 per cent nitroxylene and traces of other related compounds as by-products. The yield was 95.8 per cent of theory.

VI. SULFIDE REDUCTIONS

General

The method of sulfide reductions, although more expensive than iron and acid or catalytic reduction, has a wide field of application, particularly with respect to partial reductions and reductions in the anthraquinone series. Sodium sulfide, sodium hydrosulfide (the "sulfhydrate" of commerce), sodium polysulfides, ammonium sulfide, etc., are employed. Quite a number of benzene derivatives are normally reduced by this general method, and it is noteworthy that the first reduction of nitrobenzene was that by Zinin in 1842, using ammonium hydrosulfide. Where the presence of free alkali is harmful, sodium sulfide is not used without the addition of magnesium salts, which remove the sodium hydroxide as it is formed by precipitation of magnesium hydroxide.

Alkaline reductions are milder than the iron and acid reductions, and for this reason, modifications of this process find extensive use in technical operations. By utilizing alkali or metal sulfides, it is possible to control better the rate and degree of reduction. Although ammonium sulfide is sometimes used, sodium sulfide or sodium disulfide is most frequently employed. The sulfides of iron and manganese have also been found of value in reduction processes but thus far have not found widespread industrial applications.

The more important uses of alkali or metal sulfides are (1) preparation of nitroamines from dinitro compounds, (2) reduction of nitrophenols,[1] (3) reduction of nitroanthraquinones, and (4) preparation of aminoazo compounds from the corresponding nitro derivatives. Stronger reducing agents reduce the azo linkage as well.

The activity of alkali sulfides in the reduction of nitro compounds is due to the ease with which the former take up oxygen. The reactions may be represented as follows:

$$4RNO_2 + 6Na_2S + 7H_2O \rightarrow 4RNH_2 + 3Na_2S_2O_3 + 6NaOH \qquad (1)$$

$$RNO_2 + Na_2S_2 + H_2O \rightarrow RNH_2 + Na_2S_2O_3 \qquad (2)$$

$$4RNO_2 + 6NaHS + H_2O \rightarrow 4RNH_2 + 3Na_2S_2O_3 \qquad (3)$$

These equations represent more or less idealized conditions, and very often other side reactions take place, necessitating an altered ratio of components.

At one time, an appreciable proportion of the aniline production was made according to Eq. (2). This process runs very satisfactorily and is devoid of problems relating to the separation and disposal of iron sludge. It would, indeed, be a very attractive procedure if a profitable use or outlet were found for the by-product sodium thiosulfate to offset the comparatively higher cost of the sulfide reducing agent.

Sulfide reductions, particularly those using ammonium sulfide, are employed very extensively for the partial reduction of dinitrobenzene derivatives to nitroamines in the dye intermediate industry. In the case of nitroanthraquinones, reduction is usually carried out with sodium sulfide in the presence of sodium hydroxide.

In general it may be said that 1.8–4.0 moles of sodium sulfide, 1.8–4.0 moles of sodium hydrosulfide, and 1.6–3.0 moles of ammonium sulfide are used per mole of nitro compound.

No general rules concerning the method of carrying out the reaction can be given, since the best order of addition of reagents varies from compound

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[1] See Astle and Cropper, *J. Am. Chem. Soc.*, **65**, 2395 (1943), for mechanism of reaction.

to compound and the optimum temperature ranges from room temperature to reflux (generally 50–100°C). A solvent such as ethyl alcohol is very helpful at times in promoting a smooth reduction in good yield. A water-immiscible solvent, such as naphtha, is sometimes used to prevent overreduction. If labile halogen or nitro groups are present, they are often converted to thiols, sulfides, and disulfides.

Ward and coworkers have carried out a rather comprehensive study of the reduction of dinitrobenzenes and dinitronaphthalenes with alkali sulfides.[1] They have found that the following general reactions predominate:

o-dinitrobenzene → bis(2-nitrophenyl)sulfide
m-dinitrobenzene → *m*-nitroaniline
p-dinitrobenzene → 4,4′-dinitroazobenzene + *p*-nitroaniline
1,2-dinitronaphthalene → bis(2-nitro-1-naphthyl)sulfide
1,4-dinitronaphthalene → bis(4-nitro-1-naphthyl)sulfide
1,5-dinitronaphthalene → 5-nitro-1-naphthylamine + 5-nitro-1-naphthalenethiol
1,6-dinitronaphthalene → 5-nitro-2-naphthylamine + 5-nitro-2-naphthalenethiol
2,7-dinitronaphthalene → 7-nitro-2-naphthylamine + 7-nitro-2-naphthalenethiol

Manufacture of *m*-Nitroaniline

✓ First, 100 parts of *m*-dinitrobenzene is added to 1,000 parts of water at 90°C contained in a reducer fitted with a reflux condenser and a propeller-type stirrer. Upon emulsification, 245 parts of sodium sulfide ($9H_2O$), dissolved in a minimum of water, is gradually run in. The dinitro compound is gradually reduced to *m*-nitroaniline, the end point being determined by the formation of a definite black streak when ferrous sulfate solution is added to filter paper spotted with some of the reducer liquor.

A modification of the preceding process involves the use of an organic solvent, which is immiscible with water, for the *m*-dinitrobenzene. Accordingly, 100 parts of technical dinitrobenzene, 90 per cent purity, and 160 parts of either solvent naphtha or toluene are put into the reducer, and the mixture is warmed to 60°C to effect solution. Then, 4,000 parts of hot water is added, and the *m*-dinitrobenzene solution is stirred and heated to 95°C. A hot polysulfide (Na_2S_3) solution—made by heating 720 parts of 7 per cent Na_2S with 40 parts of flowers of sulfur—is then added rather rapidly. The reaction of the polysulfide is distinctly exothermic, and the charge boils vigorously, but overheating is avoided because of the vaporization of the solvent. Reduction of the dinitrobenzene to *m*-nitroaniline is found to take place very quickly under such conditions.

The hot reduction mass is first filtered to remove any free sulfur, and the

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[1] *J. Chem. Soc.*, **1949**, 1316; **1954**, 2974, 4545.

solvent naphtha in the filtrate is distilled with steam. The dissolved *m*-nitroaniline crystallizes out in the form of bright yellow crystals when the residual liquor is cooled. After washing, the product has a melting point of about 113°C (cp = 114°C) and can be used directly in the manufacture of azo dyes. A yield of approximately 90–92 per cent of theory is attainable, and the process is applicable to other *m*-dinitro compounds, e.g., the *m*-dinitro derivatives of toluene and xylene.

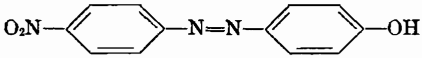
Manufacture of 2-Amino-4-nitrophenol

Two hundred and seventy parts of an aqueous solution containing 51 parts of sodium sulfide is added to a solution of 180 parts of ferrous sulfate in 240 parts of water. The mixture is thoroughly stirred until a suspension of freshly precipitated ferrous sulfide is obtained. There is then added 61.8 parts of the sodium salt of 2,4-dinitrophenol dissolved in 480 parts of water, and the mixture is heated slowly to approximately 60–80°C until the reduction of one nitro group is complete.

The batch is filtered and the filtrate neutralized carefully by the addition of hydrochloric acid. The precipitated 2-amino-4-nitrophenol is then filtered off.

Manufacture of 4-Amino-4′-hydroxyazobenzene

When *p*-nitroaniline is diazotized and coupled with an amine or a phenol, a nitro azo compound is formed:



Strong reducing agents will reduce not only the nitro group but the azo group as well, with the production of *p*-phenylenediamine and *p*-aminophenol. The nitro compound is therefore dissolved in a weak alkaline solution, and at a temperature of 40–50°C 2 moles of sodium sulfide as 30 per cent crystals is slowly added. The charge is thoroughly stirred until spot tests show a change of color, thus indicating that the selective reduction is complete. The 4-amino-4′-hydroxyazobenzene is then separated by either salting out or neutralizing the solution with dilute mineral acid.

Manufacture of 5-Nitro-1-naphthylamine

When naphthalene is dinitrated, a mixture of 1,5- and 1,8-dinitroaphthalenes is obtained. Upon reduction under controlled conditions with sodium sulfide, the 1,5-isomer is partially reduced selectively, while the 1,8-derivative remains substantially unaltered.[1] Thus, a suspension of 55 parts of the mixture of isomers in 400 parts of water is heated to 90°C, and a solution containing 23.2 parts sodium sulfide crystals and 6.2 parts of sulfur in 80

[1] Hodgson, U.S. 1,988,493 (1935).

parts of water is added. The mixture is stirred for 15 min and then cooled and filtered. The residue on the filter is washed with water and then is treated with dilute hydrochloric acid to dissolve any nitro amino compound. The acid mixture is filtered, and the residue, which is relatively pure 1,8-dinitronaphthalene, is washed with water. The filtrate contains the hydrochloride of 5-nitro-1-naphthylamine.

Manufacture of 2-Amino-7-chloroanthraquinone

Gubelmann[1] has shown that 2-nitro-7-chloroanthraquinone can be reduced satisfactorily in alkaline sulfide solutions without appreciable replacement of the chloro substituent. This procedure is of interest in view of the fact that the halogen substituent is loosely bound by virtue of the presence of the $—NO_2$ and $>CO$ groups. The reduction is carried out by suspending 287 parts of 2-nitro-7-chloroanthraquinone in 5,000 parts of water containing 40 parts of caustic soda and 625 parts of sodium sulfide ($9H_2O$). The mass is heated to the boiling point and boiled for 1–2 hr. The amino compound is then filtered off and washed with hot water.

VII. ELECTROLYTIC REDUCTIONS

The production of amines by electrolytic reduction has been studied extensively, and a great deal has been written on this subject in journals, books, and patents.[2] Although work has, thus far, in the main been limited to the laboratory and pilot plant, this method represents a potentially economic method of manufacturing certain amines. It should not be excluded from consideration by the chemist and chemical engineer when partial reduction of complex or sensitive organic compounds is required, where power cost is low, or where such operation can be combined with other existing electrochemical facilities. In general, reductions can be controlled carefully, high yields are often obtained, and by-products are few. Reductions of aliphatic and aromatic mono-, di-, and trinitro compounds to nitroso, hydroxylamino, azoxy, azo, hydrazo, and amino compounds have been described.

Apparatus. The source of current may be a generator, storage battery, or rectified alternating current with provisions to avoid fluctuations. An ammeter and a voltmeter are required. Electrodes may be solid or porous, bars of most any shape, sheets, gauze, or liquid (as mercury). Carbon,

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[1] Gubelmann, U.S. 1,810,012 (1931).

[2] SWANN, Electrolytic Reactions, in Weissberger (ed.), "Technique of Organic Chemistry," vol. II, Interscience Publishers, Inc., New York, 1956. This contains an excellent tabulation of electrolytic reductions. For early work, see HABER, *Z. Elektrochem.*, **4**, 506 (1898); *Z. physik. Chem.*, **32**, 193 (1900). For recent work, see papers by DEY and coworkers in *J. Sci. Ind. Research* (*India*), 1946–1950.

copper, zinc, cadmium, mercury, nickel, platinum, lead, tin, amalgamated lead and zinc, and Monel metal have been used as cathodes. Iron, nickel, platinum, carbon, and lead have been employed as anodes.

Electrolytes used are sulfuric acid, hydrochloric acid, sodium hydroxide, inorganic salts, and organic salts. Glacial acetic acid, methyl alcohol, and ethyl alcohol have also been found useful. Promoters are stannous chloride, copper sulfate, mercurous sulfate, antimony oxides, ketones, and salts of lead, titanium, molybdenum, and vanadium.

The cell may be constructed of suitable resistant material, generally glass in the laboratory. The diaphragm is usually made of alundum or asbestos. It should readily allow the diffusion of inorganic ions, but not the organic materials used. There should be excellent contact between the cathode and the organic nitrogen compound to be reduced. This may be accomplished by the use of solvents, wetting agents and by stirring. Very often stirring electrodes are used for this purpose. Provisions may also be made for cooling, heating, refluxing, distilling, etc.

The important factors which influence yield and quality are current density, current concentration, temperature, composition of electrodes, electrolyte, and promoters. Very often the electrodes must be activated by blank electrolytic runs.

Nitro Compounds. Both aromatic and aliphatic nitro compounds have been reduced to amines under varying conditions.

$$RNO_2 + 6H^+ + 6e \rightarrow RNH_2 + 2H_2O$$

Most of the catholytes have been aqueous or aqueous alcoholic solutions of mineral acids. In most cases the promoters used have been stannous chloride, cupric chloride, titanium chloride, vanadyl sulfate, and molybdic acid. Copper, nickel, lead, carbon, and mercury cathodes have been used.

When strong sulfuric acid is used with aromatic nitro compounds containing a free para position, rearrangement of the intermediate phenylhydroxylamine to a *p*-aminophenol takes place. A smooth platinum cathode

$$C_6H_5NO_2 + 4H^+ + 4e \rightarrow p\text{-}HOC_6H_4NH_2 + H_2O$$

has been used, as well as a copper cathode and also a carbon cathode with benzophenone as a promoter. More recently, *p*-aminophenol was prepared on a pilot-plant scale in 73 per cent yield by employing a Monel-metal cathode and mercury and cerium salts as promoters.[1] Other examples are the formation of aminocresols from *o*- and *m*-nitrotoluenes, the formation of 2,4-diaminophenol from *m*-dinitrobenzene or *m*-nitroaniline and of *m*-chloro-*p*-aminophenol from *o*-chloronitrobenzene.

Nitroguanidine has been reduced to aminoguanidine, using a lead cathode and platinum anode in strong sulfuric acid at 10–15°C. A number of

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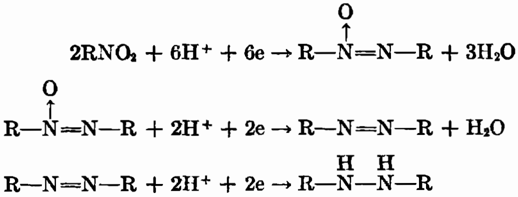
[1] DEY et al., *J. Sci. Ind. Research (India)*, **4**, 574 (1946).

2-aminoethyl compounds have been formed by the reduction of α,β-unsaturated nitro compounds at a lead cathode in hydrochloric acid solution.

Reduction of nitro compounds to azoxy compounds has generally been carried out by suspending or dissolving the nitro compound in an alkaline catholyte at a nickel cathode. A cathode of low hydrogen overvoltage is used to avoid rapid reduction of the formed azoxy compound. Reduction proceeds to the azo stage when there is added to the catholyte, alcohol or salts of aromatic sulfonic acids and the temperature is maintained near the boiling point of the catholyte. If the current density is then lowered to about one quarter of its previous value, reduction proceeds to the hydrazo stage.



$$2RNO_2 + 6H^+ + 6e \rightarrow R{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}R + 3H_2O$$

$$R{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}R + 2H^+ + 2e \rightarrow R{-}N{=}N{-}R + H_2O$$

$$R{-}N{=}N{-}R + 2H^+ + 2e \rightarrow R{-}\overset{H}{N}{-}\overset{H}{N}{-}R$$

Substituted aliphatic and all types of aromatic *amides* have been reduced to the corresponding amines.[1] A lead cathode is used, and the catholyte contains sulfuric acid and arsenic and antimony oxides as promoters. Corresponding *thioamides* have also been reduced similarly to amines.

Reduction of several aliphatic and aromatic *nitriles* to the corresponding amines has also been reported.[2] A palladium-coated nickel cathode, a carbon anode, and dilute hydrochloric acid have been used.[3] A copper cathode, a graphite anode, and a promoter such as Raney nickel have been found satisfactory for the reduction of long-chain fatty nitriles.

VIII. METAL AND ALKALI REDUCTIONS

Zinc or Iron and Strong Alkali

When nitrobenzene or its homologues are treated in alkaline solution in the presence of finely divided zinc or iron, they can be reduced step by step to the hydrazo stage. Such hydrazo compounds—hydrazobenzene, hydrazotoluene, hydrazoanisole—may be converted readily to benzidine, tolidine, and dianisidine by intramolecular rearrangement in cold concentrated hydrochloric or sulfuric acid.

The several steps in the reduction of nitroaryl compounds are repre-

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[1] GOODINGS and WILSON, *Trans. Electrochem. Soc.*, **88**, 77 (1945).

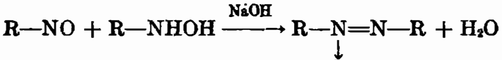
[2] OHTA, *J. Chem. Soc. Japan*, **63**, 1762 (1942); *Bull. Chem. Soc. Japan*, **17**, 485 (1942). Ishifuku et al., Jap. 180,563 (1949). Janardhan, India 44,230 (1952).

[3] OHTA, *loc. cit.*

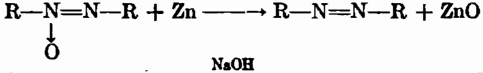
sented by the following equations, where R represents phenyl, tolyl, methoxyphenyl, chlorophenyl, etc.

$$R{-}NO_2 + Zn \xrightarrow{NaOH} R{-}NO + ZnO \tag{1}$$

$$R{-}NO + Zn + H_2O \xrightarrow{NaOH} R{-}NHOH + ZnO \tag{2}$$



$$R{-}NO + R{-}NHOH \xrightarrow{NaOH} R{-}\underset{\underset{\displaystyle O}{\downarrow}}{N}{=}N{-}R + H_2O \tag{3}$$



$$R{-}\underset{\underset{\displaystyle O}{\downarrow}}{N}{=}N{-}R + Zn \xrightarrow{NaOH} R{-}N{=}N{-}R + ZnO \tag{4}$$

$$R{-}N{=}N{-}R + Zn + H_2O \xrightarrow{NaOH} R{-}NH{-}NH{-}R + ZnO \tag{5}$$

From the above, it is seen that in the presence of an adequate supply of NaOH solution, in the proper concentration, hydrazo compounds are formed by the reduction in steps to nitroso and hydroxylamine derivatives [Eqs. (1) and (2)], followed by condensation to give the azoxy compound [Eq. (3)]. These steps necessitate the relatively strong alkalinity of concentrated sodium hydroxide and the sodium zincate formed from the hydrous zinc oxide that is generated under the aqueous conditions employed.

$$H_2ZnO_2 + 2NaOH \rightleftharpoons Na_2ZnO_2 + 2H_2O$$

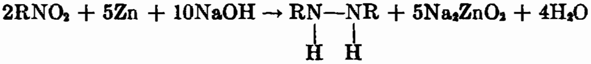
The next steps, viz., reduction to azo [Eq. (4)] and hydrazo compounds [Eq. (5)], are carried out in less alkaline solution. If the alkali concentration at the start is too low, reduction may proceed to the amine:

$$R{-}NHOH + Zn \rightarrow R{-}NH_2 + ZnO$$

Precautions must also be taken to avoid excessive heating of the hydrazo compound, which may decompose to azo compound and amine.

$$2R{-}NHNH{-}R \rightarrow R{-}N{=}N{-}R + 2R{-}NH_2$$

The reduction of the nitro compound to the hydrazo stage may be represented by the following over-all equation:



$$2RNO_2 + 5Zn + 10NaOH \rightarrow R\underset{\underset{\displaystyle H}{|}}{N}{-}\underset{\underset{\displaystyle H}{|}}{N}R + 5Na_2ZnO_2 + 4H_2O$$

Technical Operations. In technical operations, an excess of 15–50 per cent of zinc (based on the preceding equation) is used. The quantity of alkali employed is, however, only about 2–10 per cent of the theoretical. Here, as in the case of acid reductions, there is a hydrolysis of the intermediate soluble catalytic agent that is favored by the presence of metals. In this process, the sodium zincate is hydrolyzed, with the regeneration of sodium hydroxide and precipitation of an insoluble hydrous zinc oxide:

$$Na_2ZnO_2 + (x + 1)H_2O \overset{Zn}{\rightleftharpoons} ZnO(H_2O)_x + 2NaOH$$

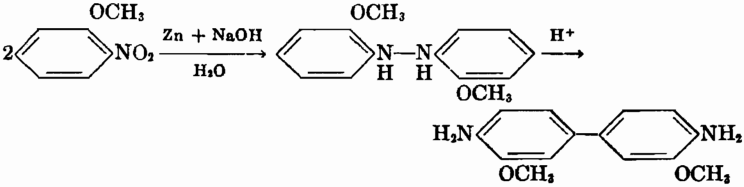
In the presence of zinc, the regenerated sodium hydroxide carries on the preceding cycle of reactions.

Ethanol and methanol are sometimes used in the latter stages (azo to hydrazo) of zinc and alkali reductions to moderate the activity of the reducer system, which then tends toward the formation of primary amine. Numerous modifications of the process have been developed to permit recovery of the residual zinc, alkali, and alcohol. Solvents, such as naphtha, have at times been used. In the I. G. Farbenindustrie procedure, described later in this section, no solvents or diluents are employed.

The effect of impurities in zinc powders used in the alkaline reduction of nitrobenzene to hydrazobenzene has been studied.[1] Iron inhibits the reaction, while lead (up to 2.5 per cent) improves the yield, shortens the reaction time, and counteracts the effect of iron. Cadmium appears not to affect the reaction.

It has been shown that iron prepared by the reduction of oxides may be used instead of zinc.[2] The molar ratio of nitrobenzene to iron and alkali, respectively, in this instance is approximately 2:4:8. The reduction procedure is similar to that using zinc, and the course of the reaction may be observed by determining the setting point on a sample of the charge (Fig. 5-18), since this changes with each phase of the reaction. Because it is difficult to separate hydrazobenzene from the iron sludge, benzene is introduced in sufficient quantities to dissolve the hydrazobenzene, which is then decanted from the sludge. Ferrosilicon (containing 15 per cent silicon) and alkali give 88–92 per cent yields of hydrazobenzene.[3]

Manufacture of 2,2′-Dimethoxyhydrazobenzene and Dianisidine Using Zinc and Alkali



In operations at I. G. Farbenindustrie, Leverkusen,[4] 250 kg (1.63 moles) *o*-nitroanisole and 1 kg 50 per cent sodium hydroxide solution are delivered to a cast-iron steam-jacketed 1,000-liter reducer. The temperature of the charge is raised to 75°C, and at regular intervals during a 24-hr period there are added concurrently 235 kg of zinc dust (90 per cent; 3.3 moles) in 2.5-kg

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[1] Tajima and Sasuga, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 116 (1954).

[2] Dreyfus, U.S. 2,010,067 (1935).

[3] Iida et al., *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 47 and 830 (1954).

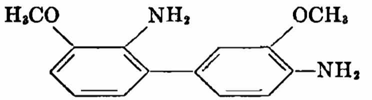
[4] *F.I.A.T. Final Rept.* 1313, vol. 1, p. 134.

portions and 50 liters of 50 per cent sodium hydroxide in approximately 0.5-liter portions. The first third of the reduction, from nitro to the azo stage, is done at 75°C and the final third at 80°C. If a sudden temperature rise occurs, which may happen if the reduction gets out of hand, the charge is drowned with water admitted by a special 4-in. line.

Approximately 200 liters of water is added and the temperature raised to 85°C. The reduction is continued from the azo stage at this temperature by the addition in small portions of 85 kg zinc dust (1.2 moles) and water during a 6-hr period, maintaining a thick but stirrable paste. Complete reduction of the azoanisole to hydrazoanisole is indicated by the absence of orange color in the benzene layer of an extract of a sample. When the test is satisfactory, the reducer is filled with water and the charge blown to a brick-lined agitated dezincing vat. Here, three reducer batches are combined and cooled to 10°C or lower, with water in a lead coil.

Sulfuric acid, 30°Bé, is run into the vat until a weak Congo acidity, stable for 20 min, is obtained. The charge is filtered, and the hydrazoanisole press cake is washed free of zinc sulfate. During a 4–5 hr period, the hydrazo paste is introduced into an acid-proof brick-lined vessel containing 3,300 liters water and 2,200 liters 30°Bé sulfuric acid at 0–5°C. Stirring is continued at 0–5°C until rearrangement to dianisidine is complete. The time varies from batch to batch and is usually about 1–1.5 days. Cooling is maintained by the circulation of water through a lead coil.

By means of suction the charge is drawn into another brick-lined vessel containing 5,000 liters 60°Bé sulfuric acid at 20°C. The stirred slurry of dianisidine sulfate is filtered, and the press cake (after washing with 50 per cent sulfuric acid) is delivered to a 20-cu m wooden tub containing water and made up to 11,000 liters. Now 500 liters of 33 per cent hydrochloric acid is added, and the contents are heated to 95°C by means of a rubber-covered steam leg to dissolve the dianisidine hydrochloride. About 1,000 liters of 2 per cent sodium sulfide solution is introduced to precipitate any residual zinc. After the addition of 25 kg Terrana (a type of mineral filter aid), the charge is permitted to settle. The supernatant liquor is drawn off into the brick-lined precipitation kettle, where 900 kg salt is added, and allowed to cool to 20°C (no coil) to precipitate the hydrochloride of *o*-dianisidine. The charge is filtered, and the press cake is washed twice with saturated salt solution. The product is dried on enamel trays at 60°C in air or vacuum. The yield is 75 per cent of theory, about 15–20 per cent "diphenyline" derivative being formed from ortho-para rearrangement.

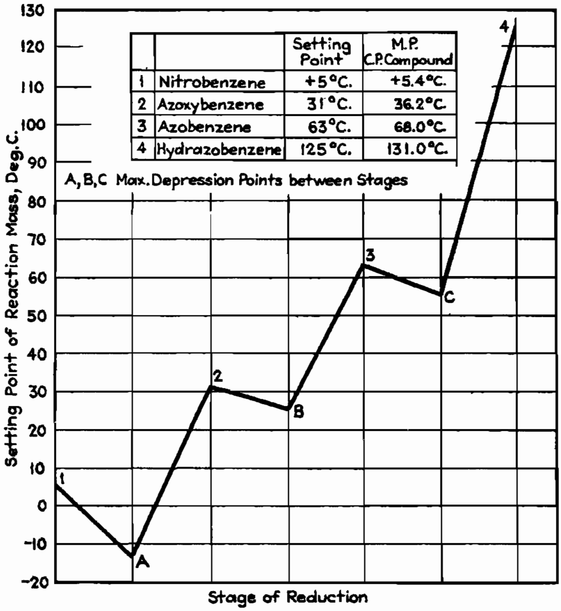


After four charges, the settled precipitate of zinc sulfide, Terrana, etc., is diluted with water, settled again, and the decanted solution used for dissolving the next charge. The residues are discarded.

Because of low labor costs and a large quantity of available equipment, I. G. Farbenindustrie placed great emphasis on material utilization, and as a consequence, this and similar processes are extremely complicated and time-consuming from the viewpoint of labor and equipment. Judged from American standards, the yield is satisfactory and the quality of the product at least equal to "normal" domestic production.

Manufacture of Hydrazobenzene Using Iron and Alkali

First, 100 kg of nitrobenzene and 50 kg of fine iron borings are stirred together and warmed to about 90°C. Then 80 kg of 55°Bé (60 per cent) caustic soda solution is added gradually, and the temperature maintained at 100–120°C by running steam or cooling water through the jacket of the reducer vessel. The course of the reaction may be observed by the change of color and the disappearance of the odor of nitrobenzene. A more exact indication may be obtained by determining the setting point on a sample of the charge (Fig. 5-18), since this changes with each phase of the reaction. As the reduction proceeds, the setting point drops from about 5 (corresponding to nitrobenzene) to a minimum of −13°C, at which time about 40 per cent of the nitro compound is converted to azoxybenzene. The setting



		Setting Point	M.P. C.P. Compound
1	Nitrobenzene	+5°C.	+5.4°C.
2	Azoxybenzene	31°C.	36.2°C.
3	Azobenzene	63°C.	68.0°C.
4	Hydrazobenzene	125°C.	131.0°C.

Fig. 5-18. Iron and alkali reduction of nitrobenzene.

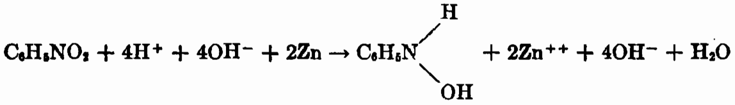
point then gradually rises to 31°C, at which time the odor of nitrobenzene has disappeared and the azoxy compound can be discharged.

Azobenzene can be obtained upon further reduction of the azoxy compound by adding a paste consisting of 16 parts iron and 40 parts 60 per cent caustic soda and heating at 110–120°C. The setting point of the reduction mass first sinks to a minimum of 25°C and then it rises to about 63°C. The apparatus may be stopped at that point and the azobenzene discharged.

In order to proceed to the next stage of reduction, that is, to hydrazobenzene, it is necessary again to add 16 kg of iron and 40 kg of 60 per cent caustic soda solution. The setting point of the mass sinks to a minimum of 55°C and then rises to 122–125°C. In order to prevent the reduction mass from solidifying, it is necessary either to raise the temperature to 130°C or to add some solvent, such as benzene, to the reaction mixture. The introduction of benzene in sufficient quantities also affords a convenient means of separating and decanting the hydrazobenzene from the iron-alkali residues.

It is difficult to remove the hydrazobenzene from the iron sludge at this point, and a number of modifications of this process have consequently been advocated. One method involves the removal of azobenzene and reducing this compound by zinc in alcoholic alkaline solution at 60°C. The reduction mass is filtered, and the zinc residues are boiled up with fresh alcohol. The filtrate separates into two layers, of which the lower contains aqueous sodium zincate, while the upper is an alcoholic solution of hydrazobenzene. The alcoholic layer is separated and saturated with carbon dioxide to precipitate the alkali. After filtering, the alcoholic solution is evaporated to obtain the hydrazobenzene, for which practically quantitative yields have been claimed.

Zinc and Weak Alkali. The mechanism of reduction with zinc and strongly alkaline solutions leads to the formation of azoxybenzene as the first stable product in the reduction of nitrobenzene. Bamberger[1] has shown that, when faintly alkaline systems are employed, the principal initial stable product of reduction is N-phenylhydroxylamine. The systems —zinc + calcium chloride and zinc + ammonium chloride—are not neutral but quite alkaline to phenolphthalein. In the preparation of N-phenylhydroxylamine from nitrobenzene by means of zinc dust and aqueous calcium chloride, the reduction liquid has a pH between 10.5 and 11.7, which corresponds to the alkalinity of 0.01 *N* alkali. When NH_4Cl is substituted for $CaCl_2$ in the reducing system, the pH is between 8 and 9.



$$C_6H_5NO_2 + 4H^+ + 4OH^- + 2Zn \rightarrow C_6H_5N\begin{matrix}H\\ \\ OH\end{matrix} + 2Zn^{++} + 4OH^- + H_2O$$

$$2Zn^{++} + 4OH^- \rightleftharpoons 2Zn(OH)_2$$

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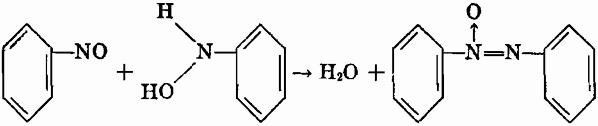
[1] See Brand and Modersohn, *J. prakt. Chem.*, **120**, 160 (1928).

Zinc and ammonium chloride can also be used advantageously for the reduction of nitroparaffins to alkylhydroxylamines:

$$CH_3NO_2 \xrightarrow{Zn + NH_4Cl} CH_3NHOH$$

Brand and Mahr showed that the formation of azoxybenzene in the reduction of nitrobenzene is brought about by the condensation of nitrosobenzene and phenylhydroxylamine, the latter being intermediate products of reduction.[1]



Ferrous Sulfate and Alkali. Although ferrous sulfate in alkaline solutions acts as a strong reducing agent, the system has only a limited usefulness in the commercial reduction of nitro compounds. The amount of ferrous sulfate used is slightly in excess of that required by theory, which is 6 moles of ferrous sulfate to 1 mole of the nitro compound.

$$RNO_2 + 6FeSO_4 + H_2O \rightarrow RNH_2 + 2Fe_2(SO_4)_3 + Fe_2O_3$$

m-Nitrobenzaldehyde can be converted to the amino compound utilizing this procedure, by putting it into solution as a bisulfite compound with double its weight of a 30 per cent solution of sodium bisulfite. This solution is slowly delivered to a vat containing the required quantity of ferrous sulfate in 3 parts of water, to which one-third of its weight of calcium carbonate has been added. The mixture is boiled with stirring. Carbon dioxide is given off with effervescence, and the reduction takes place rapidly. The amino compound can be extracted from the solution after first acidifying with hydrochloric acid to expel the sulfur dioxide.

IX. SODIUM HYDROSULFITE REDUCTIONS

Sodium hydrosulfite (hyposulfite), $Na_2S_2O_4$, in alkaline solutions has come to play an important part in the reduction of anthraquinone and indigoid derivatives to the leuco compounds. Although it is an active reducing agent, it finds only a limited use in the reduction of nitro compounds because of its comparatively greater cost.

Sodium hydrosulfite can be used as the white crystalline product of commerce, or it can be prepared in the course of the reaction by adding zinc dust to a solution of sodium bisulfite. The latter procedure has been employed for the reduction of indigo and for the preparation of *o*-aminophenol from the corresponding nitro derivative. The reaction involved is as follows:

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[1] Brand and Mahr, *J. prakt. Chem.*, **131**, 119 (1931).

$$2NaHSO_3 + SO_2 + Zn \rightarrow Na_2S_2O_4 + ZnSO_3 + H_2O$$

The required sulfur dioxide is obtained by the introduction of a mineral acid to the reaction mixture during reduction. Indigo, $C_{16}H_{10}N_2O_2$, which is insoluble, is reduced by the hydrosulfite to the leuco compound, $C_{16}H_{12}N_2O_2$, which goes into solution:

$$Na_2S_2O_4 + 2H_2O \rightarrow 2NaHSO_3 + 2(H)$$
$$C_{16}H_{10}N_2O_2 + 2(H) \rightarrow C_{16}H_{12}N_2O_2$$

Sidgwick and Callow,[1] in studying the solubility of *o*-aminophenol, prepared their amino compound by mixing *o*-nitrophenol with 4.5 molecular proportions of sodium bisulfite, $NaHSO_3$, as a 25 per cent solution. The charge is warmed, and zinc dust is added at such a rate that the liquid keeps boiling. Completion of the reaction is indicated by the disappearance of the yellow color when spotting on filter paper. The *o*-aminophenol is obtained by filtering the hot solution and permitting the filtrate to cool, whereupon the amino compound crystallizes out.

This method is useful for certain sensitive nitro compounds, which cannot be reduced by a more economical process, and for very insoluble nitro compounds. The reactions in the presence of alkali may be represented as follows:

$$RNO_2 + 3Na_2S_2O_4 + 6NaOH \rightarrow RNH_2 + 6Na_2SO_3 + 2H_2O$$
$$RNO_2 + Na_2S_2O_4 + 2NaOH \rightarrow RNH_2 + 2Na_2SO_4$$

Generally, 1.2–3.0 moles of sodium hydrosulfite is used per mole of nitro compound, together with alkali, to prevent the formation of sulfuric acid which would decompose the hydrosulfite. The use of tertiary amines in the place of alkali for use with nitro compounds containing labile halogen atoms has been described.[2]

X. SULFITE REDUCTIONS

A relatively unfamiliar method of reduction, which is limited in its applicability although very cheap and convenient where usable, is reduction by means of sodium bisulfite.[3] This reduction, discovered by Piria in 1851, may be represented by the following four reactions:

$$RNO_2 + 3Na_2SO_3 + H_2O \rightarrow RNH_2 + 3Na_2SO_4$$
$$2RNO_2 + 6NaHSO_3 + 2H_2O \rightarrow 2RNH_2 + 3Na_2SO_4 + 3H_2SO_4$$
$$R(H)NO_2 + 2Na_2SO_3 + NaHSO_3 \rightarrow R(SO_3Na)NH_2 + 2Na_2SO_4$$
$$2R(H)NO_2 + 6NaHSO_3 \rightarrow 2R(SO_3H)NH_2 + 3Na_2SO_4 + H_2SO_4$$

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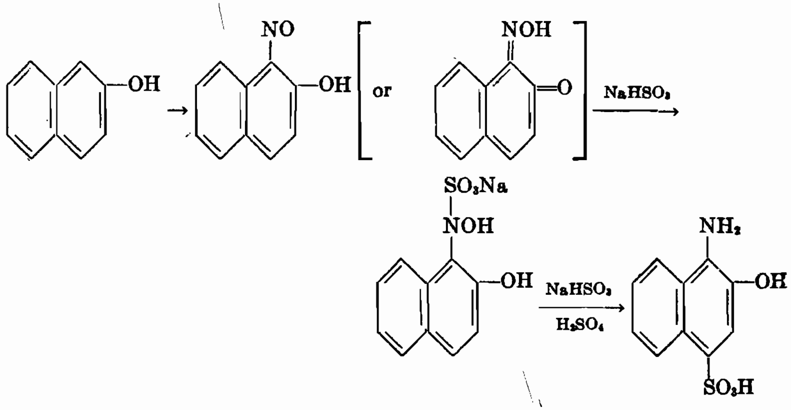
[1] SIDGWICK and CALLOW, *J. Chem. Soc.*, **125**, 2452 (1924).

[2] Werner, U.S. 2,631,167 (1953).

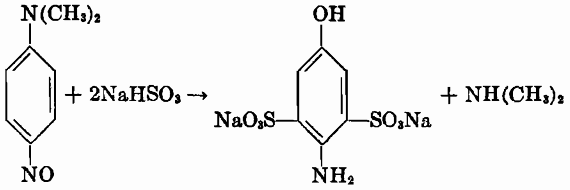
[3] See HUNTER and SPRUNG, *J. Am. Chem. Soc.*, **53**, 1432, 1443 (1931).

It is significant in that it gives not only amines but also *o*- and *p*-amino sulfonic acids, all in one reaction. It is generally carried out with excess sodium bisulfite (4.5–6.0 moles per mole of nitro compound), usually with the addition of enough caustic soda to form the required amount of neutral sulfite. A solvent, such as ethyl alcohol or pyridine, often helps to speed up the reaction, particularly for nitro compounds that are either difficultly soluble or wettable. It is interesting to note that sulfamic acids have also been isolated from this reaction in certain cases. Examples of nitro compounds that may be reduced by the Piria method are *p*-nitrotoluene, which forms *p*-toluidine in about 70 per cent yield; *p*-nitrobenzoic acid, which forms 4-amino-3-sulfobenzoic acid; and 4-nitronaphthalic anhydride, which forms 4-amino-3-sulfonaphthalic anhydride.

The well-known dye intermediate 1,2,4-acid, or 4-amino-3-hydroxy-1-naphthalenesulfonic acid, is made by this general method from 1-nitroso-2-naphthol. The reactions may be represented as follows:



The over-all yield from 2-naphthol is about 90 per cent of theory. This method is also used for the preparation of 4-amino-1-phenol-3,5-disulfonic acid from *p*-nitrosodimethylaniline by the following reaction:



Pearl and Lewis[1] studied the reduction of nitrobenzene with sulfite-pulp waste liquor with respect to the variables of time, temperature, pressure, order of addition, concentration, and composition of the liquor. At atmos-

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[1] *Ind. Eng. Chem.*, **36**, 664 (1944).

pheric pressure, aniline, azoxybenzene, and sodium *p*-azobenzenesulfonate were formed, with maximum yields of 67.5 per cent for the azoxy and 24.4 per cent for the sulfonic acid. Under pressure, aniline (maximum yield 67.5 per cent) and azoxybenzene (maximum yield 65 per cent), depending upon the ratio of reactants, were obtained. Vanillin is a by-product of the simultaneous oxidation of lignin in the waste liquor.

XI. MISCELLANEOUS REDUCTIONS

Metal Hydrides. A number of patents and publications have appeared describing the use of lithium aluminum hydride in the reduction of nitro compounds, nitriles, amides, oximes, and azides to amines. Moderate to high yields have been obtained. This process is useful in the selective reduction of compounds sensitive to catalytic hydrogenation, but is quite costly.

Finholt and coworkers[1] have studied the use of sodium aluminum hydride. With nitrobenzene, azobenzene is obtained in 78 per cent yield. With nitrobutane, butylamine is produced in 73 per cent yield. With benzonitrile, the yield of benzylamine is 92 per cent of theory.

Brown and Subba Rao[2] have found that sodium borohydride reduces nitriles to amines, but does not affect nitro groups or amides.

Sodium Hydroxide and Methyl Alcohol. On reacting nitrobenzene with methanol and caustic soda, azoxybenzene is the main reduction product formed. Sodium formate is obtained as the oxidation product of the methanol used. Naphthoquinone and its substitution products are promoters of this reaction.[3]

Nitrobenzene can also be reduced to azoxybenzene and azobenzene with magnesium and methanol.

Sodium Amalgam. Sodium amalgam reduces nitrobenzene to azobenzene as well as to hydrazobenzene and oximes to amines. The I. G. Farbenindustrie, in its development of mercury cells for the production of chlorine and caustic, found that it could use the intermediate sodium amalgam for the reduction of nitrobenzene to azobenzene on a very economical basis.[4] The operation was carried out in batches in nickel reactors, and 50 per cent caustic soda was obtained simultaneously. It was not found feasible to produce hydrazobenzene directly by this method. Hallie[5] has, however, obtained a patent on the reduction of nitrobenzene to hydrazobenzene using sodium amalgam in aqueous alcohol.

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[1] *J. Am. Chem. Soc.*, **77**, 4163 (1955).

[2] *J. Am. Chem. Soc.*, **77**, 3164 (1955).

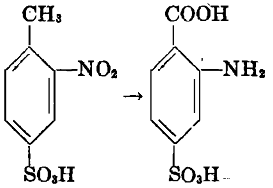
[3] Sogn, U.S. 2,684,358 (1954).

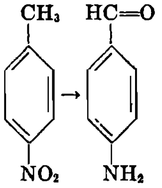
[4] *F.I.A.T. Final Rept.* 818; *B.I.O.S. Final Rept.* 853.

[5] U.S. 2,486,358 (1949).

In addition to this reaction, *o*-nitrophenoxyacetic acid can be reduced to the corresponding azo compound, and 2,7-dinitroanthraquinone-3,6-disulfonic acid is reduced directly to the diamine by this method.

Oxidation Reduction of Nitrotoluenes by Strong Alkali. Strong caustic often promotes a simultaneous oxidation reduction of nitrotoluenes whereby the nitro group is reduced to amino and the methyl group is oxidized to a carboxylic or a formyl residue. This is similar to the Cannizzaro reaction that strong alkali induces in aldehydes. Thus, 2-nitrotoluene-4-sulfonic acid, on treatment with strong caustic soda solution near the boil, forms 2-amino-4-sulfobenzoic acid. Also, *p*-nitrotoluene, on treatment with hot caustic soda in the presence of sulfur, forms 4-aminobenzaldehyde. Although the yield is generally rather low in these cases, they have been used industrially to provide a simple one-step method of producing the corresponding amines from inexpensive starting materials. The reactions may be represented as follows:





Others. Sodium and alcohol have been used to reduce oximes to amines. Hydrazine sulfate in liquid ammonia has been employed at 100°C under pressure to reduce nitroquinolines to aminoquinolines. Tetrahydronaphthalene can be used for the partial reduction of dinitro compounds. Buckley and Ray[1] have published some interesting studies involving reductions with carbon monoxide at rather high temperatures and superatmospheric pressures. Nitrobenzene, when treated with carbon monoxide at 250°C and 45,000 psig, gives a good yield of azobenzene and carbon dioxide. Nitrosobenzene, at 150°C and 45,000 psig, similarly gives azobenzene together with tarry by-products. Azoxybenzene, at 200°C and the same pressure, is reduced to azobenzene in good yield. Phenylhydroxylamine, treated exactly as azoxybenzene, gives rise to both azobenzene and aniline.

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[1] *J. Chem. Soc.*, **1949**, 1154.

Aliphatic nitro compounds could not be similarly reduced below their decomposition points.

Sargent and Pedlow[1] have described the reduction of aromatic nitro compounds to hydrazo compounds using caustic soda solution and aluminum in the presence of zinc oxide. Lacey and Brouillard[2] have found that *o*-chloronitrobenzene can be reduced to 2,2′-dichloroazoxybenzene by reacting with caustic soda and a reducing sugar.

[1] U.S. 2,570,866 (1951).

[2] U.S. 2,383,134 (1945).

CHAPTER 6

HALOGENATION

BY J. S. SCONCE, P. H. GROGGINS, AND H. P. NEWTON

I. INTRODUCTION

Halogenation may be defined as the process whereby one or more halogen atoms are introduced into an organic compound.

The preparation of organic compounds containing fluorine, chlorine, bromine, and iodine can be accomplished by a variety of methods. The conditions and procedures differ, not only for each member of the halogen family but also with the type and structure of the compound undergoing treatment.

The chlorine derivatives, because of the greater economy in effecting their preparation, are by far the most important of the technical halogen compounds and for this reason are given primary consideration. The bromine derivative, however, sometimes has certain advantages because of the greater ease in effecting the replacement of this halogen in subsequent reactions or because it possesses certain pharmaceutical or dyeing properties.

The fluorine derivatives are well established in the fields of refrigerants and aerosol propellants because of their stability and low boiling points.

As may be observed from the following examples, halogenations may involve reactions of (1) addition, (2) substitution, i.e., of hydrogen, (3) replacement, i.e., of groups, for example, the hydroxyl or sulfonic acid group.

$$HC{\equiv}CH + 2Cl_2 \xrightarrow{FeCl_3} Cl_2HC{-}CHCl_2 \tag{1a}$$

$$C_6H_6 + 3Cl_2 \xrightarrow{h\nu} C_6H_6Cl_6 \tag{1b}$$

$$CH_3COOH + Cl_2 \xrightarrow{PCl_3} CH_2ClCOOH + HCl \tag{2}$$

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O \tag{3}$$

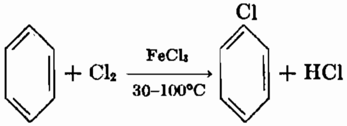
From the preceding formulations, it becomes clear that each type of reaction may involve not only a specific halogenating agent but also a suitable catalyst or activator. Many of the catalysts are halogen carriers. Iron, antimony, and phosphorus, which are able to exist in two valencies as halogen compounds, are used as they are less stable at the higher valence and give up part of their halogen during the process. In the presence of free halogen, such compounds alternately add on and give up halogen to carry on the reaction. Iodine, bromine, and chlorine which are capable of forming mixed halogens are also frequently employed as catalysts in halogenation processes. Active carbon, clays, and other compounds also serve to catalyze halogenation processes. Where the halogen is energized to an activated state by means of light, heat, nuclear energy, or free radicals, it may then proceed to react by addition as in reaction (1*b*) or by substitution without the need of a catalyst.

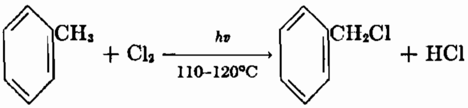
Chlorination. A number of methods are available for organizing the material relating to halogenation processes, all of which are necessarily complex. Here, as in other chapters, the principal classification is based on the (halogenating) agents employed. The most important methods for preparing chlorine compounds are the following:

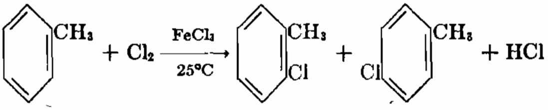
Direct Action of Chlorine Gas:

$$H_2C{=}CH_2 + Cl_2 \xrightarrow{FeCl_3} ClH_2CCH_2Cl$$

$$CH_4 + Cl_2 \xrightarrow{400\text{–}500°C} CH_3Cl + CH_2Cl_2 + HCl$$







Hydrochloric Acid as the Chlorinating Agent:

Addition reaction, direct action:

$$HC{\equiv}CH + HCl \xrightarrow{HgCl_2} H_2C{=}CHCl$$

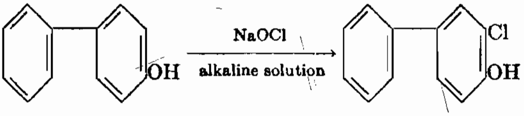
Substitution reactions, indirect action:

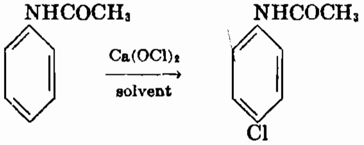
$$2C_6H_6 + 2HCl + O_2 \xrightarrow{CuCl_2 \text{ on } Al_2O_3} 2C_6H_5Cl + 2H_2O$$

Replacement reactions:

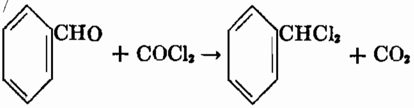
$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

Sodium Hypochlorite as Chlorinating Agent:





Chlorination with Phosgene ($COCl_2$) *and Benzotrichloride* ($C_6H_5CCl_3$):

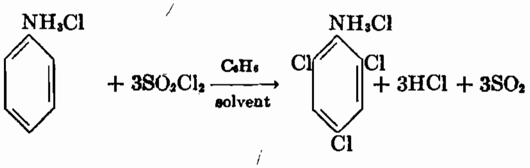


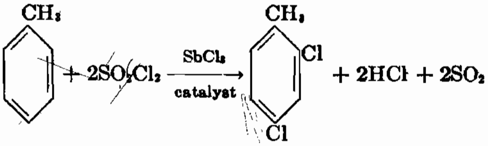
$$CH_3COOH + C_6H_5CCl_3 \rightarrow CH_3COCl + C_6H_5COCl + HCl$$

Chlorination with Thionyl Chloride ($SOCl_2$):

$$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$
$$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$$

Chlorination with Sulfuryl Chloride (SO_2Cl_2):





Chlorination with Phosphorus Chlorides:

$$3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$$
$$3RCOONa + PCl_5 \rightarrow 3RCOCl + NaPO_3 + 2NaCl$$

Preparation of Chlorine Derivatives by the Sandmeyer and Gattermann Reactions:

$$RN_2Cl + Cu_2Cl_2 \xrightarrow{HCl} RCl + N_2 + Cu_2Cl_2 \qquad \text{(Sandmeyer)}$$
$$RN_2Cl \xrightarrow[Cu]{HCl} RCl + N_2 \qquad \text{(Gattermann)}$$

Bromination. In many instances, brominations may be carried out in a manner similar to that employed for the preparation of chlorine derivatives. Thus, bromine, bromides, bromates, and alkaline hypobromites may be employed instead of the corresponding chlorine compounds. The Sandmeyer and Gattermann reactions also may advantageously be used for the preparation of bromine compounds.

Reactions involving addition and substitution are common. Bromine dissolved in water is frequently employed, particularly in the bromination of phenols. Potassium bromide is generally added to aqueous bromine solutions to increase the concentration of soluble molecular halogen. Concentrated bromine solutions are thus made available, presumably because of the following equilibrium:

$$Br_2 + KBr \rightleftharpoons KBr_3$$

Bromine, hydrobromic acid, and alkali hypobromites, like the corresponding chlorine compounds, find employment in technical brominations.

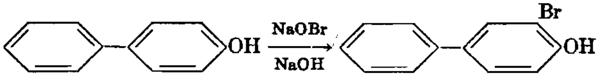
Addition Reaction:

$$H_2C{=}CH_2 + Br_2 \rightarrow BrH_2C{-}CH_2Br$$

Replacement Reaction:

$$C_2H_5OH + \xrightarrow[H_2SO_4]{KBr} C_2H_5Br + KHSO_4 + H_2O$$

Substitution Reaction:



A number of organic carriers for bromine to produce specific types of bromine-containing compounds have been explored through the use of N-bromosuccinimide, N-bromoacetamide, 1,3-dibromo-5,5-dimethylhydantoin, and associated compounds.

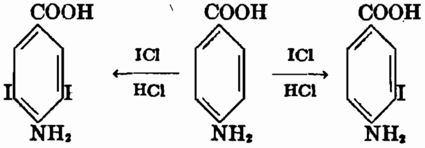
Iodination. The methods employed in iodination differ somewhat from those for chlorination or bromination. The relatively weak C-I bond, which is indicated by the low heat of reaction and which distinguishes iodine from other halogens, makes permanent, direct union of carbon to iodine by the replacement of hydrogen possible only in exceptional cases. Such iodinations are reversible in character, as, for instance, the iodination of acetic acid:

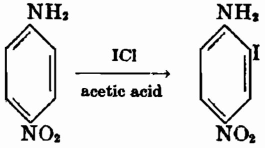
$$CH_3COOH + 2I \rightleftharpoons CH_2ICOOH + HI$$

and are governed largely by the conditions employed. The hydrogen iodide tends to effect deiodination of the halogenated compounds and, indeed, is sometimes thus employed. The removal of the hydrogen iodide by such means as oxidation or absorption in alkali is consequently essential for successful iodination. When nitric acid is employed as the oxidant, practically all the iodine enters the organic compound. In the ordinary direct halogenation in the absence of an oxidizing agent, half the reacting halogen is converted to the hydrogen halide.

Catalysts are only infrequently employed in iodination, phosphorus being the principal accelerator. Iodine monochloride, because of its activity under mild operating conditions, is a useful catalyst for the iodination of amino compounds:

$$I + Cl \rightleftharpoons ICl$$





Hydriodic acid and alkali hypoiodites, like the corresponding chlorine and bromine compounds, find employment in iodinations:

$$H_2C{=}CH_2 + HI \longrightarrow CH_2ICH_3$$

$$CH_3COCH_3 + 3KOI \xrightarrow{\text{alkali}} CH_3COCI_3 + 3KOH$$

$$CH_3COCI_3 + KOH \longrightarrow CH_3COOK + CHI_3$$

Fluorination. Fluorine acts directly on hydrocarbons to produce fluorides, but the reaction is violent and constitutes an explosion hazard. Some reactions can be carried out by careful control of temperature and fluorine concentration, but even then there may be a cleavage of carbon-carbon bonds. The bonds holding the atoms in the fluorine molecule are stronger than in the other halogens; but once the reaction is initiated and fluorine atoms are available, they combine more readily with hydrogen and hydrocarbons than do the halogens of higher molecular weight. Furthermore, the new bonds that are formed are so strong and the heat liberated is so great that precautions must be taken to moderate the reaction so as to keep it under control.

Despite all these problems and the high cost of elemental fluorine, commercial processes of fluorination are being operated and university and industry laboratories are rapidly adding to this technology.

Direct Fluorination. Direct vapor-phase fluorination using elemental fluorine is accomplished by using large volumes of an inert gaseous fluorine and hydrocarbon carrier, such as nitrogen, a mixing system that rapidly and intimately brings the two reactants into contact, and a reactor design that effectively removes the heat of reaction. Under these conditions, hydrocarbons can be fluorinated to their corresponding fluorides:

$$CH_4 + 4F_2 \rightarrow CF_4 + 4HF$$

Dilute fluorine reacts with metal carbides such as UC_2, ThC_2, and CaC_2, producing fluorocarbons and metal fluorides. All these direct fluorination reactions are accompanied with high-energy type of condensation reactions where fluorocarbons of higher carbon chain length are formed. Miller[1] claims the use of elemental fluorine as a condensing agent in liquid-phase reactions to form higher-molecular-weight compounds.

Liquid-phase fluorinations have been demonstrated on a number of compounds, but the hazards of violent detonations and the wide diversity of products so far have limited the use of these procedures.

Fluorine reacts with graphite under a variety of conditions to form solids other than the usual C_nF_{2n+2} structure. Carbon tetrafluoride can also be produced if the temperature is high.

HF *as a Fluorinating Agent.* Hydrogen fluoride adds in vapor phase by means of catalysts to acetylene:[2]

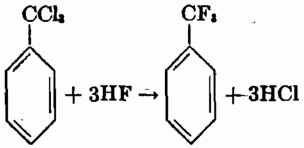
$$CH{\equiv}CH + HF \xrightarrow[\Delta]{\text{catalyst}} CHF{=}CH_2$$

$$CH{\equiv}CH + 2HF \xrightarrow[\Delta]{\text{catalyst}} CHF_2CH_3$$

Hydrogen fluoride may also replace chlorine in aliphatic chlorofluorocarbons, liberating hydrogen chloride:

$$R_2CClCF_2R + HF \xrightarrow[\Delta]{\text{catalyst}} R_2CFCF_2R + HCl$$

Hydrogen fluoride in a liquid-phase reaction readily replaces chlorine in many organic compounds:



Fluorination with Metal Fluorides. The majority of organic fluorides produced today are still made by the antimony halide process, starting with hydrogen fluoride and antimony pentachloride:

$$CCl_4 + 2HF + Cl_2 \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl + Cl_2$$

$$CCl_4 + 3HF + Cl_2 \xrightarrow{SbCl_5} CClF_3 + 3HCl + Cl_2$$

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[1] U.S. 2,716,141 (1955).

[2] U.S. 2,462,359 (1949); 2,471,525 (1949); 2,401,850 (1946); 2,716,143 (1955).

The reaction proceeds through the antimony pentahalide salts, with the major reactants believed to be a mixture of $SbCl_2F_3$ and more highly fluorinated halides[1] including SbF_5.

A number of the polyvalent metal fluorides are excellent fluorinating agents and are used in commercial reactions. Their use is limited by their high cost, as they usually are regenerated by reaction with elemental fluorine. Antimony pentafluoride, silver difluoride, lead tetrafluoride, manganic trifluoride, and cobalt trifluoride are examples of these commonly used salts.

$$2CoF_2 + F_2 \xrightarrow{200\text{–}350°C} 2CoF_3$$

$$2CoF_3 + CF_2{=}CClF \xrightarrow{100\text{–}350°C} CF_3CClF_2 + 2CoF_2$$

$$2_nCoF_3 + (CH_2CH_2)_n \xrightarrow{275\text{–}350°C} (CF_2CF_2)_n + 2_nCoF_2 + 4_nHF$$

Electrochemical Process. The preparation of a great number of fully fluorinated compounds by introducing starting products such as acids, amines, hydrocarbons, nitriles, and alcohols into cool anhydrous hydrogen fluoride in an electrolytic cell under about 5 volts potential is a very ingenious economical means for many of these products. This process is limited to saturated perfluoro compounds. Nonelectrolyte raw materials complicate this operation.

Interhalogen Fluorination. The use of halogen fluorides as a means of fluorination has been of military importance since their manufacture in World War II as potential incendiary agents. They have also been used as sources of high-energy fuel for rocketry. At low to moderate temperatures, reaction results in the addition of fluorine to the double bond or the substitution of hydrogen or other halogen. At flame temperature the end products[2] will be mainly CO, CO_2, HF, F_2, or O_2.

Fluorination with Alkali Metal Fluorides. Sodium and potassium fluorides react with alkyl hydrogen sulfates and with acid chlorides to produce organic fluorides:

$$RHSO_4 + NaF \rightarrow RF + NaHSO_4$$

Methyl and ethyl fluorides may be produced in this manner.

$$RCOCl + KF \rightarrow RCOF + KCl$$

Diazo Reactions. Aromatic diazo compounds react with hydrogen fluoride and boron trifluoride to form aromatic fluorides with the liberation of nitrogen.

$$RN{=}NCl + HF \rightarrow RF + HCl + N_2$$

$$RN{=}NBF_4 \overset{\Delta}{\rightarrow} RF + N_2 + BF_3$$

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[1] U.S. 2,410,358 (1946).

[2] ALTMAN and FARBER, Basic Research on Rocket Propellants, *Armed Services Technical Information Agency Progress Rept.* 9-26.

These are still the best methods of obtaining ring-fluorinated aromatic compounds.

II. THERMODYNAMICS AND KINETICS OF HALOGENATION REACTIONS

Many reactions of halogens with organic compounds are recorded in the literature, and some of them are utilized in commercial processes. The great variety of results reported for a wide variety of conditions precludes a complete, clear interpretation of these phenomena, but an analysis of some of the results and application of some theoretical considerations will throw light on the subject.

In order to analyze experimental results on chemical reactions, a clear separation of equilibrium and reaction-rate effects must be made. Sometimes equilibrium determines the product observed, and sometimes rate of reaction does. In the consideration of both equilibrium and reaction rates, reference to the "bond energies" of the chemical bonds involved is frequently helpful; some pertinent bond energies are given in Table 6-1.

TABLE 6-1. BOND ENERGIES AT 25°C IN KILOCALORIES

Type of bond	F	Cl	Br	I
X—X	63.5[1]	57.8	46.1	36.3
H—X	147.6	102.9	87.4	71.6
C—X	103.8	66.6	53.0	38.7

C—C	56.2	I—Br	42.9
C=C	95.8	I—Cl	51.0
C≡C	124.5	Br—Cl	52.7
C—H	87.7	Cl—F	86.4
H—H	103.8		

[1] Recent work may indicate a much lower value; DOESCHER, *J. Chem. Phys.*, **20**, 330 (1952), claims 37 k cal.

The heat of a reaction is given approximately by the sum of the energies of the bonds formed minus the sum of the energies of the bonds broken. The ΔH of reaction is the negative of this.

Thermodynamics of Halogenation Reactions[1]

Substitution Halogenation. A survey of the thermodynamics of substitution halogenation reactions shows that ΔH (change in heat content) is

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[1] The symbols used here are in accord with Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923, where ΔH = change in heat content, ΔS = change in entropy, and ΔF = change in free energy.

extremely exothermic in the case of fluorine, highly exothermic for chlorine, moderately exothermic for bromine, and endothermic for iodine and that ΔS is very small in all cases. The equilibrium is in favor of the right-hand side of the reaction at all temperatures for fluorine, chlorine, and bromine but in favor of the left-hand side at all temperatures for iodine. These deductions are illustrated by data on the following reactions at 25°C, in which all reactants and products are in the gaseous state at 1 atm.

	Kg-cal G Mole Halogen
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	−24.3
$CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$	−24.0
$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$	−23.7
$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$	−24.0
$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$	−24.1
$C_2H_6 + 6Cl_2 \rightarrow C_2Cl_6 + 6HCl$	−24.9
$C_6H_{14} + Cl_2 \rightarrow C_6H_{13}Cl + HCl$	−33.4
$CH_4 + Br_2 \rightarrow CH_3Br + HBr$	−6.4
$CH_4 + I_2 \rightarrow CH_3I + HI$	+10.4
$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$	−31.4
$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$	−29.7
$C_6H_4Cl_2 + Cl_2 \rightarrow C_6H_3Cl_3 + HCl$	−29.3
$C_6H_3Cl_3 + Cl_2 \rightarrow C_6H_2Cl_4 + HCl$	−27.5

The ΔH of chlorination of aliphatic compounds tends to increase with the chain length and the possibility of substitution in other than the primary position.

Addition Halogenation. A survey of the thermodynamics of the addition of halogens to double bonds shows that ΔH is highly exothermic for all the halogens and $\Delta S°$ is of the order of −20 cal per mole deg, since there is a change of negative one in the number of molecules. $\Delta F°$ is therefore negative, and equilibrium is in favor of the right-hand side of the reaction at all temperatures up to about 1000°C for Cl, up to about 700°C for Br, and up to about 50°C for I. These conclusions are illustrated by the accompanying reactions, in which the data are for the same conditions as given above.

	Kg-cal G Mole Halogen
$C_2H_4 + Cl_2 \rightarrow CH_2ClCH_2Cl$	−43.8
$C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$	−32.0
$C_2H_4 + I_2 \rightarrow CH_2ICH_2I$	−9.6
$C_2H_2Cl_2 + Cl_2 \rightarrow C_2H_2Cl_4$	−37.8
$C_2HCl_3 + Cl_2 \rightarrow C_2HCl_5$	−34.0
$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_6$	−32.0

A surprising trend was noted in vapor-phase heats of chlorination determined at 90°C on fluorine-containing olefins.[1]

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[1] Studies on Organic Fluorine Compounds III, Lacher et al., *A.S.T.I.A.*, *A.D.* 75655.

	Kg-cal G Mole Cl_2
$C_2F_4 + Cl_2 \rightarrow CClF_2CClF_2$	-57.3
$C_2ClF_3 + Cl_2 \rightarrow CClF_2CCl_2F$	-48.8
$C_2Cl_2F_2 + Cl_2 \rightarrow CClF_2CCl_3$	-41.0

Hydrohalogenation-Dehydrohalogenation. A survey of the thermodynamics of this type of reaction shows that ΔH is highly endothermic in all cases (for the dehydrohalogenation reactions as written below) and ΔS° is of the order of $+30$ cal per mole deg, since there is a change of positive one in the number of molecules. ΔF° is therefore negative, and equilibrium is in favor of dehydrohalogenation at all temperatures above about 250°C for Cl and above about 200°C for Br and I. These deductions are illustrated by the following reactions in which the data are for the same conditions as given above.

	Kg-cal G Mole Halogen
$C_2H_5Cl \rightarrow C_2H_4 + HCl$	$\Delta H = +16.2$
$CH_2ClCH_2Cl \rightarrow C_2H_3Cl + HCl$	$\Delta H = +16.2$
$C_2H_5Br \rightarrow C_2H_4 + HBr$	$\Delta H = +14.2$
$C_2H_5I \rightarrow C_2H_4 + HI$	$\Delta H = +14.0$

This equilibrium is quite important in determining the results of chlorination, particularly since chlorine is a powerful homogeneous catalyst for the dehydrochlorination reaction. Some experimental results on chlorination of ethylene and vinyl chloride given in a later section agree with this equilibrium picture. This discussion has not included reactions for the type $C_2H_3Cl \rightarrow C_2H_2 + HCl$, which would probably have quite different thermodynamics, since triple bonds are involved.

Reduction of Chlorinated Hydrocarbons. Vapor-phase heats of reduction of chlorinated aliphatic compounds with hydrogen have been determined[1] and calculated at 25°C.

	Kg-cal G Mole Cl_2
$CH_3Cl + H_2 \rightarrow CH_4 + HCl$	-19.3
$C_2H_5Cl + H_2 \rightarrow C_2H_6 + HCl$	-16.6
$C_2H_3Cl + 2H_2 \rightarrow C_2H_6 + HCl$	-51.2
$CH_2{=}CHCl + H_2 \rightarrow C_2H_5Cl$	-34.5
$CH_2{=}CH_2 + HCl \rightarrow C_2H_5Cl$	-16.2

Mechanisms and Kinetics of Halogenation Reactions

The rate of a chemical reaction is determined primarily by the magnitude of the activation energy. This quantity is related to the rate of reaction by the relations

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[1] LACHER et al., Reaction Heats of Organic Compounds IV, AEC Contract AT (11-1) -168.

$$k = se^{-A/RT}$$

or

$$\frac{d \ln k}{dT} = \frac{A}{RT^2}$$

where k is the specific reaction rate constant, A is the activation energy, and s is a proportionality constant which has only a small temperature variation. The lower the magnitude of A, the faster a reaction will be. Owing to the exponential effect, one reaction will predominate over another if its activation energy is only 1 kg-cal lower than that of a competing reaction, provided that their s factors are of comparable magnitude.

A is a complex function of the energies of bonds broken and formed in the reaction, so that, for most reactions, A is an experimental quantity only. However, in reactions in which one of the reactants is a free atom or a free radical, A can be estimated approximately from bond energies. Furthermore, A can be calculated for some more complex reactions by the methods of quantum mechanics, but the method is very laborious, and the results are subject to considerable error because of necessarily rough approximations.

The mechanisms and rates discussed in this section apply primarily to homogeneous, noncatalytic thermal gas-phase reactions. However, the effect of homogeneous and heterogeneous catalysts and of irradiation will be mentioned in some cases. Many of the ideas discussed apply also to liquid-phase reactions, depending on the solvent.

The reactions of halogens with organic compounds, especially hydrocarbons, have some analogies to the simpler reactions of halogens with hydrogen, which will therefore be discussed briefly first.

Reactions of the Halogens with Hydrogen. Two possible mechanisms suggest themselves:

$$\text{I.} \quad H_2 + X_2 \rightarrow 2HX \qquad (1)$$

$$\text{II.} \begin{cases} \tfrac{1}{2}X_2 \rightarrow X & (2) \\ X + H_2 \rightarrow HX + H & (3) \\ H + X_2 \rightarrow HX + X & (4) \\ \text{etc.} \end{cases}$$

Mechanism I involves simply bimolecular collisions between the two species of reacting molecules. Mechanism II is a chain reaction initiated by halogen atoms from partial dissociation of halogen molecules. The activation energy of mechanism I can be calculated only by laborious methods of quantum mechanics or determined experimentally in case that is the actual mechanism of the reaction. The over-all activation energy of mechanism II is given by the heat absorbed by reaction (2) plus the activation energy of reaction (3). The activation energy of atomic reactions, such as (3) and (4), is nearly zero if the reaction is exothermic and is approximately equal to the heat of reaction if the reaction is endothermic. The required heat of reaction can be estimated from the difference in bond energies of bonds formed and broken. Reaction (4) does not enter into the calculation of the activation energy, since such reactions involving atomic hydrogen are always exothermic and therefore fast.

Table 6-2 gives some activation energies calculated by quantum mechanics by Eyring for the bimolecular reactions (except iodine) and by the bond-energy method for the atomic reactions of type (3).[1] These calculated activation energies are in good accord with experimental evidence. Table 6-2 predicts that the reactions of F, Cl, and Br with hydrogen will be chain reactions rather than bimolecular reactions, whereas the reaction with I will be a bimolecular reaction. These are known to be true from the kinetic equations found experimentally for these reactions and from the effect of surfaces and of oxygen on the reactions with Cl and Br. Morris and Pease have deduced from experimental data activation energies of 6.0, 17.7, and 33 kg-cal for reactions (3) for Cl, Br, and I, respectively.[2] These values give 34.5, 40.3, and 50.7 for the activation energies of the over-all reactions, respectively, which compare very well with the figures in Table 6-2. A more complete analysis would have to take into account the rates of the back reactions, but this is usually a minor factor.

TABLE 6-2. CALCULATED ACTIVATION ENERGIES FOR REACTIONS OF HALOGENS WITH HYDROGEN IN KILOCALORIES*

		F	Cl	Br	I
I.	$H_2 + X_2 \rightarrow 2HX$	79	75	62	40†
II.	$\frac{1}{2}X_2 \rightarrow X$ (ΔH_0)	31.3	28.5	22.6	17.7
	$X + H_2 \rightarrow HX + H$	0(exo)	0.9	16.4	32.2
	Sum = A (over-all)	31.3	29.4	39.0	49.9

* EYRING, *J. Am. Chem. Soc.*, **53**, 2537 (1931).

† Experimental value from BODENSTEIN, *Z. physik. Chem.*, **29**, 295 (1898).

These activation energies apply only to the noncatalytic thermal reactions. The reactions with Cl and Br (and probably with F, too) proceed more rapidly under the influence of light or if catalyzed by H, Na, or K atoms.

The noncatalytic homogeneous combination of H_2 and F_2 would not be expected to proceed at room temperature or below, since an activation energy of 31.3 kg-cal corresponds to a measurable reaction rate only above about 100°C. Eyring and Kassel experimentally confirmed the nonre-

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[1] EYRING, *J. Am. Chem. Soc.*, **53**, 2537 (1931).

[2] MORRIS and PEASE, *J. Chem. Phys.*, **3**, 796 (1935).

activity of mixtures of H_2 and F_2 at ordinary temperatures and showed that the explosive reactions sometimes observed were probably due to surface catalysis.[1]

The reaction between H_2 and I_2 is one of the best-known bimolecular reactions and was studied extensively by Bodenstein in the temperature range of 200–500°C.[2]

Substitution Halogenation. One might expect mechanisms analogous to those for the reactions with hydrogen. Three possible mechanisms, using methane as an example, would be

$$\text{I.}\quad CH_4 + X_2 \rightarrow CH_3X + HX \qquad (5)$$

$$\text{II.}\quad \begin{cases} \tfrac{1}{2}X_2 \rightarrow X & (6) \\ X + CH_4 \rightarrow CH_3X + H & (7) \\ H + X_2 \rightarrow HX + X & (8) \\ \text{etc.} & \end{cases}$$

$$\text{III.}\quad \begin{cases} \tfrac{1}{2}X_2 \rightarrow X & (9) \\ X + CH_4 \rightarrow HX + CH_3 & (10) \\ CH_3 + X_2 \rightarrow CH_3X + X & (11) \\ \text{etc.} & \end{cases}$$

The activation energies for the bimolecular mechanism have never been calculated; but in the case of chlorine and bromine, at least, it is known that the reaction is a chain reaction because of the inhibitory effect of oxygen. Table 6-3 gives the activation energies for the two possible chain mechanisms calculated by the bond-energy method. Reactions of types (8) and (11) are always exothermic and therefore fast.

TABLE 6-3. CALCULATED ACTIVATION ENERGIES FOR REACTIONS OF HALOGENS WITH METHANE IN KILOCALORIES

			F	Cl	Br	I
II	$\tfrac{1}{2}X_2 \rightarrow X$	(ΔH_0)	31.3	28.5	22.6	17.7
	$X + CH_4 \rightarrow CH_3X + H$		0(exo)	21.1	34.7	49.0
	Sum = A (over-all)		31.3	49.6	57.3	66.7
III	$\tfrac{1}{2}X_2 \rightarrow X$	(ΔH_0)	31.3	28.5	22.6	17.7
	$X + CH_4 \rightarrow CH_3 + HX$		0(exo)	0(exo)	0.3	16.1
	Sum = A (over-all)		31.3	28.5	22.9	33.8

These figures indicate that the reactions with Cl and Br probably follow mechanism III; the reaction with F may follow either mechanism II or III (but probably not mechanism I by analogy with the hydrogen reactions); and the reaction with I may follow either mechanism I or III. Pease and Walz found the experimental activation energy of the chlorination of meth-

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[1] EYRING and KASSEL, *J. Am. Chem. Soc.*, **55**, 2796 (1933).

[2] BODENSTEIN, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1898).

ane to be 31.6 kg-cal, which compares well with 28.5 kg-cal given in Table 6-3.[1] The chain mechanism for Cl is confirmed by the strong inhibitory effect of oxygen.

The chlorination of paraffins is promoted by light and catalyzed by H, Na, and K atoms just as is the reaction with hydrogen. In addition, it is catalyzed by lead tetraalkyls or other source of free alkyl radicals that initiate chains.

The substitution halogenation of olefins (i.e., substitution of hydrogens on olefinic carbons only) would be expected to proceed by the same mechanisms as the halogenation of paraffins; and from the simple bond-energy point of view, the activation energies would be expected to be about the same in the two cases. However, Sherman, Quimby, and Sutherland have calculated the activation energies for the substitution halogenation of ethylene by quantum mechanics with the following results (in kilocalories):[2]

Reaction	Cl	Br	I
Bimolecular	43.4	46.0	51.2
Chain	45.0	47.0	54.0

Unfortunately these differences are not sufficiently large to say which is probably the true mechanism, in view of the uncertainties in the method of calculation. However, it is interesting to note that, regardless of the mechanism, they are all much higher than the corresponding activation energies for the halogenation of methane, indicating that the substitution halogenation of ethylene should be much slower than that of methane and other paraffins. This is indeed the case, as will be discussed below.

Addition Halogenation. Two possible mechanisms for this type of reaction, using ethylene as an example, would be

$$\text{I.}\quad C_2H_4 + X_2 \rightarrow CH_2XCH_2X \qquad (12)$$

$$\text{II.}\quad \begin{cases} \tfrac{1}{2}X_2 \rightarrow X & (13)\\ X + C_2H_4 \rightarrow CH_2CH_2X & (14)\\ CH_2CH_2X + X_2 \rightarrow CH_2XCH_2X + X & (15)\\ \text{etc.} \end{cases}$$

Mechanism I is a simple bimolecular mechanism, whereas mechanism II is a chain reaction. Still a third over-all reaction is possible, $C_2H_4 + X_2 \rightarrow CH_3CHX_2$, but this involves a molecular rearrangement, and no reasonable mechanism can be deduced for it. Calculation of the activation energies of mechanisms I and II have been made by Sherman, Quimby, and Sutherland with the following results (in kilocalories):

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[1] Pease and Walz, *J. Am. Chem. Soc.*, **53**, 3728 (1931).

[2] Sherman, Quimby, and Sutherland, *J. Chem. Phys.*, **4**, 732 (1936).

Reaction	Cl	Br	I
Bimolecular	25.2	24.4	22.4
Chain	28.5	22.6	20.5

Again, these values are too close together to draw any conclusions, in view of the possible errors in the calculations. The fact that oxygen has a strong inhibitory effect on the chlorination of ethylene indicates that it is probably a chain reaction. However, the activation energy for either mechanism is much lower than that for the corresponding substitution halogenation of ethylene, so that addition on ethylene would be expected to be much faster than substitution. This is confirmed by experimental results, as will be discussed below.

Hydrochlorination-Dehydrochlorination. Activation energies have never been measured or calculated for the simplest reactions of this type involving ethylene and ethyl chloride. However, Sherman, Quimby, and Sutherland have calculated activation energies for the following reactions:

$$CH_2XCH_2X \rightarrow C_2H_3X + HX \quad (16)$$

$$C_2H_3X + HX \rightarrow CH_2XCH_2X \quad (17)$$

which lead to some interesting conclusions.

Considering first reaction (16), they calculated activation energies as follows (in kilocalories):

Reaction	Cl	Br	I
Unimolecular	75.7	68.3	64.2
Chain, catalyzed by X_2	57.0	46.0	51.2

These values probably have little meaning in absolute magnitude; but in a relative sense they show that the X_2-catalyzed chain reaction should be much faster than the unimolecular thermal decomposition. This prediction is confirmed by the observed catalytic effect of chlorine in promoting dehydrochlorination. Mugdan and Barton reported dehydrochlorination of ethylene dichloride to vinyl chloride and HCl in the presence of ½ per cent chlorine as 30 per cent at 300°C, 50 per cent at 350°C, and 70 per cent at 370°C for a flow rate of 38 g per hr through a 600-mm length of hot zone.[1] In the absence of chlorine, there was only 2 per cent dehydrochlorination at 400°C and 30 per cent at 500°C with the same experimental setup. The mechanism used by Sherman, Quimby, and Sutherland for this catalyzed chain reaction was as follows:

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[1] U.S. 2,378,859 (1945).

$$\tfrac{1}{2}X_2 \rightarrow X \qquad (18)$$

$$X + CH_2XCH_2X \rightarrow CHXCH_2X + HX \qquad (19)$$

$$CHXCH_2X \rightarrow C_2H_3X + X \qquad (20)$$

etc.

Considering now reaction (17), Sherman, Quimby, and Sutherland calculated activation energies as follows (in kilocalories):

Reaction	Cl	Br	I
Bimolecular	43.5	41.9	36.4
Chain	39.3	29.0	27.0

The activation energies of the chain reactions are clearly lower, and their relative values are in agreement with the experimental fact that HBr and HI add to ethylene readily whereas HCl does so much more slowly, except in the presence of a catalyst such as $FeCl_3$.

Chlorination of Hydrocarbons and Chlorohydrocarbons

The published knowledge under this heading is well summarized in three papers and several patents by Vaughan and Rust.[1] Certain data extracted from these papers and patents are summarized in Tables 6-4 and 6-5. These data are rather fragmentary and represent comparable rate data only in a rough way. Nevertheless, intercomparison of these figures leads to some interesting conclusions:

1. *The rate of substitution chlorination of hydrogens on saturated carbons is greater than the rate of substitution of hydrogens on unsaturated carbons.* This conclusion is evident from a comparison of ethane and propane with ethylene and vinyl chloride. In fact, the rate of substitution on paraffins is greater than the rate of substitution plus addition on unsaturates. The difference in rate is such that, in the chlorination of mixtures of paraffins and olefins, substitution on paraffins (or on saturated carbons in olefins) is the predominant reaction, particularly above 300°C. This is illustrated by the chlorination of a mixture of 1 mole Cl_2:1 mole C_2H_6:1 mole C_2H_4:3 moles N_2 at 314°C at a total flow rate of 300 cc per min, which gave a product 67.8 mole per cent ethyl chloride, 22.6 per cent 1,1-dichloroethane, 3.6 per cent vinyl chloride, 2.5 per cent 1,2-dichloroethane, 2.2 per cent 1,1,1-trichloroethane, 1.3 per cent heavier products. Another illustration is the technically important chlorination of propylene at temperatures of 350°C and up, which gives a high yield of allyl chloride. Quantitatively,

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[1] Vaughan and Rust, *J. Org. Chem.*, **5**, 449 (1940); Rust and Vaughan, *ibid.*, **5**, 472 (1940); **6**, 479 (1941); U.S. 2,246,082; 2,249,922 (1941); 2,278,527; 2,284,479; 2,284,482; 2,299,441 (1942).

TABLE 6-4. DATA ON CHLORINATION OF HYDROCARBONS AND CHLOROHYDROCARBONS*

	240°C	280°C	320°C	360°C	400°C
Ethane	19	85	95		
Propane	18	97			
To 1-chloropropane	9				
To 2-chloropropane	9				
Ethylene	11	60	..	Large	Large
Substitution	1	8	..	Large	Large
Addition	10	52	..	Small	Small
Propylene	26	80	..	Large	Large
Substitution	10	50	..	Large	Large
Addition	16	30	..	Small	Small
Ethyl chloride	7	26	59	96	100
To 1, 1-dichloroethane	..	..	47		
To 1, 2-dichloroethane	..	..	12		
Vinyl chloride	12	47	72	84	90
Substitution	0	1	19	54	84
Addition	12	46	53	30	6

* Figures are percentage of Cl_2 reacted for mixture 1 mole Cl_2: 2 moles reactant: 3 moles N_2 or CO_2 at total flow rate of 300 cc per min.

it may be noted that the total rate of substitution of the paraffinic portion of propylene (three hydrogens) is about one-half the rate of substitution of ethane (six hydrogens).

TABLE 6-5. DATA ON CHLORINATION OF PROPYL AND BUTYL CHLORIDES*

	200–208°C	260°C	312–319°C	340°C	380–383°C
n-Propyl chloride:					
To 1, 1-dichloropropane	..	14	..	6	34
To 1, 2-dichloropropane	..	24	.	4	0
To 1, 3-dichloropropane	..	14	..	7	36
Isopropyl chloride:					
To 1, 2-dichloropropane	40	..	22	..	21
To 2, 2-dichloropropane	50	..	32	..	64
n-Butyl chloride:					
To 1, 1-dichlorobutane	15	..	17	..	10
To 1, 2-dichlorobutane	14	..	0	..	0
To 1, 3-dichlorobutane	59	..	43	..	23
To 1, 4-dichlorobutane	40	..	38	..	17
sec-Butyl chloride					
To 1, 2-dichlorobutane	0	..	0	..	0
To 1, 3-dichlorobutane	31	..	33	..	32
To 2, 2-dichlorobutane	19	..	22	..	22
To 2, 3-dichlorobutane	30	..	16	..	0

* Figures are grams of product recovered in particular experiments.

Conclusion 1 was predicted by the calculated activation energies of Sherman, Quimby, and Sutherland despite the large errors possible in the quantum mechanical methods used. They calculated activation energies of about 30 and 45 kg-cal, respectively, for the substitution chlorination of paraffinic and olefinic hydrogens.

2. *The rate of substitution chlorination of hydrogens on saturated carbons is greater than the rate of addition chlorination to double bonds at high temperatures; the reverse is true at low temperatures.* See the discussion under conclusion 1. The calculated activation energies for the two reactions are 28.5 and 25.2 kg-cal, respectively, but these calculated values are too close together to draw valid conclusions.

3. *The rate of addition chlorination on double bonds is greater than the rate of substitution of hydrogens on unsaturated carbons.* This is certainly true at temperatures around 240–280°C, as shown by the data for ethylene and vinyl chloride in Table 6-4. It may also be true at higher temperatures, despite the data in Table 6-4, since the substituted products that predominate at higher temperatures may be formed by addition of chlorine followed by a rapid dehydrochlorination to reach or approach equilibrium. The relative amounts of substitution and addition products as a function of temperature given in Table 6-4 are approximately the equilibrium amounts for this reaction.

The theoretically calculated activation energies, 25.2 kg-cal for addition chlorination and 43.4 kg-cal for substitution of ethylenic hydrogens, are in agreement with conclusion 3.

4. *The rate of substitution of hydrogens α to a chlorine is about the same as the normal rate of substitution of hydrogens on the type of carbon atom concerned.* The rate of substitution of ethyl chloride (largely on the 1-carbon atom) at 260 and 280°C is about one-third the rate of substitution of ethane, which has six equivalent hydrogen atoms.

5. *The rate of substitution of hydrogens β to a chlorine is markedly less than the normal rate of substitution of hydrogens on the type of carbon atom concerned.* Compare the results of chlorination of propyl and butyl chlorides in Table 6-5, giving proper weight to the relative rates of substitution of hydrogens on primary and secondary carbon atoms. This effect is more pronounced with increasing temperature so that the amounts of 1,2-dichloropropane, 1,2-dichlorobutane, and 2,3-dichlorobutane decrease relative to the 1,1;2,2; and 1,3 types of compounds with increasing temperature.

6. *The rate of substitution of hydrogens γ to a chlorine is only slightly less than the normal rate of substitution of hydrogens on the type of carbon atom concerned. For hydrogens δ and farther removed from a chlorine, the rate of substitution is the normal one.* Compare the amounts of 1,3-dichloropropane, 1,3-dichlorobutane, and 1,4-dichlorobutane obtained, giving proper

weight to the relative rates of substitution of hydrogens on primary and secondary carbon atoms.

A number of other interesting semiquantitative deductions can be drawn from the above data, which will be left to the reader. There do not appear to be any theoretical considerations bearing on conclusions 4, 5, and 6.

The substitution chlorination of hydrocarbons in the presence of oxygen to give greater yields of chlorinated product for a given consumption of Cl_2 reported by Cass is an equilibrium effect in the oxidation of HCl to Cl_2 according to the Deacon reaction.[1] Equilibrium is in favor of Cl_2 in the Deacon reaction at all temperatures below about 600°C. This reaction must be carried out at a sufficiently high temperature to overcome the inhibitory effect of oxygen on the substitution reaction but yet low enough to have favorable equilibrium in the Deacon oxidation reaction.

III. SURVEY OF HALOGENATIONS

CHLORINATION

It is difficult to overestimate the economic importance of the compounds obtained by the halogenation of the saturated and unsaturated lower paraffins. To a considerable extent, these halogen derivatives are used per se as cleaning fluids ($CHCl{=}CCl_2$), refrigerants (CCl_2F_2), anesthetics ($CHCl_3$), general solvents (CCl_4), etc. By and large, however, the saturated and unsaturated halogeno paraffins are used as the raw materials for an exceedingly large number of syntheses, e.g., the preparation of alcohols, alkylene oxides, ethers, amines, hydrocarbons, alkaryl compounds, etc. Because the paraffinic hydrocarbons and chlorine are widely available and cheap, this segment of chemical activity has increased greatly in recent years and is destined to expand further.

Halogenation with Chlorine Gas

Chlorination Rules: Paraffins. On the basis of extensive research, Hass and coworkers have postulated the following rules regarding the chlorination of paraffins.[2] Such operations can be carried out in the apparatus shown diagrammatically in Fig. 6-5.

1. Carbon skeleton rearrangements do not occur during either photochemical or thermal chlorinations if pyrolysis temperatures are avoided. Every possible monochloride derivative without such rearrangement is always formed. As far as is known, this generalization extends also to the polychlorides.

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[1] U.S. 2,327,174 (1943).

[2] HASS and MARSHALL, *Ind. Eng. Chem.*, **23**, 352 (1931); HASS, MCBEE, and WEBER, *ibid.*, 27, 1190 (1935); **28**, 333 (1936); HASS and WEBER, *Ind. Eng. Chem., Anal. Ed.*, 7, 231 (1935); HASS, MCBEE, and HATCH, *Ind. Eng. Chem.*, **29**, 1335 (1937).

2. The hydrogen atoms are usually substituted at rates that are in the order primary < secondary < tertiary. In applying this rule, conditions must be selected so that pyrolysis is substantially eliminated and only a very small amount of monochloride is carried to a higher state of chlorination.

3. At increasing temperatures, there is increasingly close approach to equal rates of substitution in both the liquid and vapor phase. Evidence for this generalization is given in Fig. 6-1, where the relative rates of secondary and tertiary hydrogen atoms are shown to vary with temperature in both vapor and liquid phases. The relative substitution rate of a primary hydrogen atom is taken as 1.

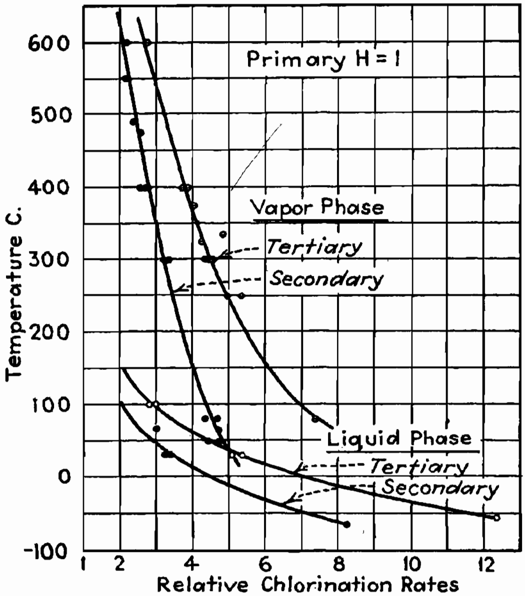


FIG. 6-1. Rule 3, halogenation.

By the use of these graphs, an approximation may be made of the isomeric monochloride compositions obtained by chlorination of a number of paraffin hydrocarbons.

Certain precautions must be observed in applying these curves. The different monochlorides may chlorinate to dichlorides, trichlorides, etc., at different rates. This would change their ratios in the monochloride fraction so that results are most accurate when not more than a small proportion of monochloride is converted to dichloride. This is the condition always used in commercial operations for obtaining monochlorides, for reasons of economy. At low temperatures, where substantially no olefin formation occurs, results are not complicated by selective pyrolysis; but when operating at temperatures above 300°C, one can easily get the impression that a nonselective chlorination is taking place, whereas actually the tertiary and/or secondary chlorides are being preferentially decomposed. When pyrolysis becomes appreciable, (1) the organic chlorine fails to balance the chlorine present as hydrochloric acid, (2) olefins appear in the recovered hydrocarbon, and (3) especially if recycling is used, chloroolefins appear in the organic chloride fractions.

4. Liquid-phase chlorination gives relative rates of primary, secondary, and tertiary substitution which are obtainable only at much higher temperature in vapor phase. This is obvious from an inspection of Fig. 6-1.

A given temperature change produces a much greater difference in relative reaction rates of primary, secondary, and tertiary hydrogens when one is operating in liquid phase than when the chlorination takes place in gaseous phase. This means that the isomeric ratios are much more readily controllable in liquid than in vapor phase. Maximum yields of either primary isomers (at high temperatures) or secondary or tertiary isomers (at low temperatures) can be obtained by operating with the reagents in liquid form. In case the critical temperature of the hydrocarbon is inconveniently low, the chlorination may be carried out using carbon tetrachloride as a solvent.

5. The presence or absence of the following factors does not affect appreciably the relative rates of primary, secondary, and tertiary substitution: (*a*) moisture, (*b*) carbon surfaces, and (*c*) light.

6. Excessive temperatures and/or reaction times result in appreciable pyrolysis of the chlorides in the order primary < secondary < tertiary.

This has already been commented on in connection with rule 3 in so far as excessive temperatures are concerned, but it may be added that the extent of the pyrolysis is more than would be predicted from data obtained by passing the pure chlorides through a hot reactor in the absence of chlorine. This result would be expected on the basis of free radical formation, since the radicals may decompose as follows:

$$C_nH_{2n+1} \rightarrow C_nH_{2n} + H$$

The free hydrogen atoms would continue the chlorination chain as follows:

$$H + Cl_2 \rightarrow HCl + Cl$$

Excessive polychloride formation is presumably caused by the following types of reactions:

$$C_5H_{11}Cl \rightarrow C_5H_{10} + HCl$$
$$C_5H_{10} + Cl_2 \rightarrow C_5H_{10}Cl_2$$
etc.

7. If a molar excess of hydrocarbon is used and the chlorination conditions are maintained constant, the yield of monochlorides versus polychlorides may be obtained from the equation

$$X = KY$$

where X = weight ratio of monochlorides over polychlorides
Y = ratio of moles of hydrocarbon over moles of chlorine
K = a constant peculiar to the hydrocarbon and the conditions

As evidence, Fig. 6-2 is presented. In applying this graph, conditions are chosen so that all the chlorine reacts.

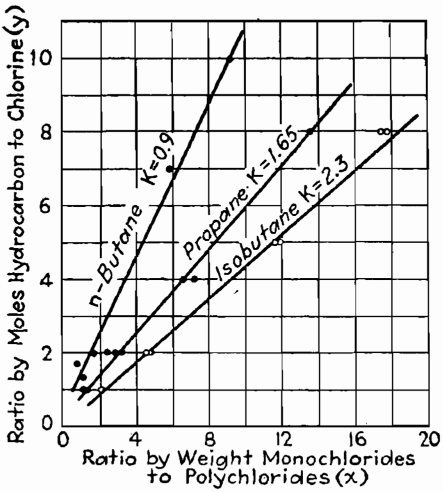


FIG. 6-2. Rule 7, halogenation.

The practical import of rule 7 is that the yield of overchlorinated material may be suppressed to any desired degree if only a small percentage of the material to be chlorinated is allowed to react at each pass through the chlorinator. This applies to any stage of chlorination. An economic balance must be struck between the advantages of the higher yields of monochlorides, which are caused by the lower chlorine concentrations in the reacting hydrocarbon, and the increased cost of additional recycling. When chlorination is achieved thermally, recycling involves the expense of heating and cooling large quantities of materials. In the case of the further thermal chlorination of the homologous alkyl chlorides, too many passes through the hot reactor may increase the amount of pyrolysis unduly, so that too much recycling is undesirable from that standpoint also.

One of the advantages of liquid-phase thermal chlorination is that, because of the lower temperatures involved, the pyrolysis is almost completely eliminated and the amount of heat put into the reacting materials and removed from the reaction products is lessened.

8. Dichlorination proceeds by two mechanisms: (*a*) loss of hydrogen chloride followed by addition of chlorine to the resulting olefin and (*b*) progressive substitution. Slow thermal chlorination favors mechanism 1, whereas with rapid liquid-phase or vapor-phase single-pass thermal reaction or low-temperature photochemical conditions, mechanism 1 is substantially eliminated.

In view of the large amount of work that has been performed on the addition of chlorine to olefin bonds, it is evident that conditions conducive to the formation of unsaturates must result in at least some union of chlorine with these products, unless the temperature is too high. Thus, a prolonged vapor-phase thermal chlorination of *n*-pentane at 100°C in the absence of light yields a much higher ratio of polychlorides to monochlorides than if the reaction is carried out rapidly at the same temperature in the presence of light. This is due to the pyrolysis of the secondary chlorides which, though very slow, is appreciable at this temperature, followed by saturation of the double bonds with chlorine.

Conclusive evidence that dichlorination occurs also by progressive substitution is available in the formation of large quantities of 1,3-disubstitution products which cannot be produced by the addition, under these conditions, of either hydrogen chloride or chlorine to any olefin or chloroolefin.

9. In vapor-phase chlorination, the presence of a chlorine atom on a carbon atom tends to hinder further reaction upon that carbon atom during the second substitution.

The data obtained in the dichlorination of propane and isobutane shows that only small amounts of dichlorides containing both chlorine atoms on the same carbon atom are found to be present. In the case of propane, the boiling points of the dichlorides are as follows: 2,2-dichloride, 69.7°C; 1,1-dichloride, 86°C; 1,2-dichloride, 96.8°C; 1,3-dichloride, 120.4°C. A rectification analysis is therefore conclusive and relatively easy.

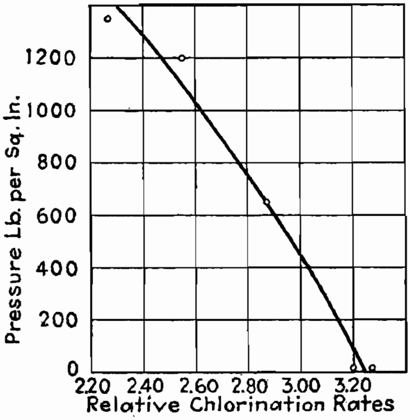


FIG. 6-3. Chlorination of propane, at 300°C. Effect of pressure on relative chlorination rates of primary and secondary hydrogen atoms.

10. In vapor-phase chlorination of saturated hydrocarbons, increased

pressure causes increased relative rates of primary substitution. The influence of pressure, in the chlorination of propane in the vapor phase, is shown by the curve of Fig. 6-3.

SUBSTITUTION REACTIONS

In a chain reaction, once a source of energy activating the chlorine has been applied, the rate of reaction of chlorine gas with vapors of paraffin hydrocarbons is a function of the molar composition of the mixture. Within certain limits this reaction will become so rapid that inflammation of the mixture will occur because of lack of heat dissipation, and within still narrower limits the flame velocity will increase into detonation rates. An approximate range for these limits of propane and chlorine is presented in Fig. 6-4.

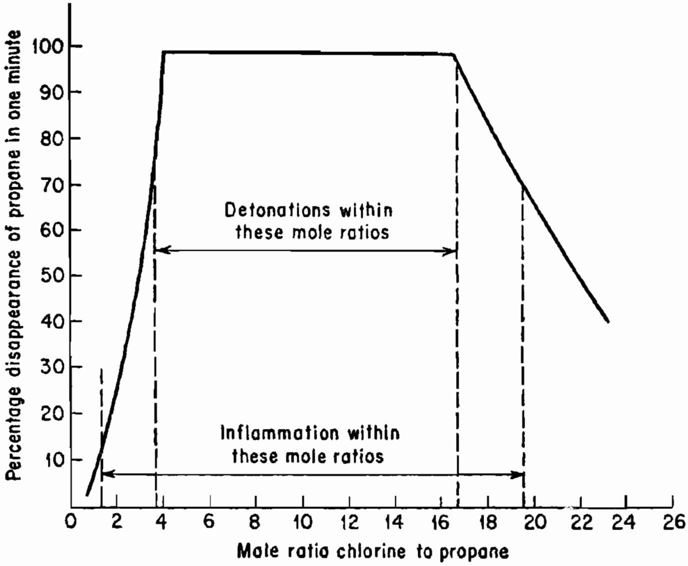


FIG. 6-4. Effect of mole ratio on rate of reaction of chlorine and propane.

Each hydrocarbon and partially halogenated hydrocarbon appears to have the same general type of reaction curve with a halogen. Once the safe working limits are clearly established, practical commercial processes can be designed and operated safely outside these hazardous conditions. This rule also applies to fluorine but is complicated by the ease with which molecular fluorine can be converted to a high-energy reaction state. Thus at the point of mixing of fluorine with the reactant, extreme care must be taken to ensure that, during the process of mixing, activated fluorine and the reactant do not contact each other in a proportion within the detonating range. The following are some of the methods proposed for moderating and controlling the reaction:

1. Employing a considerable excess of the hydrocarbon vapors.
2. Carrying out the reaction in the presence of diluent gases such as nitrogen, recycle gases, or the hydrogen halide that is liberated.
3. Introducing the reacting gases into a liquid cosolvent.
4. Employing a halogen gas that reacts mildly and then replacing the combined halogen with chlorine or fluorine.
5. Effecting halogenation in successive stages by mixing only part of the halide with the hydrocarbon.

Chlorination of Methane. The chlorination of methane can most economically be accomplished by treating a mixture of chlorine with an excess of the hydrocarbon at elevated temperatures. Actinic rays, iodine, activated carbon, and the chlorides of copper, iron, and antimony have been suggested as catalysts for this reaction, but the presence of a catalyst is not necessary.

In the thermal method, a close correlation between temperature and reaction time must be observed. Temperatures of approximately 300°F may be used at relatively long contact periods, whereas 0.01 sec is sufficient for operations at 800–850°F. The products of chlorination depend on the temperature and the chlorine ratio; but in all cases a mixture is obtained. It is possible, however, to control conditions to obtain a preponderance of one of the chloromethanes.

The thermal chlorination of methane is carried out on a large scale in this country by Dow Chemical Company, Diamond Alkali Company, and Allied Chemical & Dye Corporation, Solvay Process Division.[1] High-purity methane is mixed with cycle gas and then with chlorine and the mixture introduced into a packed reactor heated to 350–400°C, where chlorine is completely reacted in the excess of hydrocarbon and chlorinated hydrocarbon. The effluent gases contain excess methane and all the chlorinated methanes, which may be separated after condensation by fractional distillation.[2] When reaction temperatures are increased, a competing reaction develops with the formation of perchloroethylene.

$$2CCl_4 \rightarrow C_2Cl_4 + 2Cl_2$$

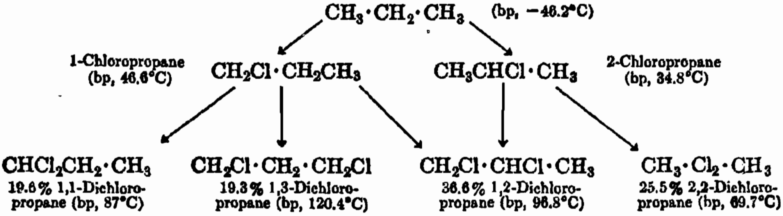
Chlorination of Ethane. Ethane may be chlorinated in the vapor phase either thermally as in the case of methane or by light activation. A mixture of mono- and polychlorides is produced. Ethyl chloride is pro-

[1] Economics, *Chem. Eng.*, **274,** September, 1955.

[2] Chlorinated Methanes, *Petroleum Refiner*, **21,** 11, 124 (1942).

duced commercially by the hydrochlorination of ethylene, the reaction of hydrogen chloride on ethyl alcohol, or the direct chlorination of ethane.

Chlorination of Propane. When propane is chlorinated under conditions that avoid excessive pyrolysis, every possible monochloride and polychloride derivable without carbon-skeleton rearrangement is always formed in accordance with Hass's rule.[1] According to this generalization, the chlorination of propane to the dichloride stage occurs according to the following diagram.[2]



The dichlorination may be carried out in apparatus shown diagrammatically in Fig. 6-5, at 150–250°C and preferably under superatmospheric pressures.[3]

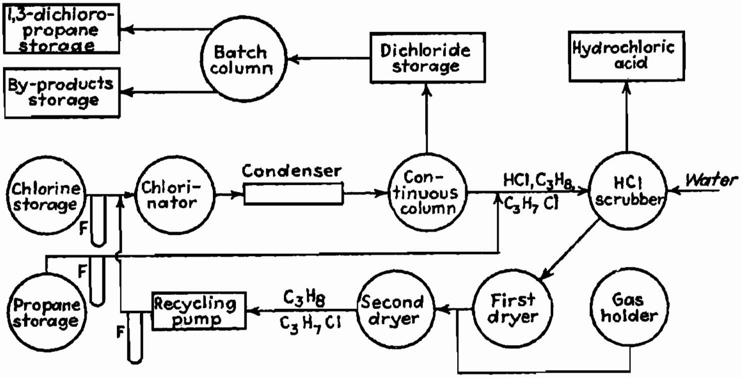


FIG. 6-5. Flow diagram, chlorination of propane.

By means of flowmeters (*F*), a molar excess of material to be chlorinated (propane and monochlorides) over chlorine, of approximately 10:1, is maintained in the gases flowing to the chlorinator. This excess, in combination with complete removal of dichlorides from the recycled gas by means of the continuous rectifying column, ensures a low concentration of

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[1] Hass, McBee, and Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935).

[2] Hass, McBee, and Hatch, *Ind. Eng. Chem.*, **28**, 1178 (1936).

[3] Hass and McBee, U.S. 2,105,733 (1938).

trichlorides in the crude dichloride mixture. The chlorine is allowed to react completely in the chlorinator, and the material flowing to the condenser and hence to the continuous rectifying column consists essentially of propane, both monochloropropanes, all four dichloropropanes, and hydrogen chloride. The effluent from the base of the continuous column consists of dichloropropanes with minor amounts of more highly chlorinated material. The hydrogen chloride, propane, and monochlorides pass up through the column in which a sufficient monochloride reflux is maintained to remove the dichlorides efficiently from the overhead product. The make-up propane is introduced immediately after the continuous column and assists in preventing condensation of monochlorides in the hydrochloric acid scrubber, in which the hydrogen chloride is removed.

The photochlorination of propanes to a mixture of polychloropropanes is accomplished by introducing chlorine and propane in separate streams in a light-activated chamber containing products of the reaction.[1] The composition of the products range from dichlorides up to octachlorides. This mixture is suitable for further chlorination to carbon tetrachloride and perchloroethylene by thermal or catalytic procedures. The over-all reaction is

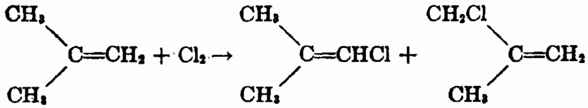
$$C_3H_8 + 8Cl_2 \rightarrow CCl_4 + C_2Cl_4 + 8HCl$$

Chlorobutanes. Chlorobutanes can be obtained by diverse procedures, such as (1) the liquid-phase or thermal chlorination of butane, (2) addition of chlorine or hydrogen chloride to butenes, (3) reaction of hydrochloric acid with butanols and butylene glycols, (4) chlorination of chlorobutenes and chlorobutadienes, and (5) hydrochlorination of tetramethylene oxide (tetrahydrofuran) and butadiene.

The thermal chlorination of butane is similar to that of propane and can be carried out according to the procedures developed by Hass and coworkers.[2] The product contains 1-chloro- and 2-chlorobutane as well as 1,2-dichloro- and 1,3-dichlorobutanes. In the photochemical chlorination, chlorine is introduced into a body of *n*-butane that is cooled to −25°.[3]

Butene-1 and butene-2 add chlorine in the presence of light at low temperatures to yield 1,2- and 2,3-dichlorobutanes, respectively.

Isobutylene, however, does not yield a saturated chloro derivative on chlorination but yields the two chlorobutenes:



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[1] McBee and Devaney, U.S. 2,473,161 (1949).

[2] Hass, McBee, and Weber, *op. cit.*, p. 1191; U.S. 2,105,733 (1938).

[3] Carter and Johnson, U.S. 2,381,037 (1945).

Reeve, Chambers, and Puckett[1] propose a two-step reaction, the first step involving addition of a positive chlorine to the center of high electron density of the olefin. Then the chloro tertiary butyl carbonium ion loses a proton to form the unsaturated methallyl chloride.

When a gas mixture containing 1.0 part by weight of *n*-butane and 0.53 part chlorine is passed at a uniform rate into a molten mixture of potassium chloride and aluminum chloride, the products are 20 per cent monochlorobutane, 29.2 per cent butylene, and 44 per cent unreacted butane.[2]

Chlorination of Cycloparaffins. Cyclohexyl chloride can be made by two general methods: (1) direct chlorination of cyclohexane in the presence or absence of light and (2) hydrochlorination of cyclohexanol. In batch operations, the method of direct chlorination ordinarily leads to the formation of a considerable proportion of polychlorocyclohexanes even when half of the stoichiometric quantity of chlorine is used.

According to the procedures developed by Levine and Cass, cyclohexane admixed with about 3 per cent anhydrous stannic chloride is subjected to the action of dry chlorine in the absence of light.[3] The chlorination is slow but smooth when the temperature is maintained at 40°C. A yield of 89 per cent monochlorocyclohexane and about 10 per cent dichlorocyclohexanes is obtained when 38 per cent of the chlorine necessary for complete halogenation is used. When the reaction is carried out in the presence of light in a lead-lined vessel, the reaction is more rapid. A yield of 82.5 per cent monochlorocyclohexane is obtained when 53 per cent of the chlorine necessary for complete monochlorination is introduced.

When cyclohexyl chloride is the desired product for use in the preparation of cyclohexylamine or for condensations according to the Friedel and Crafts reaction, it appears advantageous to chlorinate in the presence of light and to use at least a 10:1 molar ratio of cyclohexane to chlorine in a cyclic process.[4] The products of reaction are continuously withdrawn from the reaction chamber to a still (Fig. 6-6) where the unconverted cyclohexane is distilled off, condensed, and returned to the chlorinator which is provided with an encased battery of electric lights. The chlorinator, which is maintained at 55–65°C, is preferably made of lead, nickel, or Monel metal in order to provide better resistance against the corrosive action of the reaction products. A yield of about 94 per cent cyclohexyl chloride is thus obtained in batch operations when about half of the chlorine theoretically required to convert all the cyclohexane to cyclohexyl chloride has been reacted.

Chlorination of cyclohexane does not produce the 1,2,3,4,5,6-hexachloro-

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[1] REEVE, CHAMBERS, and PUCKETT, *J. Am. Chem. Soc.*, **74**, 5369 (1952).

[2] Kennedy and Russell, U.S. 2,224,155 (1940).

[3] Levine and Cass, U.S. 2,154,049 (1939).

[4] Britton and Perkins, U.S. 2,287,665 (1942).

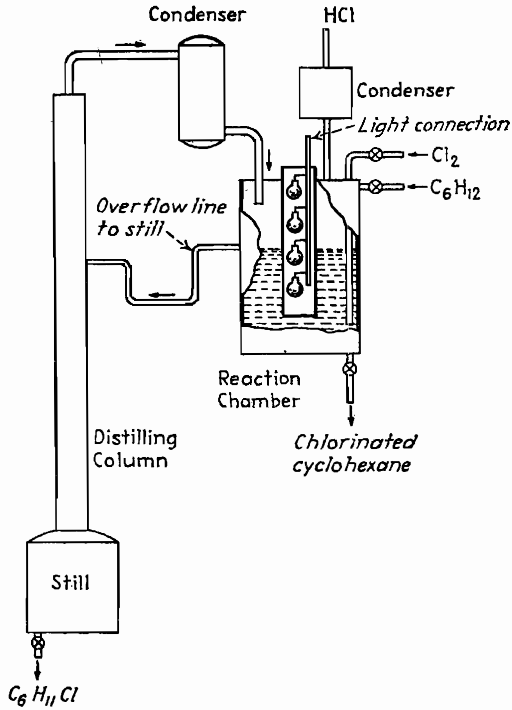
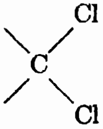


FIG. 6-6. Photochlorination of cyclohexane.

cyclohexane commonly called benzene hexachloride and used as an insecticide, because of the ease of forming the  structure. This compound is commonly produced by the additive chlorination of benzene.

Chlorination of Ethanol. *Chloral.* Either 95 per cent or absolute ethyl alcohol can be chlorinated to produce trichloroacetaldehyde (chloral) through a series of reactions frequently represented as follows:

$$C_2H_5OH + Cl_2 \rightarrow C_2H_5OCl + HCl \qquad (1)$$

$$C_2H_5OCl + C_2H_5OH \rightarrow CH_3CH(OH)OC_2H_5 + HCl \qquad (2)$$

$$CH_3CH(OH)OC_2H_5 + 3Cl_2 \rightarrow CCl_3CH(OH)OC_2H_5 + 3HCl \qquad (3)$$

If the above three equations are combined, the over-all effect may be represented as Eq. (4):

$$2C_2H_5OH + 4Cl_2 \rightarrow CCl_3CH(OH)OC_2H_5 + 5HCl \qquad (4)$$

This equation represents a theoretical requirement of 2 moles of alcohol and 4 moles of chlorine to produce 1 mole of the hemiacetal. However, it has been found feasible to hydrolyze the hemiacetal by the addition of water, thereby releasing chloral hydrate and alcohol. The alcohol is then subjected to further chlorination so that the composite of all the reactions can be represented by Eq. (5).

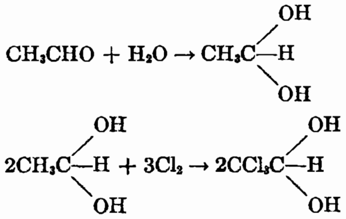
$$C_2H_5OH + 4Cl_2 + H_2O \rightarrow CCl_3CH(OH)_2 + 5HCl \qquad (5)$$

This equation indicates a requirement of only 1 mole of alcohol per mole of chloral hydrate produced rather than the 2 moles indicated in the generally accepted equation (4). While the exact mechanism of the series of reactions is in doubt, proof of the existence of the hydrolysis type of reaction is in the actual yields obtained in commercial operations.[1] Based on Eq. (5), conversion of alcohol to chloral will run as high as 85 per cent. Some manufacturers have been reported as using ferric chloride to catalyze the chlorination of alcohol, but water appears to be as effective and offers other advantages. While Eq. (5) may represent the ultimate result, in practice it has been found desirable to add the required water after the chlorination is partially completed. It is also desirable to operate with an excess of chlorine to avoid excessive formation of ethyl chloride.

Chlorination of Acetaldehyde. In some commercial processes for chloral, acetaldehyde, or its condensation product, paraldehyde is chlorinated under hydrous conditions. In some cases this has an advantage over the chlorination of ethanol as only 3 moles of chlorine are required as compared with the 4 moles used in the ethanol process:

$$CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl$$

Cave[2] demonstrated that the reaction proceeds by the aqueous HCl blocked chlorination:



Aliphatic Acids. By the appropriate choice of chlorinating agents, aliphatic carboxylic acids can be converted either to chloro derivatives by substitution of H in the alkyl chain or to acid chlorides by replacement of the $-OH$ of the carboxyl group.

The chlorination of liquid carboxylic acids generally takes place at tem-

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[1] Coster, U.S. 2,669,585 (1954).

[2] The Chlorination of Acetaldehyde, *Chemistry in Can.*, **35**, June, 1949.

peratures lower than are necessary for the paraffins. A diversity of procedures and catalysts have been employed for such compounds. The catalysts include iodine, sulfur, phosphorus and their halides; sulfuric, phosphoric, and chloroacetic acids; acetic anhydride; mixed esters of phosphorus halides and organic acids; and a number of metal chlorides. The reason for this large diversity of catalysts is the hope of directing chlorine into one specific isomeric mono- or dichloride, but so far very little comparable technical information has been published.

The reported commercial catalysts for monochloroacetic acid are acetic anhydride or acetyl chloride with hydrogen chloride;[1] phosphorus, probably entering the reaction as a phosphite acetate ester;[2] and acetic anhydride or acetyl chloride with an ionic peroxide inhibiting catalyst such as chromium acetate or manganese acetate.[3]

Sulfuryl chloride, in the presence of an organic peroxide, can also be effectively used for the preparation of chloroaliphatic carboxylic acids, their alkyl esters, and chloroacyl halides.

At Höchst, trichloroethylene is hydrolyzed in 74 per cent sulfuric acid at 130–140°C to form monochloroacetic acid free from dichloroacetic acid:

$$CCl_2{=}CHCl + 2H_2O \xrightarrow{H_2SO_4} CH_2ClCOOH + 2HCl$$

2,2-Dichloropropionic acid, of importance as a herbicide, can be prepared by the liquid-phase chlorination of the acid at 90–100°C, using selective catalysts such as phosphorus trichloride. β-chloropropionic acid is made by the hydrochlorination of acrylic acid.[4]

Chlorination in the Side Chain of Aromatic Compounds. When chlorine is passed into boiling toluene in the presence of chlorine-activating light, a mixture of different chlorinated products is obtained. The degree of halogenation will depend on the quantity of chlorine consumed, the principal products being those in which chlorine is substituted in the side chain.

Generally, a higher temperature of chlorination (120–130°C) favors substitution in the side chain, while chlorination at a lower temperature (30–50°C), in the presence of a catalyst, e.g., iron, favors the replacement of nuclear hydrogen.

$$C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl + HCl$$
$$C_6H_5CH_3 + 2Cl_2 \rightarrow C_6H_5CHCl_2 + 2HCl$$
$$C_6H_5CH_3 + 3Cl_2 \rightarrow C_6H_5CCl_3 + 3HCl$$

The ratio of formation of benzyl-, benzal-, and benzotrichloride is a function of the moles of chlorine used and the mole ratio of the chlorinating

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[1] U.S. 2,503,334 (1950); 2,539,238 (1951).

[2] U.S. 3,595,899 (1952).

[3] U.S. 2,688,634 (1954).

[4] U.S. 2,759,018 (1956).

products present. For highest yields of either benzyl or benzal chloride, a batch or multistage continuous process is indicated.

Xylenes readily chlorinate in the side chain under similar high-temperature batch procedures using chlorine-activating light. Meta- and para-xylene proceed to the hexachloride, but the structure of ortho-xylene is such that the sixth chlorine cannot be introduced.

Ethylbenzene, isopropylbenzene, and higher alkylbenzenes chlorinate at elevated temperature in the side chain with substitution occurring preferentially on the α-carbon. However, at elevated temperatures, dehydrochlorination readily occurs, producing reactive double-bond groups and tar formation. Because of this reaction, the aryl methane reaction, and the catalyst-promoted ring chlorination reaction, much work has been done to inhibit these side reactions. The most promising to date include the use of peroxides and the sequestering agents such as amides.

Chlorination in the Nucleus of Aromatic Compounds. Substitution of chlorine for hydrogen in the benzene ring takes place readily. The reaction is greatly facilitated by the presence of a halogen carrier, such as iron or aluminum. Previously, it has been shown that side-chain chlorination occurs with the alkylbenzenes when chlorination is carried out at comparatively elevated temperatures and in the presence of light. At low temperatures and in the presence of a halogen carrier, if reaction takes place, the halogen replaces hydrogen atoms in the ring.

Liquid-phase Chlorination of Benzene. The chlorination of benzene is carried out in iron vessels, usually with ferric chloride as a catalyst. Anhydrous benzene takes up chlorine readily in the presence of a carrier, and the heat of the reaction must be controlled by cooling or refluxing systems to maintain optimum temperature. When only monochlorobenzene is desired, optimum yields may be obtained in a batch reactor at 30–40°C, using 0.6 mole of chlorine per mole of benzene.

Rectification after introduction of a full mole of chlorine will give the fractions indicated in the accompanying table.

Distillation products	Per cent	Boiling range, °C
Benzene	3	79–81
Benzene and chlorobenzene	10	81–125
Chlorobenzene	75	126–133
Chlorobenzene and dichlorobenzenes	10	133–180
Resinous materials and loss	2	

The yield of monochlorobenzene decreases and the yield of dichlorobenzene increases as the temperature is increased.

MacMullin has made a mathematical analysis of the benzene chlorination process which provides theoretical curves of performance that are in close agreement with experimental evidence.[1] The curves of Fig. 6-7 show the relative quantities of chlorobenzenes formed as functions of X (moles chlorine per mole of benzene) and of the method of chlorination. It is clear that, under the conditions used, batch chlorination permits a greater production of monochlorobenzene; the actual maximum (M on curve B) being reached when 1.07 moles of chlorine per mole of benzene is used. The maximum for dichlorobenzenes (curve C) is reached when 2.04 moles of chlorine per mole of benzene is used. It is noteworthy that continuous chlorination results in a greater proportion of higher chlorinated products than batch chlorination for all values of X. Continuous chlorination is, therefore, less favorable for monochlorobenzene production than batch chlorination, but it can be made equally favorable by chlorinating to a lower value of X and recycling underchlorinated material (see pp. 286–287). Two-stage chlorination gives products intermediate between single-stage continuous chlorination and batch operations.

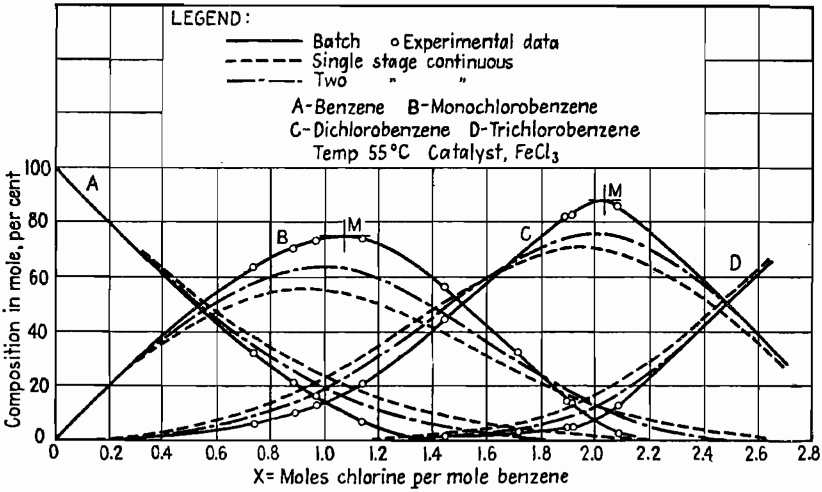

FIG. 6-7. Chlorination of benzene by substitution distribution of reaction products.

The chlorination of benzene has been studied by Weigandt and Lantos with the object of determining the factors contributing to an increased content of p-dichlorobenzene.[2] They found:

1. Distribution of the reaction products, benzene, mono-, di-, and trichlorobenzenes, is not affected by the type of catalyst (iron, $FeCl_3$, $SbCl_5$,

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[1] MACMULLIN, *Chem. Eng. Progr.*, **44** (3), 183 (1948).

[2] WIEGANDT and LANTOS, *Ind. Eng. Chem.*, **43**, 2167 (1951); LANTOS, Cornell Thesis, 1950.

I_2, $AlCl_3$, etc.), its concentration, or the rate of feeding chlorine to the reactor. Higher temperature, however, gives higher yields of polychlorinated benzenes at any chlorination level.[1] Lower reaction temperatures favor formation of para isomer.

2. Single or multistage continuous chlorination gives higher yields of polychlorinated benzene at any chlorination level than batch chlorination.
3. Ortho-dichlorobenzene converts more rapidly to trichlorobenzene than does para-dichlorobenzene. Thus the percentage of para in the dichloro fraction increases further after the trichloro begins to form.
4. Ortho-dichlorobenzene added to the charge increases the selectivity of the reaction to para-dichlorobenzene, probably as a result of mass action and increased polarity of the chlorinating mass.
5. The choice of catalyst and the catalyst concentration have important influences on the para-ortho isomer ratio; $FeCl_3$ or $SbCl_5$ at low concentration is effective in producing better yields of para.

The commercial development of markets for tetrachlorobenzene and trichlorophenol has extended the range of the data shown in Fig. 6-7 in the expected comparable manner. The formation of tetrachlorides begins with the consumption of 2.2 moles of chlorine, rising to a peak at about 4.05 moles of chlorine. The 1,2,3,4-tetrachlorobenzene is converted more rapidly to higher chlorides than the 1,2,4,5-tetrachloro isomer. If 1,2,4,5-tetrachlorobenzene is desired as a pure product, ortho-dichlorobenzene and 1,3,4-trichlorobenzene may be used as starting materials and 1,2,4,5-tetrachlorobenzene crystallized from the chlorinated product.

Vapor-phase Chlorination of Benzene. Chlorine reacts with benzene above 400°C and preferably at 500°C to form a different series of polychlorobenzenes than by liquid-phase reaction.[2] Meta- or 1,3-dichlorobenzene is the preponderant dichloride and chlorinates further to the symmetrical 1,3,5-trichloride.

If the ratio of chlorine to benzene materially exceeds 1:1, inflammation may occur at the mixing point, but a cyclic operation with recycle of lower chlorinated benzenes allows easy chlorination to tri- and tetrachlorobenzenes. There is little change in the ratio of mono- to dichlorobenzenes at temperature increases above 400°C, but above 500°C pyrolysis and condensation reactions occur, with the formation of carbon, hexachlorobenzene, and chlorinated biphenyls.

Chlorination in the Nucleus of Substituted Aromatic Compounds. The effect of substitutents in the benzene ring is a most important factor in additional substitutions in the ring. R. T. Sanderson[3] states: "Newly

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[1] In accordance with the findings of Burion, *Compt. rend.*, **180**, 1319 (1920); and MacMullin, *op. cit.*

[2] Mason et al., *J. Chem. Soc.*, **1931**, 3150; U.S. 2,470,336 (1949); 1,784,267 (1930); 1,835,754 (1931).

[3] *Science*, **122**, 599 (1955).

available information on charge distribution in molecules,[1] even though it is somewhat speculative, should certainly be of interest in the field of aromatic substitution where no completely satisfactory interpretive theory has yet been developed."

Table 6-6 lists the substituents in order of decreasing electron release to, or increasing withdrawal from, the ring. The partial charge on the atom of the substituent group that is directly attached to the ring, as well as the partial charges on carbon and hydrogen atoms, is given. Also indicated are the possibility of substituent conjugation with the ring and the usual orientation effect. It is extremely important in studying the charge data to keep in mind that they represent solely the partial charges that would be expected from bond polarities resulting from initial electronegativity differences. The mobility of certain electrons in these multiple-bonded systems also has an important influence on the over-all charge distribution in the

TABLE 6-6. EFFECT OF SUBSTITUENTS IN BENZENE RING

Substituent	Charge* withdrawal (+) from ring	Charge* on atom next to ring	δ C*	δ H*	Conjugation with ring	Orientation effect
O	−0.627	−0.373	−0.084	−0.025	None	*o,p*
$Si(CH_3)_3$	−0.241	0.289	0.049	0.011	None	*o,p* (weak)
$C(CH_3)_3$	−0.085	−0.035	−0.035	0.025	None	*o,p*
CH_3	−0.052	−0.032	−0.032	0.028	None	*o,p*
H	−0.030	0.030	−0.030	0.030	None	
C_6H_5	0	−0.027	−0.027	0.033	Possible	*o,p*
NH_2	0.092	−0.176	−0.019	0.042	None	*o,p*
CH_2Cl	0.171	−0.012	−0.012	0.049	None	*o,p*
OCH_3	0.174	−0.309	−0.012	0.049	None	*o,p*
CN	0.180	−0.011	−0.011	0.050	Possible	*m*
$COCH_3$	0.181	−0.011	−0.011	0.050	Possible	*m*
OH	0.247	−0.303	−0.005	0.056	None	*o,p*
Cl	0.251	−0.251	−0.005	0.056	None	*o,p*
CHO	0.252	−0.005	−0.005	0.056	Possible	*m*
$CHCl_2$	0.400	0.008	0.008	0.070	None	*o,p*
$N(CH_3)_3^+$	0.446	−0.148	0.012	0.074	None	*m*
COOH	0.480	0.015	0.015	0.007	Possible	*m*
CCl_3	0.634	0.029	0.029	0.091	None	*m*
NO_2	0.671	−0.129	0.033	0.095	Possible	*m*
SO_3H	0.736	−0.039	0.038	0.101	Possible	*m*
NH_3^+	0.805	−0.120	0.043	0.105	None	*m*
CF_3	0.975	0.060	0.060	0.123	None	*m*

* All charge values were calculated by the methods described in *Science,* **122,** 599 (1955); and *J. Chem. Ed.*, **31** (2), 238 (1954); **32,** 140 (1955).

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[1] *J. Chem. Ed.,* **31,** 238 (1954); **32,** 140 (1955); and *Science,* **121,** 207 (1955).

molecule, but the quantitative effect of this influence cannot easily be reckoned.

If the general reactivity of a benzene ring may be taken as a reflection of the availability of π electrons, the data of Table 6-6 are of especial interest. Electron availability will be determined chiefly by two factors: the charge on the carbon atom and the capacity of the rest of the molecule to supply electrons without resulting in excessive positive charge on any one atom. The first factor is evaluated in Table 6-6; the lower the positive charge or the higher the negative charge on carbon, the greater the electron availability. The second factor depends essentially on the number and kinds of atoms of the substituent group: if the electron release to the ring is equal for two different substituents, the substituent that is the better electron reservoir will contribute more to the availability of π electrons.

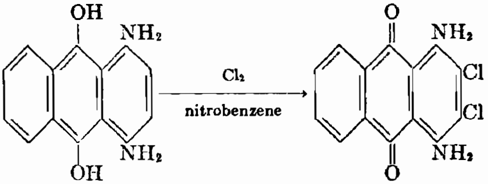
Chlorination of Naphthalene and Biphenyl. In organic synthesis, it is often necessary, in carrying out reactions, to employ inert solvents or solvents that, although normally reactive, will remain substantially inert under the conditions of reaction employed.

α-Chloro- and polychloronaphthalenes can be prepared by dissolving naphthalene in α-chloronaphthalene, adding ferric chloride, and chlorinating to the desired product. If hexachlorobutadiene is used as a solvent, naphthalene may be fully chlorinated to octachloronaphthalene. In addition to the unreactive carbon tetrachloride often used as a solvent for such reactions, the more reactive solvents, benzene, acetic acid, and acetylene tetrachloride have been commercially employed.

Halogenation of Anthraquinones. Ordinarily, the halogenated anthraquinones are derived from the corresponding keto acids, which in turn are prepared according to the Friedel-Crafts reaction. Thus, not only chlorobenzene but also *o*- and *m*-dichlorobenzenes have been utilized in the synthesis of halogenated benzoylbenzoic acids by condensing with phthalic anhydride as well as its halogen derivatives. Under certain conditions, particularly when halogeno-amino derivatives are required, it is desirable to chlorinate the anthraquinone compounds directly in order to obtain a specific intermediate for vat dye manufacture.

The chlorination of 2-aminoanthraquinone can be carried out by suspending 10 parts of the amine in 100 parts of nitrobenzene and then passing in chlorine until the increase in weight indicates monochlorination. With constant agitation, the mixture is boiled vigorously for ½ hr and then permitted to stand overnight. The 2-amino-3-chloroanthraquinone that crystallizes out is filtered off and washed with nitrobenzene, alcohol, and finally water.

An aminoanthraquinone can also be chlorinated in nitrobenzene solution if it is first converted to the leuco compound. Upon oxidation, the chlorinated aminoanthraquinone is obtained.



Carbon Tetrachloride: Chlorination of Carbon Disulfide. The fundamental reaction of carbon disulfide with chlorine may be expressed as follows:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2 \qquad (1)$$

This reaction readily goes to completion and is an economic procedure for the manufacture of carbon tetrachloride when the demand for sulfur monochloride is sufficient. When the demand for both products is not in balance, it is desirable to employ the sulfur monochloride as a chlorinating agent. The reaction between carbon disulfide and sulfur monochloride can be carried out so as to leave no unreacted S_2Cl_2 by the use of an excess of CS_2 as follows:

$$3CS_2 + 4S_2Cl_2 \rightleftharpoons 2CCl_4 + 12S + CS_2 \qquad (2)$$

To obviate difficulties in separating the carbon tetrachloride from sulfur dichloride (bp, 59°C), it is customary to use reactions (1) and (2) alternately. Part of the carbon tetrachloride (bp, 76.74°C) is distilled after reaction (1), and the residual sulfur monochloride (bp, 138°C) is transferred and treated in accordance with Eq. (2). When the carbon disulfide and carbon tetrachloride which are recycled to reaction (1) are distilled, all the liberated elemental sulfur is removed. During this distillation, some reversal occurs.

Carbon tetrachloride can also be made by the direct chlorination of methane (see process description and flow sheet on p. 299) and recycling the unreacted and partially reacted products.

ADDITION REACTIONS

Olefins combine readily with chlorine and bromine. In these reactions, the characterizing double bond is replaced by a single bond, and two halogen atoms become attached to the adjacent carbon atoms which were previously united by a double bond:

$$CH_3CH{=}CH_2 + Cl_2 \rightarrow CH_3CHClCH_2Cl$$
$$CH_3CH{=}CCl_2 + Cl_2 \rightarrow CH_3CHClCCl_3$$

The addition reactions are usually carried out in the presence of a solvent that may be some of the finished product or unwanted higher chlorinated derivatives. Any of the lesser active polychlorinated compounds such as CCl_4 and $C_2H_2Cl_4$ may also be used.

When the hydrogen halides are similarly allowed to react with olefinic hydrocarbons, the halogen, in accordance with Markownikoff's rule, ordinarily attaches itself preponderantly to that carbon with which are combined the least number of hydrogen atoms, while the hydrogen adds on to the terminal carbon atom.

$$CH_3CH{=}CH_2 + HCl \rightarrow CH_3CHClCH_3$$
$$CH_3CH_2CH{=}CH_2 + HCl \rightarrow CH_3CH_2CHClCH_3$$

If this reaction were universally true, only secondary and tertiary halogeno compounds could be obtained from the higher olefins. Kharasch has, however, shown that the addition of HBr to the double bonds of olefinic hydrocarbons is influenced by the presence of either peroxides or antioxidants, the former serving to produce primary and the latter secondary or tertiary halogen derivatives.[1]

In Chap. 13, it is shown that, when a mixture of olefins is treated with sulfuric acid, the butylenes and propylene will react under milder conditions of temperature, pressure, and acid concentration than ethylene. Similarly, it is feasible to effect the selective chlorination of the higher olefins and, after separation of the liquid chloropropanes, butanes, etc., to chlorinate the residual ethylene.

√**Preparation of Ethylene Dichloride.** The addition of chlorine to ethylene may be effected in the liquid phase in the presence of a cosolvent or in the vapor phase in the presence of metal contact agents.

The use of solvents ordinarily leads to considerable substitution as well as addition, even at relatively low temperatures. From 10–20 per cent polychloroethanes are obtained when operating at 0–40°C. The cosolvent may be some of the desired product, viz., dichloroethane or a polychlorohydrocarbon, which can be recovered and reused.

According to Hammond, the addition of relatively small amounts (0.05–0.25 per cent, based on the weight of dichloroethane used as a cosolvent) of anhydrous ferric chloride will serve to depress substitution reactions.[2] The reaction can be carried out in the apparatus shown in Fig. 6-8. Chlorine and ethylene, under moderate pressure, are introduced into a reactor containing a body of dichloroethane and provided with a plurality of tubes through which cooling water is circulated. Ferric chloride may be introduced as such but, because of its hygroscopicity, may be first dissolved in anhydrous ethanol or delivered to the reactor with the replacement dichloroethane.

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[1] Kharasch, *J. Am. Chem. Soc.*, **55**, 2468, 2521, 2531 (1933); **56**, 244, 712, 1212, 1643, 1782 (1934); **57**, 2463 (1935); **59**, 195 (1937).

[2] Hammond, U.S. 2,393,367 (1946).

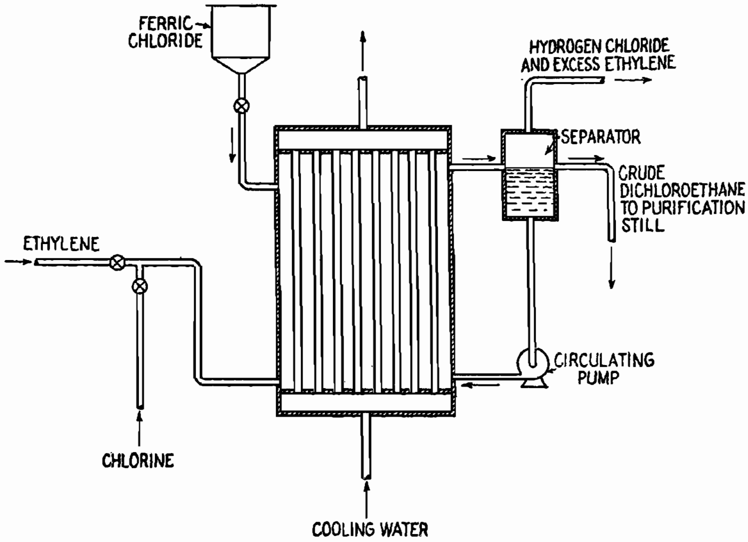


FIG. 6-8. Manufacture of dichloroethane.

When ethylene and chlorine in a mole ratio of 1.1:1 react in a liquid bath of dichloroethane, maintained at a temperature of 40°C, about 85.6 per cent of the chlorine reacts by addition, and about 7.7 per cent reacts to form higher chlorination products. If, however, the preceding reaction is carried out in the presence of 0.05–0.25 per cent of ferric chloride—based on dichloroethane—97.2 per cent of the chlorine reacts by addition to yield dichloroethane, while only 1.75 per cent enters into substitution reactions.

When the addition of chlorine to ethylene is carried out in the vapor phase and in the presence of metal contact agents, higher proportions of 1,2-dichloroethane are obtained. Equimolecular proportions of chlorine and ethylene reacting at 80–100°C in the presence of copper or iron give about 90–95 per cent of the theoretical yield of dichloroethane. The reactions may be carried out in tubes that are packed with shavings or particles of the preferred metal. When small amounts of dichloroethane are recirculated to the reaction zone, the exit gases can be scrubbed more easily. In many plants, the concurrent formation of polychloroethanes is considered desirable, for such compounds are subsequently submitted to dehydrochlorination and yield desired chloroolefins.

Chlorination by the Action of Hydrochloric Acid with and without Oxidants

Reactions in this group include chlorination with (1) hydrochloric acid and (2) chlorides and chlorates in the presence of mineral acids. The syntheses made possible by the action of hydrochloric acid and generated chlorine comprise reactions involving *addition*, *substitution*, and *replacement*.

ADDITION REACTIONS

Preparation of Alkyl Halides from Olefins. There are two general methods for the synthesis of alkyl halides: (1) by the interaction of an alcohol with a halogen hydride—a procedure that may reasonably be discussed under esterification or halogenation and, also, under the Friedel-Crafts synthesis when a metal halide is used to catalyze the reactions—and (2) by the addition of a halogen hydride to an unsaturated hydrocarbon. This reaction may be catalyzed by metal halides and by sulfuric acid. In the latter instance, the ethylsulfuric acid first formed is converted to the halide by gaseous chlorine or chlorine liberated *in situ* by action of sulfuric acid on a halide.

It has long been known to students of the Friedel-Crafts reaction that olefins could be employed instead of the corresponding alkyl halides in alkylation reactions, since they were transformed into the alkyl halide by the added or liberated halogen hydride. The preparation of the alkyl halide may be presented as follows:

$$R{-}HC{=}CH_2 + HCl \xrightarrow[\text{catalyst}]{\text{Friedel-Crafts}} R{-}CHClCH_3$$

Aluminum chloride, ferric chloride, bismuth trichloride, zinc chloride, and stannic chloride have been variously employed to catalyze the reaction.

The synthesis may be carried out as a batch process by bringing the olefin and halogen hydride together in a pressure vessel containing the catalyst (1) suitably distributed over an absorbent material or (2) dissolved in an inert solvent. The synthesis may also be effected by passing the reactants as vapors over a solid catalyst, e.g., zinc chloride on charcoal at approximately 100°C.

In general, the ease of synthesis of alkyl halides from olefins is dependent on the molecular weights of the hydrocarbons and the particular hydrogen halide. Thus, as was explained earlier in this chapter, the reaction becomes more difficult in passing from iodides through bromides to chlorides. Likewise, olefins containing several carbon atoms react much more readily than those of a lower order.

Preparation of Chloroolefins and Diolefins by Hydrochlorination. When a gaseous mixture of acetylene and hydrogen chloride is passed through a reaction chamber packed with highly activated charcoal or silica gel impregnated with a solution containing about 20 per cent calcium chloride, 10 per cent barium chloride, and 1 per cent mercuric chloride[1] or mercurous chloride,[2] vinyl chloride is obtained.

$$HC\equiv CH + HCl \xrightarrow[200°C]{\substack{HgCl_2 \\ \text{impregnated charcoal}}} CH_2{=}CHCl$$

Vinylacetylene can be hydrochlorinated in a continuous manner in the presence of an aqueous cuprous chloride solution. The principal reaction is the formation of chloroprene, 2-chlorobutadiene-1,3.

$$HC\equiv C{-}CH{=}CH_2 + HCl \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2{=}CCl{-}CH{=}CH_2$$

A secondary reaction involving the formation of 1,3-dichlorobutene-2 occurs concurrently.

$$H_2C{=}CCl{-}CH{=}CH_2 + HCl \rightarrow CH_3{-}CCl{=}CH{-}CH_2Cl$$

To obtain high yields of chloroprene, the circulation rate of vinylacetylene through the reaction zone needs to be great, and it must be used in excess of the rate at which it is consumed. The aqueous solution containing hydrogen chloride, cuprous chloride, and ammonium chloride passes downward through the reactor maintained at 40–65°C and reacts with the rising vinylacetylene vapors. The used hydrogen chloride solution is freed of tars, fortified with fresh hydrogen chloride, passed through a column packed with copper particles, and then recirculated to the reaction zone.[3]

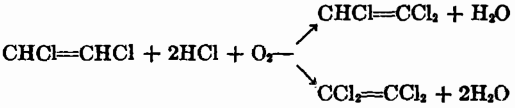
In a following section dealing with the preparation of chloroolefins by dehydrochlorination, it is shown that such compounds can be made either by chlorinating olefins with gaseous chlorine at a critical temperature range or by catalytic or thermal dehydrochlorination. Cass has shown that a mixture of hydrogen chloride and oxygen can be successfully substituted for elemental chlorine in the preparation of chloroolefins.[4] The reactions that take place may be represented by the following equations:

$$CH_2{=}CH_2 + HCl + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CHCl + H_2O \qquad (1)$$

$$CH_2{=}CH_2 + 2HCl + O_2 \rightarrow CHCl{=}CHCl + 2H_2O \qquad (2)$$

$$CH_2{=}CH_2 + 4HCl + 2O_2 \rightarrow CCl_2{=}CCl_2 + 4H_2O \qquad (3)$$

$$CH_2{=}CHCl + 2HCl + O_2 \rightarrow CHCl{=}CCl_2 + 2H_2O \qquad (4)$$



$$CHCl{=}CHCl + 2HCl + O_2 \begin{cases} \nearrow CHCl{=}CCl_2 + H_2O \\ \searrow CCl_2{=}CCl_2 + 2H_2O \end{cases} \qquad (5)$$

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[1] *F.I.A.T. Final Rept.* 843 (Field Information Agency Technical).

[2] Lazier and Whitman, U.S. 2,391,465 (1945); *O.P.B. Rept.* 208 (*Office of Publication Board*, U.S. Department of Commerce).

[3] Carter and Downing, U.S. 2,221,941 (1940).

[4] Cass, U.S. 2,308,489; 2,327,174 (1943); 2,342,100 (1944); 2,374,923; 2,379,414 (1945).

The use of an oxidation catalyst is essential (Deacon process) in order to obtain satisfactory results. Good yields are obtained by using firebrick saturated with cupric oxide, nitrate, etc. It is important to operate in a relatively narrow critical range (400–450°C) in which chlorination and dehydrochlorination reactions can occur concurrently. When the chlorination temperature is sufficiently lowered, addition reactions predominate. When the temperature is too high, the yields are low because of pyrolytic reactions which are accompanied by the liberation of carbon oxides.

Even under carefully controlled conditions, a diversity of reaction products are obtained in such "substitutive" chlorinations. Thus, when 10.3 moles of vinyl chloride, 20.9 moles of hydrogen chloride, and 15.5 moles of oxygen (as air) are passed over a copper oxide catalyst at 400–460°C, the gas effluent consists of 0.89 mole dichloroethylene, 2.12 moles trichloroethylene, and 3.35 moles perchloroethylene. More or less saturated chloroparaffins are formed, depending on the temperature of reaction.

SUBSTITUTION REACTIONS

Chlorination of Methane with Hydrogen Chloride in the Presence of Oxygen. It has been shown that the introduction of air or oxygen into the reaction chamber containing chlorine and methane makes possible the conversion of the liberated hydrogen chloride to active chlorine. Thus, methyl chloride can be made by first chlorinating methane with gaseous chlorine in the vapor phase and then employing the liberated hydrogen chloride and oxygen in an integrated catalytic conversion zone for the further chlorination of methane.[1]

$$2CH_4 + 2Cl_2 \rightarrow 2CH_3Cl + 2HCl$$

$$2CH_4 + 2HCl + O_2 \xrightarrow[400°C]{Cu_2Cl_2} 2CH_3Cl + 2H_2O$$

Thus far, the oxidation-chlorination technique has not been found practical when applied to methane. The oxygen and the liberated steam cause extensive oxidation and hydrolysis.

Benzene, however, is successfully chlorinated by an entirely similar procedure.[2] Benzene vapor is preheated to 300°C and air is preheated to 150°C in separate parts of an oil-fired furnace before being led to a vapor mixer in which hydrochloric acid (from an acid evaporator) is introduced. The gaseous mixture is then passed into a catalytic chamber containing

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[1] Riblett, U.S. 2,334,033 (1943).

[2] *F.I.A.T. Final Rept.* 768; *B.I.O.S.* (British Intelligence Objectives Sub-committee) *Final Rept.* 1841, Item 22, Rashig-Durez Process; CRAWFORD, *Chem. Eng. Progr.*, **46**, 483 (1950).

pumice impregnated with cupric and ferric chlorides at 240 C. About 10–15 per cent of the benzene is converted per pass. The products of reaction pass to a tile-lined packed column which acts as a partial condenser and which permits the separation of the mono- and polychlorobenzenes (about 10 per cent) along with some benzene. The residual benzene is condensed while the air, containing a small amount of benzene, is exhausted. For a practical application of this procedure as the first step in the technical production of phenol, see Chap. 13.

Utilization of Liberated Hydrogen Chloride. *Preparation of Alkyl Halides.* By causing the hydrogen chloride split off in direct chlorinations to react with compatible alcohols, it is not necessary to employ oxidants to obtain a maximum utilization of the chlorine introduced. Thus, methanol can be introduced into the chamber containing hydrogen chloride, hydrocarbon, and chlorinated hydrocarbon and is converted to methyl chloride. The principal reactions involved may be represented as follows:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$
$$HCl + CH_3OH \rightarrow CH_3Cl + H_2O$$

Preparation of Chloroolefins. Cass has shown that the use of oxygen in accordance with the Deacon process permits maximum utilization of the halogen in the reaction system in carrying out thermal chlorinations. The function of the oxygen is to convert any hydrogen chloride *formed* or *introduced* into active chlorine. Therefore, one O_2 needs to be used for each $2HCl$ or $2Cl_2$, water vapor being the coproduct of reaction. The utility of this technique may be exemplified by the following three sets of reactions:

$$CH_2{=}CH_2 + Cl_2 + \tfrac{1}{2}O_2 \rightarrow CHCl{=}CHCl + H_2O \qquad (1)$$
$$CH_2{=}CH_2 + 2Cl_2 + O_2 \rightarrow CCl_2{=}CCl_2 + 2H_2O \qquad (2)$$

If a 10 per cent excess of oxygen is used in reaction (2), the product comprises 5–10 per cent dichloroethylene, 25–35 per cent trichloroethylene, and 50–60 per cent perchloroethylene.[1]

Symmetrical and unsymmetrical dichloroethylene undergo similar reactions:[2]

$$2CHCl{=}CHCl + 2Cl_2 + O_2 \rightarrow 2CCl_2{=}CCl_2 + 2H_2O \qquad (3)$$
$$4CCl_2{=}CH_2 + 2Cl_2 + O_2 \rightarrow 4CCl_2{=}CHCl + 2H_2O \qquad (4)$$

Previously, it was shown that, when chloroalkanes or chloroolefins are subjected to temperatures of 350–450°C, dehydrochlorination occurs. In the presence of oxygen and an oxidizing catalyst, however, most of the hydrogen chloride is converted to chlorine, which is found in the resultant chloroolefin.

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[1] Cass, U.S. 2,327,174 (1943).

[2] Cass, U.S. 2,379,414 (1945).

$$2CH_3CH_2Cl + O_2 \rightarrow 2CH_2{=}CHCl + 2H_2O \qquad (5)$$

$$2CH_2ClCHCl_2 + O_2 \rightarrow 2CCl_2{=}CHCl + 2H_2O \qquad (6)$$

When an excess of 20 per cent oxygen is used in reaction (6), about 25 per cent of the theoretically available hydrogen chloride is found in the reaction products, the balance of the chlorine being organically bound. The products of distillation show the formation of 36.9 mole per cent trichloroethylene, 21.1 mole per cent dichloroethylene, and 5.7 per cent unconverted β-trichloroethane.[1]

The preceding reactions confirm the observations (see pp. 219–222) regarding the equilibrium that exists under certain conditions between halogenation and dehydrohalogenation.

Halogen Exchange. Alkyl halides and unsaturated aliphatic compounds can simultaneously be obtained by treating halogenated aliphatic carboxylic acids, nitriles, or esters with aliphatic alcohols and/or ethers in the temperature range 260–320°C and 700 lb pressure.[2] During the course of the reaction, hydrogen chloride is split out, the hydrogen and chlorine coming from adjacent carbon atoms. Under the conditions of reaction, the hydrogen chloride converts the reacting alcohol to the corresponding halide. The equations underlying such reactions may be expressed as follows:

$$\underset{\beta\text{-Chloropropionic Acid}}{CH_2ClCH_2COOH} + CH_3OH \xrightarrow{Al_2O_3} \underset{\text{Acrylic Acid}}{CH_2{=}CH{-}COOH} + \underset{\text{Methyl Chloride}}{CH_3Cl} + H_2O$$

$$\underset{\substack{\beta\text{-Chloropropionic}\\ \text{Methyl Ester}}}{2CH_2ClCH_2COOCH_3} + CH_3OCH_3 \xrightarrow{AlPO_4} \underset{\text{Methyl Acrylate}}{2CH_2{=}CH{-}COOCH_3} + \underset{\substack{\text{Methyl}\\ \text{Chloride}}}{2CH_3Cl} + H_2O$$

A similar halogen exchange occurs when tetrachloroethane and ethanol (or methanol) react at 280°C in the presence of an aluminum oxide catalyst.[3] The products are trichloroethylene and ethyl chloride.

$$CHCl_2CHCl_2 + C_2H_5OH \xrightarrow[280°C]{Al_2O_3} CHCl{=}CCl_2 + C_2H_5Cl + H_2O$$

Dehydrochlorination

Halogenated Olefins. Halogenated olefins can be made by the addition of a halogen or a hydrogen halide to acetylene, but most frequently they are made by the substitutive halogenation of olefins or the halogenation of olefins by addition and then dehydrohalogenation of the polychloroparaffins. Alcoholic KOH, alkali and alkaline-earth hydroxides, and nitrogen bases can be used to effect the elimination of hydrogen chloride.

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[1] Cass, U.S. 2,342,100 (1944).

[2] Andrussow and Stein, U.S. 2,210,564 (1940), German origin.

[3] U.S. 2,210,563 (1940).

The use of metal halides and thermal treatment alone have also been found to be highly effective.

Before describing some of the dehydrohalogenation processes, it is appropriate to emphasize that such operations are frequently integrated with other chlorination reactions, as follows:

$$\underset{\text{Acetylene}}{C_2H_2 + 2Cl_2} \xrightarrow{FeCl_3} \underset{\text{Tetrachloroethane}}{CHCl_2\cdot CHCl_2}$$

$$\underset{\text{Tetrachloroethane}}{CHCl_2\cdot CHCl_2} \xrightarrow[\text{or vapor-phase cracking}]{\text{active carbon}} \underset{\substack{\text{Trichloro-}\\\text{ethylene}}}{CHCl{:}CCl_2} + HCl$$

$$\underset{\text{Acetylene}}{C_2H_2 + HCl} \xrightarrow[\text{activated charcoal}]{HgCl_2\text{ on}} \underset{\text{Vinyl Chloride}}{CH_2{:}CHCl}$$

$$\underset{\text{Dichloroethane}}{CH_2Cl\cdot CH_2Cl} \xrightarrow{\text{vapor-phase cracking}} \underset{\text{Vinyl Chloride}}{CH_2{:}CHCl} + HCl$$

$$\underset{\text{Dichloroethane}}{CH_2Cl\cdot CH_2Cl} \xrightarrow[280°C,\ 1\text{ atm}]{BaCl_2\text{ on activated carbon}} \underset{\text{Vinyl Chloride}}{CH_2{:}CHCl} + HCl$$

$$\underset{\text{Trichloroethylene}}{CHCl{:}CCl_2 + Cl_2} \xrightarrow{FeCl_3} \underset{\text{Pentachloroethane}}{CHCl_2\cdot CCl_3}$$

$$\underset{\text{Pentachloroethane}}{CHCl_2\cdot CCl_3} \xrightarrow[110°C]{Ca(OH)_2} \underset{\text{Perchloroethylene}}{CCl_2{:}CCl_2} + HCl$$

$$\underset{\text{Perchloroethylene}}{CCl_2{:}CCl_2 + Cl_2} \xrightarrow{h\nu} \underset{\text{Hexachloroethane}}{CCl_3\cdot CCl_3}$$

$$\underset{\text{Trichloroethylene}}{2CHCl{:}CCl_2} \xrightarrow[\Delta]{\text{pressure}} \underset{\text{Hexachlorobutene}}{CHCl_2CCl{:}CClCHCl_2}$$

$$\underset{\text{Hexachlorobutene}}{CHCl_2CCl{:}CClCHCl_2} \xrightarrow[\text{clay catalyst}]{Cl_2} \underset{\text{Pentachlorobutadiene}}{CHCl{:}CCl\cdot CCl{:}CCl_2} + HCl$$

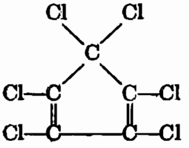
Thermal and Catalytic Dehydrochlorinations. When vapors of polychloroparaffins are heated at elevated temperatures alone or with catalysts, chloroolefins are obtained by dehydrochlorination.

$$CH_2ClCH_2Cl \xrightarrow[550°C]{\Delta} CH_2{=}CHCl + HCl$$

$$CHCl_2CHCl_2 \xrightarrow[200\text{–}300°C]{\text{active carbon}} CHCl{=}CCl_2 + 2HCl$$

$$C_3H_2Cl_6 + 2Cl_2 \xrightarrow{500°C} CCl_4 + CCl_2{=}CCl_2 + 2HCl$$

$$C_5H_6Cl_6 + 3Cl_2 \xrightarrow[400°C]{\text{clay catalyst}}$$



$+ 6HCl$

$$2CHClF_2 \xrightarrow[700°C]{\Delta} CF_2{=}CF_2 + 2HCl$$

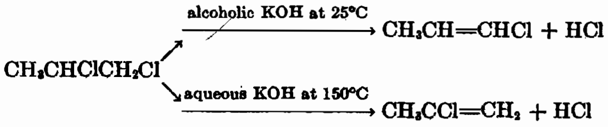
The conditions prevailing during such dehydrochlorinations where chlorine is present are probably a chain-type of reaction wherein equilibrium is more rapidly established than by the unimolecular thermal-decomposition reactions. The catalysts lower the temperature at which equilibrium is accomplished by 100–200°C.

Use of Alkali and Alkaline Earths. The preparation of vinyl chloride, vinylidene chloride, and trichloroethylene may be represented by the following equations:

$$CH_2{=}CH_2 + Cl_2 \rightarrow CH_2ClCH_2Cl + NaOH \rightarrow CH_2{=}CHCl + NaCl$$
$$CH_2{=}CHCl + Cl_2 \rightarrow CH_2ClCHCl_2 + KOH \rightarrow CH_2{=}CCl_2 + KCl$$
$$2CH{\equiv}CH + 4Cl_2 \rightarrow 2CHCl_2CHCl_2 + Ca(OH)_2 \rightarrow 2CHCl{=}CCl_2 + CaCl_2 + H_2O$$

When ethylene dichloride (bp, 84°C) is used for the preparation of vinyl chloride, it is treated with dilute sodium hydroxide at approximately 150°C in a pressure vessel provided with an agitator. By means of a suitable fractional condensing system, the vapors of dichloroethane are condensed and returned to the reactor, the water of reaction is removed, and the volatile vinyl chloride (bp, 13.9°C) is withdrawn and liquefied in a low-temperature condenser.

When propylene dichloride is treated with an alcoholic solution of potassium hydroxide at ordinary temperatures, α-chloropropylene will be formed; but when reacted with alkali hydroxides at relatively high temperatures, the product consists largely of the β-chloro derivative.



$$CH_3CHClCH_2Cl \begin{cases} \xrightarrow{\text{alcoholic KOH at 25°C}} CH_3CH{=}CHCl + HCl \\ \xrightarrow{\text{aqueous KOH at 150°C}} CH_3CCl{=}CH_2 + HCl \end{cases}$$

Trichloroethylene is prepared commercially in a continuous manner by treating tetrachloroethane with an aqueous suspension of calcium hydroxide (about 10 per cent) in a stirred reactor.

Use of Nitrogen Bases. Dehydrochlorinations can be catalyzed by nitrogen bases such as trialkylamines, dialkylamines, monoalkylamines, and their hydrochloride salts as well as by quinoline, piperidine, etc.[1] As a practical matter, it makes little difference whether the free nitrogen base is used or the hydrogen chloride salt is employed, inasmuch as the free base will react initially, at least to some extent, with the liberated hydrogen chloride. The preparation of trichloroethylene from tetrachloroethane is carried out at about 160°C in the presence of a nitrogen base and a high-boiling diluent, such as diphenyl oxide. The concentration of the nitrogen base should be 10–40 per cent by weight.

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[1] Vining, U.S. 2,361,072 (1944).

Use of Metal Halides. Metal halides and particularly zinc and aluminum chlorides have been found to be effective dehydrochlorinating agents. When pentachloroethane is heated with aluminum chloride, tetrachlorethylene is obtained.[1] The pentachloroethane is fed continously into a mixture of tetrachloroethylene and aluminum chloride (or metal aluminum particles) at 120°C. The chloroolefin distills over with hydrogen chloride, and the metal halide becomes converted to an organo aluminum chloride complex of diminishing catalytic activity. Fresh catalyst must consequently be added periodically to maintain high conversion rates.

Chlorination with Hypochlorites

Hypohalites in water or alkaline solutions are effective in producing a number of different types of halogenation. The controlling factor in many of these reactions is hydrogen-ion concentration.

When chlorine is dissolved in water with no appreciable amounts of alkaline constituents present, the following reactions take place:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$
$$HCl \rightleftharpoons H^+ + Cl^-$$
$$HOCl \rightleftharpoons H^+ + (OCl)^-$$

The dissociation constants for the above reactions are given as follows:[2]

$$\frac{(H^+)\,(Cl^-)\,(HOCl)}{Cl_2} = 4.48 \times 10^{-4}$$

and

$$\frac{(H^+)\,(OCl^-)}{HOCl} = 3.7 \times 10^{-8}$$

Increasing the H^+ concentration by the addition of a strong acid causes the reaction to proceed as follows:

$$2HOCl + 2H^+ \rightleftharpoons 2H_2O + Cl_2 \qquad (1)$$

Likewise, increasing the $(OH)^-$ concentration by the addition of NaOH or $Ca(OH)_2$ causes the action to be reversed and proceed to the formation of $(OCl)^-$ as follows:

$$HOCl + (OH)^- \rightleftharpoons H_2O + (OCl)^- \qquad (2)$$

Addition Reactions. *Preparation of Ethylene Chlorohydrin.* When ethylene is brought into contact with a hypochlorous acid solution, the principal reaction product is ethylene chlorohydrin:

$$HOCl + H_2C{=}CH_2 \rightarrow CH_2OHCH_2Cl$$

Owing to the slight solubility of ethylene in such aqueous solutions at ordinary pressure, some of the undissolved hydrocarbon reacts with the chlorine gas that is present to form ethylene dichloride. To prevent extensive dichloride formation, it is necessary to maintain an excess of

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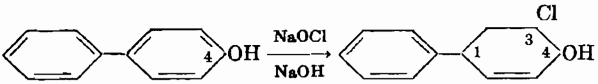
[1] Wimmer and Mugdan, U.S. 2,249,512 (1941).

[2] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899); Davidson, *Shirley Inst. Mem.*, **12**, 6–15 (1933).

ethylene or to increase the solubility of the hydrocarbon by the employment of pressure. In commercial practice, a pressure of about 2.5 atm is used.[1]

Instead of pressure, surface-active agents can be used to promote the formation of hypochlorous acid and ethylene chlorohydrin.[2] Ethylene is passed at 20–30°C countercurrent to a hypochlorous acid solution containing sodium lauryl hydrogen sulfate until the concentration of the chlorohydrin is 8 per cent. In addition to the rate of reaction being accelerated, the yield of ethylene chlorohydrin under such conditions is about doubled, being 77.6 per cent compared with 39.2 per cent for the untreated control.

Substitution Reaction. *Chlorination of Hydroxy- or Methoxybiphenyls.*



Alkali hypochlorite solutions can be employed in chlorinating hydroxy- or methoxybiphenyl. One mole of 4-hydroxybiphenyl is dissolved in 1 mole of caustic soda and 6 liters of water. The solution is cooled, and 1 mole of sodium hypochlorite in solution is added slowly, with constant stirring. The reaction mixture is allowed to stand for about 1 hr and then warmed to 40°C. After filtration and cooling, 3-chloro-4-hydroxybiphenyl is precipitated by the addition of hydrochloric acid.

Chlorination of Nitroparaffins. The nitroparaffins are readily chlorinated with alkali hypochlorite solutions. Depending on the ratio of hypochlorite solution, mono-, di-, and trichloro derivatives can be obtained.[3] In practice, the requisite quantity of chlorine is added to a 10 per cent caustic soda solution. It is important to provide an excess of about 20 per cent hypochlorite solution and to maintain the pH somewhere between 12 and 14.

The production of chlorpicrin (trichloronitromethane) can be used to illustrate the process. Here, 11.2 parts of nitromethane is added slowly to about 700 parts of a 10 per cent sodium hypochlorite solution under agitation at 20–25°C. After all the nitromethane has been introduced, stirring is continued until the temperature falls. A yield of 96 per cent of trichloronitromethane is obtained when the crude product is distilled with steam.

Phosgene ($COCl_2$) and Benzotrichloride ($C_6H_5CCl_3$)

Phosgene and benzotrichloride find important use in the preparation of acid chlorides.[4] When vapors of organic acids are mixed with phosgene in

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[1] *B.I.O.S. Final Repts.* 776 and 1059, Item 22.

[2] Valik, U.S. 2,260,547 (1941).

[3] Tindall, U.S. 2,365,981 (1944).

[4] *B.I.O.S. Final Rept.* 1153, Item 22.

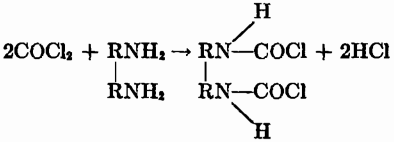
the presence of charcoal, they react readily and provide a continuous and comparatively cheap method of preparing acid chlorides. Chloroacetyl chloride is prepared by admitting gaseous phosgene at the rate of 200 liters per hr and liquid chloroacetic acid at the rate of 900 g per hr into a reaction chamber packed with charcoal and maintained at 200°C. The effluent vapors are led to a reflux condenser, and the chloroacetyl chloride (bp, 106°C) passes through, while the chloroacetic acid (bp, 187°C) is returned to the reactor. Approximately 900 g of chloroacetyl chloride per hour is thus obtained.

When acetic acid or acetic anhydride is treated with benzotrichloride in the liquid phase at elevated temperature, acetyl chloride is formed. The reaction may be stopped with the production of benzoyl chloride or carried to the benzoic acid stage.

$$C_6H_5CCl_3 + CH_3COOH \xrightarrow{\Delta} CH_3COCl + C_6H_5COCl + HCl$$

$$C_6H_5CCl_3 + 2CH_3COOH \xrightarrow{\Delta} 2CH_3COCl + C_6H_5COOH + HCl$$

The most important use of phosgene is in the preparation of diisocyanates from the corresponding amines. These compounds have reached major importance as blowing agents for elastic and rigid polymeric foams and as cross-linking agents in improved elastomers and polymers.



$$2COCl_2 + \begin{array}{l} RNH_2 \\ | \\ RNH_2 \end{array} \rightarrow \begin{array}{l} \quad\ H \\ RN\diagup\!\!-COCl \\ | \\ RN\diagdown\!\!-COCl \\ \quad\ H \end{array} + 2HCl \tag{1}$$

$$(RNHCOCl)_2 \xrightarrow{\Delta} (RNCO)_2 + 2HCl \tag{2}$$

Many modifications of the above equations have been made to allow for the formation of the amine hydrochloride, combination into single-stage high-temperature processes, etc., but a satisfactory procedure consists of dissolving the diamine into an unreactive solvent such as toluene, adding hydrogen chloride to produce a solution or suspension of hydrochloride, introduction of phosgene below the boiling point of toluene, and then distilling off the toluene to give the crude diisocyanate. Great stress has been placed in some procedures on the introduction of the amine or amine hydrochloride into a solvent containing an excess of phosgene rather than the phosgene into the hydrochloride solution, thus eliminating carbamate formation. Chemical literature leaves considerable room for improved chemical-engineering development on these processes, and there is little doubt that the major producers have made great strides in simplifying these processes.

Thionyl Chloride ($SOCl_2$)

Introduction of Chlorine. Thionyl chloride is used to introduce chlorine in place of various groups, OH, SH, NO_2, SO_3H, hydrogen and oxygen.

$$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$
$$C_6H_5CSSH + 2SOCl_2 \rightarrow C_6H_5CSCl + SO_2 + S_2Cl_2 + HCl$$
$$C_6H_5SO_3H + SOCl_2 \rightarrow C_6H_5Cl + 2SO_2 + HCl$$

Preparation of Acid Chlorides. Probably the most common use of thionyl chloride is to replace phosphorus chlorides in the preparation of acid chlorides from the corresponding acids.

$$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$$

In this reaction the side products are all gases easily removed from the acid chloride.

Thionyl chloride seldom reacts with aldehyde, ketone, or ethoxy groups, thus permitting its use with many acids where phosphorus chlorides cannot be used. Surprisingly, the OH group of salicylic acid is not attacked when the acid chloride is made by this method.

Sulfuryl Chloride (SO_2Cl_2) as a Chlorinating Agent

Treatment of Paraffin Hydrocarbons. Sulfuryl chloride reacts readily with unsaturated hydrocarbons to form the halogen derivatives. It can also be employed to advantage in the chlorination of saturated paraffins, such as methane, hexane, and octadecane.

Previously, it has been shown that the direct chlorination of saturated paraffins is accomplished with considerable difficulty, because of the tendency to explosions, unless special precautions are taken. The advantage of using sulfuryl chloride for chlorinating saturated hydrocarbons resides primarily in the fact that no great amount of heat is evolved when it is used. The dissociation of sulfuryl chloride results in the formation of sulfur dioxide and chlorine, heat being absorbed during the process. The halogen enters into reaction with the hydrocarbon that is present. Approximately two-thirds of the amount of heat evolved by the chlorination of methane or other hydrocarbons is absorbed in effecting the progressive dissociation of sulfuryl chloride. For this reason, it is difficult to cause an explosion when saturated paraffins are mixed with sulfuryl chloride, regardless of the proportions in which the reactants are present.

By regulating the quantity of sulfuryl chloride, it is possible, in the chlorination of methane, to obtain a yield of 50 per cent chloroform. When a lesser quantity of sulfuryl chloride is used, it is obvious that a larger proportion of mono- and dichloromethanes is formed. The reaction is promoted by the presence of ionizing agents such as light, heat, metallic chlorides, and activated carbon. The heat of reaction is slightly greater than the quantity absorbed by the decomposition of sulfuryl chloride. The excess of heat is sufficient to keep the temperature of the hydrocarbon gas at the optimum reaction temperature, without the application of heat after the reaction has started.

The chlorination of methane can be carried out by bubbling the hydrocarbon gas through sulfuryl chloride (bp, 69°C) at a predetermined temperature. The higher the temperature, the larger the ratio of sulfuryl chloride vapor to hydrocarbon. The mixture of gases is passed through a tube filled with inert material and maintained at about 350°C. The flow is sufficiently rapid to constitute turbulent flow. It is necessary to use only a small quantity of catalyst, e.g., carbon; otherwise, the decomposition of sulfuryl chloride will be too rapid, and the rate of formation of chlorine will then be greater than the reaction between chlorine and methane.

Instead of the use of sulfuryl chloride, SO_2 and Cl_2, which combine to give sulfuryl chloride, can be employed for vapor-phase reactions.[1] When the ratio of SO_2 to Cl_2 is adjusted, it is feasible to produce sulfonic or chlorosulfonic acid derivatives of saturated paraffins in liquid-phase reactions. According to Lockwood and Richmond, a premixed stream of sulfur dioxide and chlorine can be used for the countercurrent photochlorination of white oil (petroleum fraction, sp gr, 0.8033; bp, 283–324°C) at about 50°C.[2] The product, after hydrolysis with 30 per cent sodium hydroxide, yields an aqueous solution of the sodium salt of a sulfonic or chlorosulfonic acid. An increase in the ratio of SO_2 to Cl_2 greatly increases the yield of solubilized product. When a 3:1 ratio is used, the product contains very little chlorine and has good wetting and detergent characteristics.[3]

Sulfuryl chloride reacts readily with aliphatic compounds in the presence of light and a suitable catalyst such as pyridine or thiophenol at temperatures of 40–60°C to form alkyl sulfonyl chlorides. Yields are often as high as 70 per cent.

$$C_6H_{12} + SO_2Cl_2 \xrightarrow[\text{catalyst}]{h\nu} C_6H_{11}SO_2Cl + HCl$$

It may also react with aliphatic alcohols to form chloro sulfonates.

$$C_3H_7OH + SO_2Cl_2 \rightarrow C_3H_7OSO_2Cl + HCl$$

Treatment of Aromatic Compounds with SO_2Cl_2. In the absence of a catalyst, sulfuryl chloride, SO_2Cl_2, does not react readily with such compounds as benzene or halogenated benzene, it being necessary to operate

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[1] Reed, U.S. 2,046,090 (1936). See Reed reaction, Chap. 7.

[2] Lockwood and Richmond, U.S. 2,193,824 (1940).

[3] Fox et al., U.S. 2,202, 791 (1940).

in closed vessels at 150°C. In the presence of aluminum chloride and sulfur or sulfur chloride, chlorination of benzene occurs with vigor at ordinary temperatures. Dichlorobenzene can thus be converted substantially to the tetrachloro derivative.

Sulfuryl chloride can be employed in conjunction with numerous chlorine carriers to effect substitution in either the ring or side chain. The chlorides of antimony, iron, molybdenum, and aluminum are valuable with sulfuryl chloride in effecting substitution in the ring. The chlorides of phosphorus and, to a lesser extent, manganese, arsenic, and bromine favor side-chain substitution. Sulfur accelerates both types of substitution.

Effect of Oxidants. Kharasch has shown that, in the presence of benzoyl or other organic peroxides, sulfuryl chloride selectively chlorinates the side chain and not the nucleus of alkyl-substituted benzene. The reaction, which is carried out in the dark, is also useful for the chlorination of aliphatic compounds such as acyclic hydrocarbons, cycloparaffins, carboxylic acids, and their acid halides.[1]

TABLE 6-7. CHLORINATION WITH SULFURYL CHLORIDE IN THE PRESENCE OF BENZOYL PEROXIDE

SO_2Cl_2, moles	Organic reactant	Moles reactant	Reflux, hr	Product yields
0.75	*n*-Heptane	3.0	1	Over-all yield, 85% 15% primary heptyl chloride 85% *sec*-heptyl chlorides
0.2	*n*-Propyl chloride	0.6	4	Over-all yield, 85% 60% 1,2-dichloropropane 40% 1,3-dichloropropane
0.2	Toluene	0.4	¼	80% benzyl chloride
0.3	*m*-Xylene	1.0	½	80% *m*-xylyl chloride
0.4	Propionic acid	1.0	1½	Over-all yield, 75% 45% α-chloropropionic acid 55% β-chloropropionic acid
0.6	Cyclohexane	1.8	1½	Over-all yield, 98% 89% chlorocyclohexane 11% dichlorocyclohexane

The quantity of organic peroxide required is generally about 0.1 per cent based on the SO_2Cl_2 used. The employment of a solvent or diluent such as carbon tetrachloride is advantageous in the chlorination of carboxylic acids that react vigorously and also in the case of solid materials. The data in Table 6-7 indicate the scope and nature of the results obtained by this procedure.

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[1] Kharasch and Brown, U.S. 2,302,228 (1942).

Acid Chlorides. Previously, it was shown that thionyl chloride, $SOCl_2$, can be advantageously used for the preparation of acid chlorides from their respective carboxylic acids. Sulfuryl chloride, $SO_2 + Cl_2$, can be similarly employed to effect the conversion of the alkali metal salts of fatty acids.

$$2R{\cdot}CO{\cdot}ONa + SO_2Cl_2 \rightarrow 2R{\cdot}CO{\cdot}Cl + Na_2SO_4$$

Anhydrides may be formed by condensation during the process, but these may be converted to the desired acid chloride by using an excess of chlorinating agent.

$$R{\cdot}CO{\cdot}ONa + Cl{\cdot}OC{\cdot}R \rightarrow R{\cdot}CO{\cdot}O{\cdot}OC{\cdot}R + NaCl$$
$$R{\cdot}CO{\cdot}O{\cdot}OC{\cdot}R + SO_2Cl_2 \rightarrow 2R{\cdot}CO{\cdot}Cl + SO_3$$

Chlorination with Phosphorus Chlorides

At moderate temperatures, PCl_5 is almost as powerful a chlorinating agent as chlorine; and at higher temperatures, its behavior is approximately of the same order. The liberation of chlorine from PCl_5 takes place according to the law of mass action, as can be seen from a consideration of the following system, all the components

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \frac{(PCl_3)\cdot(Cl_2)}{(PCl_5)} = K$$

being in the vapor phase. The formation of PCl_5 is favored by the application of pressure, whereby PCl_3 and Cl_2 combine; the liberation of chlorine is favored by an increase in temperature and an opportunity for the free movement of the vapors. The dissociation of PCl_5 at various temperatures is as follows:

Temperature, °C	182	200	250	300
Percentage decomposition	41.7	48.5	80	97.3

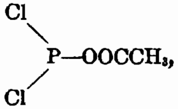
Phosphorus pentachloride is employed as an esterification agent in the treatment of alcohols, the halide becoming hydrolyzed during the reaction.

Acid Chlorides. Acid chlorides can be made from the corresponding fatty acids by treatment with phosphorus halides. When liquid carboxylic acids are reacted, the phosphorus halide, PCl_3 or $POCl_3$, may be added gradually. If the acid does not react energetically, as in the case of the higher members of the acetic acid series or with aromatic carboxylic acids, phosphorus pentachloride is used. The reactions may be represented as follows:

$$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl \tag{1}$$
$$3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3 \tag{2}$$
$$2RCOONa + POCl_3 \rightarrow 2RCOCl + NaPO_3 + NaCl \tag{3}$$

Phosphorus oxychloride is used ordinarily when treating salts of the carboxylic acids. This reaction [Eq. (3)] may be used to advantage in order to utilize more of the chlorine of PCl_5 than is the case when the latter acts upon the free acids. When the pentachloride reacts with the sodium salt, as above, $POCl_3$ is formed as an intermediate compound; and although this no longer has the capacity to act on free fatty acid, it can convert two other molecules of the salt into the acid chloride:

$$3CH_3COONa + PCl_5 \rightarrow 3CH_3COCl + NaPO_3 + 2NaCl$$

The procedure by which phosphorus chlorides react with acetic acid or anhydride was explored by Van Druten[1] and the existence at room temperature of a number of complex esters established. Presumably these are of the general structure  $Cl_2P{-}OOCCH_3$, although the pentavalent phosphates may be formed.

If optimum yields of acetyl chloride are desired, it appears that the reactants of Eq. (2) should first be mixed at low temperature and then heated to distill off acetyl chloride and hydrogen chloride.

Phosphorus trichloride is also used to convert stearic, lauric, and other higher fatty acids to the corresponding acid chlorides. An excess of PCl_3 must be used, and this is removed by washing the upper layer of the settled charge with water.[2]

Halogenation by the Sandmeyer Reaction

Replacement of Diazonium Group.

$$C_6H_5{\cdot}N_2{\cdot}Cl + Cu_2Cl_2 \xrightarrow{HCl} C_6H_5{\cdot}Cl + N_2 + Cu_2Cl_2$$

$$2C_6H_5{\cdot}N_2{\cdot}Cl + Cu_2Br_2 \xrightarrow{HBr} 2C_6H_5{\cdot}Br + 2N_2 + Cu_2Cl_2$$

$$C_6H_5{\cdot}N_2{\cdot}SO_4H + KI \xrightarrow{HI} C_6H_5I + N_2 + KHSO_4$$

The Sandmeyer reaction is a valuable procedure for the preparation of halogen derivatives, such as fluorobenzene,[3] that generally cannot be made by other more direct methods. When diazonium salts, which are unstable, and unsaturated bodies react with halogen hydracids alone or, preferably, in the presence of the corresponding cuprous salt, nuclear halogen derivatives are formed and nitrogen is evolved. Although this procedure is comparatively costly, it is thus possible to obtain specific halogenated deriva-

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[1] VAN DRUTEN, The Reaction of Phosphorus Trichloride on Acetic Anhydride, Thesis, University of Leyden (1926).

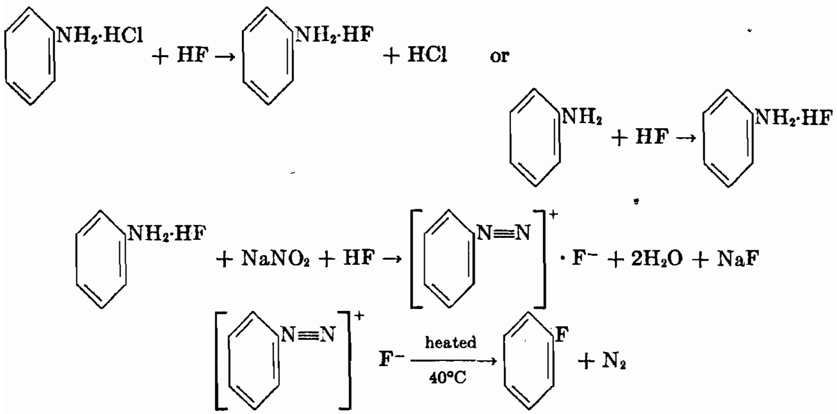
[2] *C.I.O.S. Rept.* XXVI-2, Item 22, I.G. Farbenindustrie, Höchst (Combined Intelligence Objectives Sub-committee).

[3] *B.I.O.S. Final Rept.* 986, Item 22, Part 1.

tives in a high state of purity. In a number of syntheses, the Sandmeyer reaction is used in conjunction with other methods of halogenation to secure polyhalogenated derivatives.

The reaction involves the preparation of a solution of the diazonium halide and gradually adding it to a solution of the corresponding cuprous halide. In the preparation of compounds that are volatile, it is essential to employ a reflux condenser. In some cases, the diazo solution is prepared in the presence of the cuprous halide. Under such circumstances, a solution of sodium nitrite is added to a heated acid solution of the amine and copper salt. The diazotization and replacement of the diazo group then takes place in one operation.

Fluorobenzene is prepared by a modified Sandmeyer reaction from aniline hydrochloride and hydrofluoric acid, followed by a treatment of the resultant aniline hydrofluoride with sodium nitrite.[1] The resulting diazonium salt is decomposed in a HCl-N_2 atmosphere at 40°C to give fluorobenzene. The liberated hydrofluoric acid which boils off at $>20°C$ is condensed and flows back to the decomposing tube. The several reactions in the fluorination process are



BROMINATION

In general, methods similar to chlorination with chlorine and chlorides can be employed in the preparation of bromine derivatives. Because the reaction is milder, the bromination of the paraffin hydrocarbons does not, however, proceed so rapidly or to so great a degree; and with the lower permissible operating temperature, the formation of polybromine compounds occurs to a lesser extent.

In brominations, it is generally advisable to employ a compatible solvent, not only for the organic compound but also for the bromine. Water,

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[1] *F.I.A.T. Final Rept.* 998, I.G. Farbenindustrie, Höchst.

dilute alkali, glacial acetic acid, concentrated sulfuric acid, methanol, chloroform, carbon disulfide, and carbon tetrachloride can thus be employed. The use of such cosolvents serves to ameliorate the reaction and thus subjects it to closer control.

The choice of the solvent will, of course, depend on the reactants employed and their specific reactivity in various solvents. Thus, benzaldehyde takes up bromine in carbon tetrachloride about a thousand times as rapidly as it does in chloroform or carbon disulfide.[1] The bromination leads to the formation of bromobenzyl benzoate according to the following reactions:

$$C_6H_5{\cdot}CHO + Br_2 \rightarrow C_6H_5{\cdot}COBr + HBr$$

$$C_6H_5{\cdot}COBr + C_6H_5{\cdot}CHO \rightarrow C_6H_5{\cdot}COO{\cdot}CHBr{\cdot}C_6H_5$$

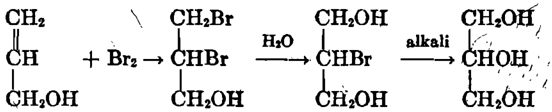
The reactivity of aromatic side-chain compounds toward brominating agents is also influenced by the nature of the solvent. Under comparable conditions, the percentage formation of benzyl bromide from bromine and toluene in various solvents is as follows:[2]

$CS_2{=}85.2$ $CCl_4{=}56.6$ $CH_3COOH{=}4.0$ $C_6H_5NO_2{=}2.0$

This same influence is exhibited not only in the dark, but also in photobrominations. From the preceding data, Bruner has concluded that solvents such as nitrobenzene and acetic acid, which have strong ionizing (dissociating) powers, favor substitution in the nucleus.

Addition Reactions with Bromine. Bromine in aqueous solution forms addition compounds readily with unsaturated organic compounds. This reaction is of considerable interest, since it provides an analytical method for the detection and estimation of double bonds.

Allyl alcohol on bromination takes on two atoms of bromine, one of which is hydrolyzed when the reaction is carried out in aqueous solutions. In the presence of an excess of alkali, the second bromine is split off with the formation of glycerol.[3]



$$\begin{matrix}CH_2\\ \Vert\\ CH\\ |\\ CH_2OH\end{matrix} + Br_2 \rightarrow \begin{matrix}CH_2Br\\ |\\ CHBr\\ |\\ CH_2OH\end{matrix} \xrightarrow{H_2O} \begin{matrix}CH_2OH\\ |\\ CHBr\\ |\\ CH_2OH\end{matrix} \xrightarrow{alkali} \begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}$$

***Addition of* HBr.** Kharasch and coworkers[4] have shown that the addition of HBr to the double bonds of olefinic hydrocarbons or substituted olefinic hydrocarbons is influenced by the presence of either peroxides or

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[1] HERZ and DICK, *Ber. duet. chem. Ges.*, **41**, 2645 (1908).

[2] BRUNER and VORBRODT, *Chem. Zentr.*, **33**, 557 (1909).

[3] STRITAR, *Chem. Ztg.*, **43**, 23 (1919).

[4] KHARASCH, *J. Am. Chem. Soc.*, **55**, 2468, 2521 (1933); **56**, 244, 712, 1212, 1782 (1934); **57**, 2463 (1935).

antioxidants. Normal additions occur in the absence of peroxides; and in practice this condition can be brought about by working under carefully controlled conditions or by the addition of antioxidants to the reaction mixture. Among the antioxidants found to be effective are diphenylamine, thiophenol, and thiocresol, the first being the least effective of the three. Benzoyl peroxide and ascaridole (Δ-2, *p*-menthene-1,4-dioxide) are useful in ensuring a peroxide-catalyzed addition of HBr and HI to olefins.

In Table 6-8 are presented typical data illustrating the influence of peroxides and antioxidants.

TABLE 6-8. INFLUENCE OF PEROXIDES AND ANTIOXIDANTS

Compound treated	Addition agent	Normal product	Addition agent	Catalyzed product
$CH_2{=}CHBr$	Diphenylamine	$CH_3{\cdot}CHBr_2$	Air	$CH_2Br{\cdot}CH_2Br$
$CH_3CH{=}CH_2$	Thiocresol	$CH_3CHBrCH_3$	Benzoyl peroxide	$CH_3CH_2CH_2Br$
$CH_3CH_2CH{=}CH_2$	None	$CH_3CH_2CHBrCH_3$	Ascaridole	$CH_3CH_2CH_2CH_2Br$
$CH_3{-}\underset{\mid \atop CH_3}{C}{=}CH_2$	Diphenylamine	$CH_3\underset{\mid \atop CH_3}{C}BrCH_3$	Ascaridole	$CH_3{\cdot}\underset{\mid \atop CH_3}{CH}{\cdot}CH_2Br$
$CH_3(CH_2)_{10}CH{=}CH_2$	Antioxidant	2-Bromotridecane	Peroxide	1-Bromotridecane

It is clear from the above data that the addition of HBr to the alkenes containing terminal double bonds results in the formation of primary bromides whenever "peroxides" are present in the reaction mixture. Secondary and tertiary bromides are formed during the normal addition in the presence of "antioxidants" in accordance with Markownikoff's rule. In general, the yields of the alkyl halides are high and the formation of the specific product is almost quantitative.

Some olefins, e.g., vinyl bromide and allyl bromide, are very sensitive to peroxides; whereas others, e.g., butene-1, are comparatively insensitive. Kharasch has found that external conditions such as solvents, light, and temperature have a very powerful effect on those systems which are sensitive to peroxides but practically no effect on those which are comparatively insensitive. Peroxides are the most important single factor governing the direction of addition; and, in all probability, this is due to their action on the hydrogen bromide or the unsaturated compound or both *before* addition actually takes place. The physical and chemical agencies such as light, solvent, and temperature exert their peculiar influence on the peroxide molecules or in activating the oxygen liberated by the decomposition of the peroxides.

Bromine Carriers. Zeigler and Spaith[1] showed that a hydrogen atom on a methylene group adjacent to an ethylenic double bond may be easily replaced with bromine by means of N-bromosuccinimide. This reaction proceeds by a free radical chain mechanism,[2] and substitution may occur on either side of the double bond.

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[1] ZIEGLER and SPÄITH, *Liebigs Ann.*, **1942**, 551, 80.

[2] WATERS, *J. Chem. Soc.*, **1937, 2007**; BLOOMFIELD, *J. Chem. Soc.*, **1944**, 114.

The side-chain bromination of toluene and ethyl benzene can be readily accomplished by use of benzoyl peroxide.[1] If Lewis acids are added, nuclear bromination of toluene in ortho and para positions occurs.[2]

IODINATION

Although chlorine and bromine react with methane and other saturated hydrocarbons, iodine enters into combination only under exceptional circumstances. Chlorine and bromine react with hydrogen with the evolution of heat, whereas under the same conditions (400°C) hydrogen iodide is formed with the absorption of heat. Since the heat of formation is a measure of the strength of the bond, then, compared with the halogens of lower molecular weight, iodine exhibits a stronger tendency to combine only loosely and to enter into reversible reactions.

Treatment of Aliphatic Compounds. *Addition.* Iodine and hydriodic acid combine readily with unsaturated paraffin hydrocarbons. When ethylene gas is passed into a warm solution of iodine in alcohol, the two substances unite:

$$H_2C{:}CH_2 + I_2 \rightarrow \underset{\text{Ethylene Diiodide}}{IH_2C{\cdot}CH_2I}$$

With hydriodic acid, the reaction takes place with the formation of ethyl iodide.

Replacement. 1. Chlorine and bromine may be replaced by iodine in many compounds by heating the derivative with an alkali iodide:

$$CH_3{\cdot}CH_2Cl + KI \rightarrow CH_3{\cdot}CH_2I + KCl$$

2. *a.* Alkyl iodides may be prepared by the reaction of PI_3 with an alcohol. In practice, this is generally accomplished by digesting red phosphorus with an anhydrous alcohol and then adding iodine. The mixture is heated under a reflux condenser and finally distilled:

$$3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + P(OH)_3$$

b. They may also be prepared by treating an alcohol with hydriodic acid, the reaction taking place according to the following equation:

$$CH_3OH + HI \rightarrow CH_3I + H_2O$$

The process may be made continuous, by adding the alcohol gradually and keeping the temperature sufficiently high so that the water distills over as it is formed. Methyl iodide is prepared by heating methyl alcohol with sodium iodide and sulfuric acid.

3. The action of iodine on either acetone or alcohol, in a mildly alkaline solution, will yield iodoform

$$C_2H_5OH + 8I + 6KOH \rightarrow CHI_3 + HCOOK + 5KI + 5H_2O$$

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[1] ANDERSON et al., *J. Chem. Phys.*, **21**, 1258 (1953).

[2] SCHMID and KARRER, *Helv. Chim. Acta*, **29**, 573 (1946).

Industrially, iodoform is prepared by electrolysis, at 60–65°C, of a solution of 60 kg of KI, 20 kg of Na_2CO_3, and 80 liters of ethanol per 400 liters of solution. The iodine set free by the current converts the ethanol and the sodium carbonate into iodoform and sodium iodide. In practice, part of the iodine reacts with the caustic alkali formed at the cathode and forms an iodate. Prevention of this reaction by surrounding the cathode with a porous cup brings the yield of iodoform up to about 90 per cent of the theoretical.

Aromatic Compounds. *Substitution.* Direct substitution of iodine into the benzene nucleus is feasible only in the presence of an oxidizing agent. The hydrogen iodide formed simultaneously with the iodo compound is unstable; the iodine in the benzene nucleus is loosely bound; and conditions must therefore be provided to avoid reversibility.

$$2C_6H_6 + I_2 + (O) \rightarrow 2C_6H_5I + H_2O$$

1. Benzene treated in a sealed tube with iodine and iodic acid under suitable conditions will yield iodobenzene. The iodic acid oxidizes the hydrogen iodide as it is formed, thus preventing the reduction of the iodobenzene to benzene.

2. The method of Varma and Panickar, which involves the use of sodium nitrite and fuming sulfuric acid, may be employed for the iodination of aromatic compounds.[1] Nitric acid can be used advantageously as the oxidant for the liberated hydriodic acid. The procedure as applied to the production of iodobenzene involves the reaction of 1.5 moles of iodine with 5.1 moles of benzene in the presence of 6.15 moles of nitric acid. The yield is in excess of 85 per cent of the theoretical. Other benzenoid compounds are iodinated in a similar manner. It should be noted that, in this reaction, all the halogen enters into the benzene compound, unlike ordinary direct halogenations in which half of the halogen used is given off as halogen hydride.

3. Phenols may be iodinated by treatment with iodine in the presence of strong ammonia. 2,4,6-Triiodophenol is prepared quantitatively by treatment of phenol in concentrated aqueous ammonia with iodine until the color of iodine persists. Phenolic compounds, in general, are susceptible to the foregoing method.

FLUORINATION

Under atmospheric conditions, fluorine attacks with violence all organic compounds; benzene, ether, and turpentine take fire immediately on contact with it. Explanations of this violent and disruptive activity that are in harmony with theoretical considerations and thermodynamic data are as follows.[2] Any halogen, X_2, may react by either of two mechanisms:

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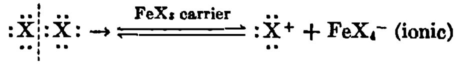
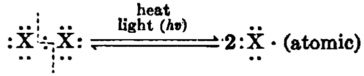
[1] Varma and Panickar, *Quart. J. Indian Chem. Soc.*, **3**, 342 (1926).

[2] Bigelow, Tompson, and Tarrant, *Ind. Eng. Chem.*, **39**, 360 (1947).

(1) ionic, carrier-catalyzed, leads to the active X^+ ion; (2) atomic, often light- and heat-catalyzed, leads to the active X atom. Since fluorine, the



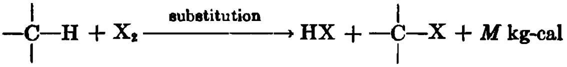
$$:\overset{..}{\underset{..}{X}}:\overset{..}{\underset{..}{X}}: \rightarrow \xrightleftharpoons{FeX_3\ \text{carrier}} :\overset{..}{\underset{..}{X}}{}^+ + FeX_4^- \ \text{(ionic)} \tag{1}$$



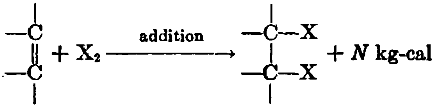
$$:\overset{..}{\underset{..}{X}}:\overset{..}{\underset{..}{X}}: \xrightleftharpoons[\ ]{\text{heat, light } (h\nu)} 2:\overset{..}{\underset{..}{X}}\cdot \ \text{(atomic)} \tag{2}$$

most electronegative of all elements, has a high positive nuclear charge, it should react atomically rather than ionically, because complete removal of an electron from it to form a positive F^+ ion would be very difficult. Consequently, in organic fluorinations fast chain reactions occur and are to be expected.

Another fundamental cause of the violence of these reactions has been mentioned previously in the section dealing with kinetics and thermodynamics, and this is the very high heat of formation of hydrogen fluoride and of carbon-to-fluorine bonds.



$$-\overset{|}{\underset{|}{C}}-H + X_2 \xrightarrow{\text{substitution}} HX + -\overset{|}{\underset{|}{C}}-X + M\ \text{kg-cal} \tag{3}$$



$$\begin{matrix} -\overset{|}{C} \\ \| \\ -\underset{|}{C} \end{matrix} + X_2 \xrightarrow{\text{addition}} \begin{matrix} -\overset{|}{C}-X \\ | \\ -\underset{|}{C}-X \end{matrix} + N\ \text{kg-cal} \tag{4}$$

If X = fluorine, M = 103, and N = 107.
If X = chlorine, M = 23, and N = 33.
Heat of dissociation of C—C bond = 71 kg-cal (approx).

Reactions (3) and (4) represent substitution and addition, respectively. When X is fluorine, the heats of reaction (M and N) exceed the heat of dissociation of a carbon-to-carbon bond by a substantial margin, even without the heat of activation; when X is chlorine, corresponding values do not do this. Consequently, fluorine would be expected to disrupt an organic molecule easily, whereas chlorine should not.

The powerful reactions actually observed can, in general, be moderated and caused to take place in an orderly fashion, first, by breaking up the reaction chains, and second, by dissipating the heat. The more common means for moderating direct fluorinations are as follows:

1. Diluting the fluorine by an inert gas.
2. Conducting the reaction in an inert solvent.
3. Fluorinating by means of compounds which easily release fluorine atoms or molecules, such as $C_6H_5IF_2$, SbF_5, PbF_4, MnF_3, CeF_4, AgF_2, CoF_3, and others.
4. Carrying out the reaction in the vapor phase, within the meshes of a metal packing, with or without other catalyst.

5. Reacting the fluorine with a relatively inert compound.
6. Various combinations of the preceding.

Of these, dilution of the fluorine with an inert gas, which surrounds the halogen with unreactive molecules, has not been successful alone. Conducting the reaction in an inert solvent, which similarly envelops the reactant, has often failed because nearly all organic liquids react with fluorine and fluorocarbons themselves are not good solvents for organic compounds. By combining techniques, Bockemüller[1] fluorinated some aliphatic compounds successfully in carbon tetrachloride solution at 0–15°C. Bigelow and coworkers,[2] however, have found that in the aromatic series these conditions often result in the formation of ClF, which causes deep-seated chlorination of the organic molecules. Liquid hydrogen fluoride has, however, been used successfully as a solvent. The reagents SbF_5 and CoF_3 that release fluorine atoms or molecules have the common advantage that a portion of the heat of fluorination is consumed in dissociating the reagents, and the over-all reaction is thus moderated to a certain extent. Their disadvantage is that they have to be regenerated unless the reactant is sufficiently inert to fluorine to permit use as carrier catalysts, which is usually not the case. Antimony pentafluoride, however, is a powerful fluorinating agent that finds commercial application. Vapor-phase fluorination within the meshes of a metal packing has also proved to be successful, since a large mass of metal (sometimes silver-plated) rapidly conducts heat away from the reaction zone, and the relatively great metal-halide surface tends to break up reaction chains.

The most important means of introducing fluorine into aliphatic compounds is the HF substitution of aliphatic chlorides in the presence of pentavalent antimony salts. A common procedure is to add carbon tetrachloride to a stainless-steel autoclave, then introduce antimony pentachloride, chlorine, and hydrogen fluoride. The autoclave is closed and heated to 100°C until reaction is complete. HCl must be vented at intervals to keep the pressure down to 30 atm.

SbF_3 alone or in the presence of HF will not react with carbon tetrachloride, but if to the mixture bromine, chlorine, or a pentavalent antimony halide is added reaction occurs, forming CCl_3F, CCl_2F_2, and $CClF_3$. Swarts[3] claims that the mixture formed is a double halide of antimony such as $SbCl_2F_3$.

Hydrocarbons may also be fluorinated with HF and $SbCl_5$ mixtures in an autoclave. The first step is the chlorination of the hydrocarbon with $SbCl_5$, followed by chlorine substitution with the pentavalent antimony halide as a second step. The above reactions with pentavalent antimony

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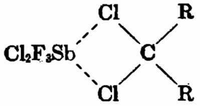
[1] BOCKEMÜLLER. *Ann.*, **506**, 20 (1933).

[2] BIGELOW, TOMPSON, and TARRANT, *loc. cit.*

[3] SWARTS, *Bull. acad. roy. Belg.*, 26R781.

halides are limited to organic halogen compounds that have at least two halides on one carbon; thus the Booth-Swinehart theory of complexes of the



type may be predicted as a logical first-step mechanism of this reaction.

The HF–pentavalent antimony halide reaction is not limited to the methane series but has been applied to longer-chain saturated and unsaturated halogenated hydrocarbons, cyclic olefins, and dienes, and certain of the silica organic derivatives.

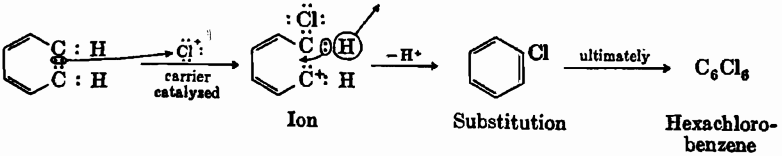
IV. CHLORINATION IN THE PRESENCE OF A CATALYST

The catalytic agents most frequently employed in chlorinations are ferric salts, cupric salts, bromine, iodine, the halides of antimony, tin, arsenic, phosphorus, aluminum, and sulfur, active carbons, and activated clays.

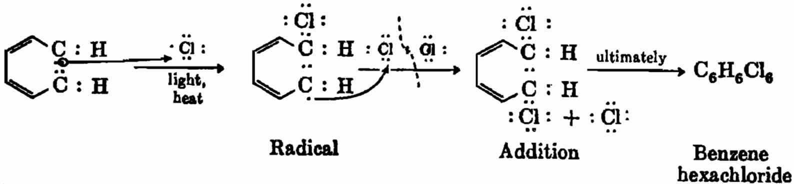
Although the halogen carriers exert a powerful influence in promoting ring substitution in the chlorination of aromatic side-chain compounds and also markedly affect the ratio of disubstituted isomers,[1] they have no considerable effect upon the relative reaction rates of primary and secondary hydrogen atoms in paraffin molecules.[2]

When chlorine acts ionically on an unsubstituted aromatic nucleus as in reaction (1) below, the result is a gradual substitution of Cl for H and the ultimate formation of hexachlorobenzene. When chlorine acts atomically as in reaction (2), in the presence of light or heat, addition occurs, with the ultimate formation of benzene hexachloride.[3]

A.



B.



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[1] Stoesser and Smith, U.S. 1,946,040 (1934).

[2] HASS, MCBEE, and HATCH, *Ind. Eng. Chem.*, **29**, 1337 (1937).

[3] BIGELOW, TOMPSON, and TARRANT, *loc. cit.*

Iron Salts as Catalysts. Ferric chloride is employed not only for reactions involving the replacement of hydrogen by chlorine in the aromatic nucleus, but also for accelerating numerous other chlorinations. The preparation of carbon tetrachloride from carbon disulfide is frequently brought about by the catalytic effects of iron. In the absence of iron, perchloromethyl mercaptan is formed.

Antimony pentachloride is an excellent chlorine carrier. It has been used extensively in the past for the manufacture of tetrachloroethane, ethylene dichloride, and tetrachlorophthalic anhydride, but most of these chlorinations have been converted to ferric chloride procedures.

Bromine and iodine, because of their capacity to form mixed halogens, e.g., BrCl, BrF_3, and ICl which have a low energy of activation, are excellent halogenation catalysts. In general, it can be stated that small quantities of iodine and bromine are frequently added along with other less costly chlorine carriers, and the literature records numerous examples of such halogenations.

The atomic reactions of iodine or bromine are often speeded up by the introduction of small amounts of chlorine or fluorine into the reaction mass. As little as 0.015 mole of elemental fluorine will initiate the reaction of atomic chlorine with benzene to form hexachlorocyclohexane.

Sulfur and sulfur chloride, S_2Cl_2, are efficacious catalysts. They have been used for the conversion of glacial acetic acid into monochloroacetic acid, the latter compound being employed for the synthesis of ω-chloroacetophenone (tear gas) and 2,4-dichlorophenoxyacetic acid. It is necessary to carry out this chlorination at the boiling point of glacial acetic acid; for, in the cold, acetyl chloride is obtained.

In the presence of sulfur or antimony pentasulfide, CS_2 is transformed into CCl_4. This reaction may be carried out in iron equipment simply by bubbling chlorine gas through boiling carbon disulfide containing free sulfur.

Chlorinations Catalyzed by Active Carbon. When carbon of different densities is subjected to superheated steam, its surface is vaporized, forming capillaries which have the property of absorbing gases and compressing them into much smaller volumes. This compression, possibly combined with the catalytic effect of the metal impurities present in the carbon, promotes reactions such as halogenation, hydrohalogenation, or dehydrohalogenation. The character of the metallic impurities, the absorption power of the carbon, the density of the carbon, and the method of capillary formation all materially influence the type of reaction and the life of the catalyst. Often materials are added to these carbons to modify their properties.

Activated Clays. A number of the so-called activated clays originally used in petroleum-refinery operation have found commercial application in halogenation reactions. The geological materials are bauxite, montmorillonite, and attapulgite which have been washed and calcined at 250–500°C to a controlled volatile hydrate content. The bauxite types based on Al_2O_3 are more drastic as chlorinating agents, often leading to unsaturation and cracking of the carbon chains; the other two minerals, based mainly on the aluminum and magnesium silicates, are gentler in action and promote halogenation without chain breakage and often ring closure. As in the case of active carbons, the metallic impurities and methods of preparation materially influence the course of the reaction and the life of the catalyst.

V. PHOTOHALOGENATION

Photohalogenation can be broadly defined as the effect of electromagnetic radiation on halogenation reactions and includes reactions which may be produced by all wavelengths from those of radio waves through x-rays, gamma rays, etc., into cosmic rays. When radiation is absorbed by molecules, they are either raised to higher energy levels or dissociated. The molecules in higher energy levels may suffer several different fates, including dissociation, loss of energy by collision, loss of energy through the emission of fluorescent light or heat, or reaction with other molecules at collision.

The amount of energy required to raise a molecule to a higher energy level is called a quantum. One of the factors that make up a quantum is a true energy value given in ergs and called Planck's constant, but the formula for a quantum is

$$h \times \text{constant/wavelength in cm}$$

thus, the requirement of energizing a molecule of halogen is ruled by the frequency of the electromagnetic radiation.

Halogen	Energy of dissociation into two normal atoms, ev	Equivalent wavelength, A	Minimum frequency to form an excited atom, A
Chlorine	2.480	5,000	4,785
Bromine	1.970	6,288	5,100
Iodine	1.542	8,000	4,989
HCl	4.300	2,800	2,500
HBr	.....	3,350	?
HI	.....	3,850–4,100	?

Unfortunately, in most photohalogenation reactions other than those involving chlorine, the competing reactions of dissociation to heat, light, normal state atoms, etc., are many times greater than the desired reaction, and as a result photohalogenation has been limited commercially to chlorinations where chain mechanisms are favored. The recent entry of private industry into nuclear reactions may change the economics of these reactions in the future.

When a gas is dissolved in a liquid or condensed to a liquid, each molecule becomes so closely surrounded by other molecules that its behavior is strongly modified by its neighbors. If the liquid is nonpolar, then the behavior of the excited atom may not differ much from that of gaseous reactions, but when the liquid is highly polar and complex formation exists, then behavior may differ widely from the gas-phase conditions.

This polar solvent effect is used to advantage by Neubauer[1] and others in modifying the chlorination of benzene to hexachlorocyclohexane.

VI. DESIGN AND CONSTRUCTION OF EQUIPMENT FOR HALOGENATION

From the preceding survey of halogenations, it is obvious that no general rules can be formulated for the design and construction of the plant. Conditions vary greatly as regards not only continuous or batch operations but also the chemical and physical characteristics of the organic compound undergoing treatment. Reactions in the vapor phase, particularly those accelerated by light (Fig. 6-9), require equipment that differs markedly from that which is suitable for the liquid-phase chlorination of olefins, paraffins, benzene, carboxylic acid, etc. For this reason, flow diagrams have been included in the technical section of this chapter which describe the design and construction of equipment for typical industrially important halogenations.

With nonaqueous media, apparatus constructed of iron and lined with plastics, such as Teflon, Kel-F, Saran, polyvinyl chloride, polyesters, epoxy resins, or with stoneware, enamel, porcelain, glass, lead, nickel, Inconel, stainless steel, Hastelloy, Duriron, glazed tile, carbon brick, Karbate, titanium, tantalum, and zirconium can be used for the whole plant or specific apparatus.

In aqueous media where hydrochloric and hypochlorous acid and halogens are present in either vapor or liquid phase, the utility of the above materials of construction is severely limited and can best be determined by rates of corrosion study during pilot laboratory operation. Tantalum, zirconium, and titanium are usually resistant but expensive. The plastics are of variable resistance and are severely limited by temperature and solvent attack. Stoneware, Karbate, glass, glazed tile, carbon brick, and enameled steel all have utility within rigid limits. The other metals and alloys are usually questionable but may be desirable for replaceable parts

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[1] Neubauer et al., U.S. 2,717,238 (1955).

subject to wear on pumps, agitators, etc. In dilute solutions, wood is satisfactory where conditions allow it to swell and seal pores, cracks, etc. Care must be taken that hoops, tie rods, etc., are coated with an inert material such as tar, pitch, silicates, epoxy and polyester resins, polyvinyl chloride, etc. For hydrochloric acid, rubber-lined steel is excellent at low temperatures and in the absence of organic solvents. Major piping advancements have been made in the cutting, welding, annealing, and installation of Pyrex glass, and many commercial plants have installed and are using this material. Rigid polyvinyl chloride and reinforced polyester piping are of major importance in handling both aqueous liquids and gases under extreme corrosion conditions.

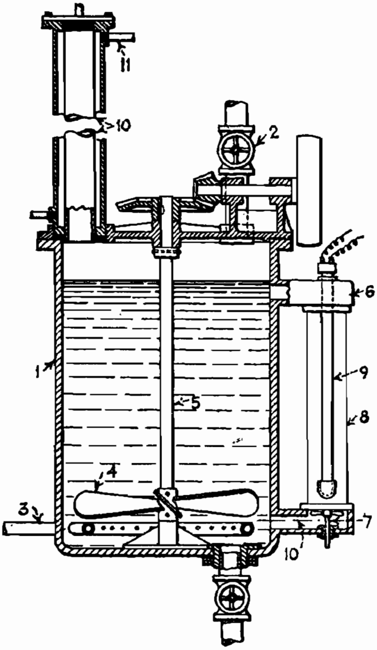
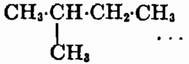
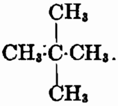


FIG. 6-9. Apparatus for photochlorinations.

Iron valves with resistant liners of porcelain, rigid polyvinyl chloride, plasticized Teflon, or Kel-F have to a great extent solved many of the major problems of valve corrosion. Gasketing materials range from Teflon to the conventional elasticized asbestos materials and if properly chosen and installed are seldom an operating problem. Light wells and piping are easily made of glass and quartz, with varieties available for transmission of frequencies as high as 2,200 A. Care must be taken in setting up a process unit to avoid use of materials which can set up galvanic action when immersed in the reaction media. It is usually desirable in the pilot laboratory stage to make measurements of potential across proposed materials under operating conditions.

VII. TECHNICAL HALOGENATIONS

Chlorination of Pentanes. The chlorination of any of the lower paraffins can be carried out according to the following procedure, which was developed by Ayres for the production of amyl alcohols.[1] The source of pentane is natural-gas gasoline, the lower fractions of which yield the following pentanes:

		Bp, °C
Normal pentane,	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$	36.0
Isopentane,	 $CH_3\cdot\underset{\displaystyle CH_3}{\underset{\vert}{CH}}\cdot CH_2\cdot CH_3$	28.0
Tetramethylmethane,	 $CH_3\cdot\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}}\cdot CH_3$	9.5

The reactions involved in this procedure may be simply expressed as follows:

$$C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$$
$$C_5H_{11}Cl + NaOH \rightarrow C_5H_{11}OH + NaCl$$

Since there are three pentanes, eight possible amyl chlorides, and therefore eight arrangements of the alcohol $C_5H_{11}OH$, the process is not so simple as indicated in the equations above. In the commercial synthesis, normal pentane and isopentane (2-methylbutane) are submitted to chlorination and subsequent hydrolysis.

The chlorination of pentane is accomplished in equipment represented diagrammatically in Fig. 6-10, as follows: pentane (normal or iso) is introduced into the system and is saturated with hydrogen chloride from the cycle of operations. The hydrocarbon is pumped at 75 psig pressure through a heater and vaporized at 85°C. It then passes into a venturi throat where it comes into contact with chlorine vapors which are supplied at 50°C and 60 lb pressure. At this point, the velocity of the pentane vapors should be above 60 mph and the volume ratio of hydrocarbon to chlorine about 15:1.

Under these conditions of excellent mixing of chlorine and hydrocarbon at low temperature and in the absence of an activating agent, no ignition occurs and the resulting mixture has such a low reaction velocity that the reaction wave will not travel backward from the reactor to the mixer.

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[1] AYRES, *Ind. Eng. Chem.*, **21**, 899 (1929).

The reaction vessel is controlled at 250–300°C. The chlorine-free reaction gases pass through the heat exchanger and a cooler before entering a rectifying tower. The rectifier is supplied with a large body of refluxing pentane and chlorinated pentane from the dephlegmator. The refluxing mixture serves to condense most of the organic compounds but permits the hydrogen chloride and some uncondensed pentane to pass on. These residual gases are cooled and bubbled through pentane entering the system. The hydrogen chloride combines with any moisture in the paraffin hydrocarbon and is separated as hydrochloric acid by agglomerization and decantation.

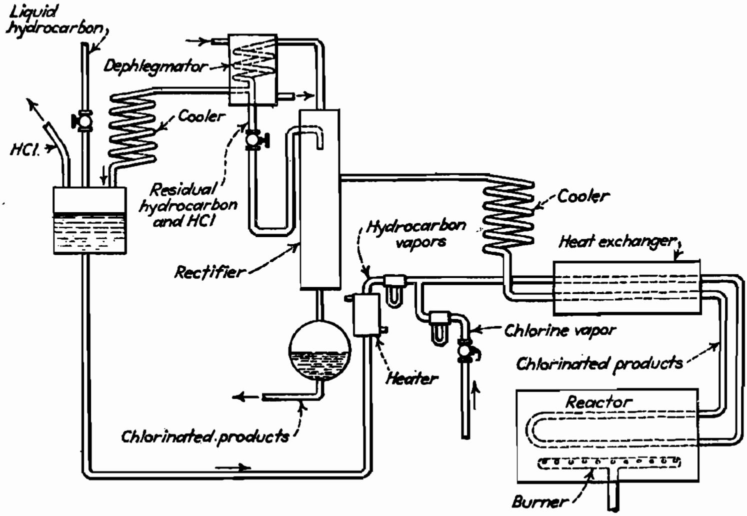

FIG. 6-10. Plant layout for chlorination of pentane and other paraffin hydrocarbons.

Any amyl chloride returned to the reaction zone may be converted to polychlorides either by dehydrochlorination to amylene followed by addition chlorination to dichloride or by direct substitution of hydrogen with additional chlorine. Even with a 15:1 hydrocarbon:chlorine ratio, about 5 per cent dichloride is formed.

According to Hass, chlorination of the pentanes yields all possible isomers, and when the reaction is carried out at 300°C, the following ratios are obtained:

From *n*-pentane: 24 per cent primary, 76 per cent secondary.

From isopentane: 50 per cent primary, 28 per cent secondary, 22 per cent tertiary.

Allyl Chloride : High-temperature Chlorination of Propylene. Allyl chloride is manufactured by the noncatalytic chlorination of propylene in the vapor phase at about 500°C in adiabatic reactors. The principal reaction involved is the substitution of an atom of chlorine for an atom of hydrogen in the propylene molecule:

$$Cl_2 + CH_2{:}CH{\cdot}CH_3 \rightarrow CH_2{:}CH{\cdot}CH_2Cl + HCl$$

The chief secondary reaction is the further chlorination of allyl chloride to 1,3-dichloropropane. Another side reaction is the additive chlorination of propylenes to 1,2-dichloropropane. This reaction is favored by low temperatures and, at a reaction temperature of 200°C or lower, takes place to the virtual exclusion of substitutive reactions. Dichloropropane is always present to an appreciable extent even with reaction temperatures as high as 600°C.

A schematic flow diagram indicating the essential equipment in the allyl chloride process is shown in Fig. 6-11.[1] Propylene from wet storage flows through a bayonet-type cooler located in the bottom of the dry propylene storage tank and then through a coalescer where water precipitated by chilling is drawn off at intervals. From the coalescer, wet propylene is directed to the driers which are packed with activated alumina and are operated alternately, one being regenerated while the other is in operation. The dried propylene flows to the dry propylene storage tank which is self-refrigerated by evaporation of propylene.

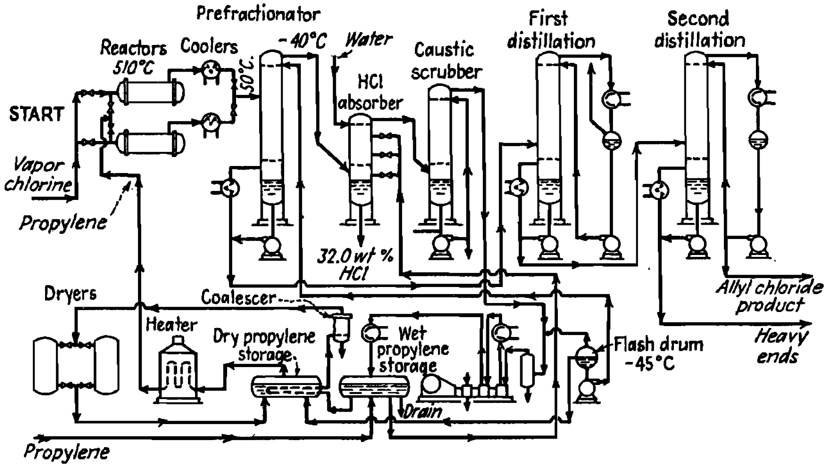

FIG. 6-11. Flow diagram of allyl chloride plant.

Gaseous propylene for chlorination is drawn as a vapor from the top of

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[1] FAIRBAIRN, CHENEY, and CHERNIAVSKY, *Chem. Eng. Progr.*, **43**, (6), 280 (1947).

the dry storage tank and flows to the heater. Here it is heated to whatever temperature is required to maintain the subsequent chlorination temperature.

Liquid chlorine drawn from storage is vaporized, using hot water for heating, and passes to the reactors at a pressure of about 60 psig. A pressure recorder-controller regulates the flow of liquid to maintain constant pressure in the vaporizer.

Each reactor has its own product cooler, and pairs of reactors and coolers operate alternately to permit cleanout of carbon. The cooled reactor product is fed directly to the prefractionator whose function is to separate the organic chlorides from propylene and hydrogen chloride. Liquid propylene from storage is used as reflux, its flow being regulated by a recorder-controller. This reflux is cooled to about −40°C, the dew point of the top stream from the prefractionator, by self-refrigeration in a propylene flash drum.

The overhead product from the prefractionator, comprising propylene and hydrogen chloride, passes into the hydrogen chloride absorber where aqueous hydrogen chloride of commercial strength is produced. Here, liquid propylene is injected to remove the heat of absorption. Propylene leaving the absorber is first scrubbed with caustic to remove traces of hydrogen chloride and is then directed to the suction side of the recycle compressor. This compressor also handles the propylene from drier regeneration and the vapor from the prefractionator reflux flash drum. After condensation, the combined propylene recycle stream is returned to the wet propylene storage tank.

Crude allyl chloride from the bottom of the prefractionator is refined by taking top and bottom cuts in two continuous distillation steps. In the topping operation, light ends and traces of propylene are removed as vapors; in the second distillation step, finished allyl chloride is taken overhead, and the bottom material is sent to storage.

Operating Factors. As can be seen from Fig. 6-12, a temperature range of 500–510°C represents an optimum for allyl chloride production. Lower temperatures are conducive to addition chlorination, while higher temperatures favor formation of benzene. The exothermic heat of chlorination is removed with the excess of propylene leaving the reactor. If the propylene ratio is increased, more sensible heat per mole of chlorine reacting is removed, and the heat input to the reactor must be increased to maintain the desired temperature. This is done by increasing the propylene preheat temperature. Pressure has little influence on the course of the principal reactions. Although increased pressure is conducive to carbonization, this factor is not severe at the relatively low pressures (about 15 psig) employed in the plant.

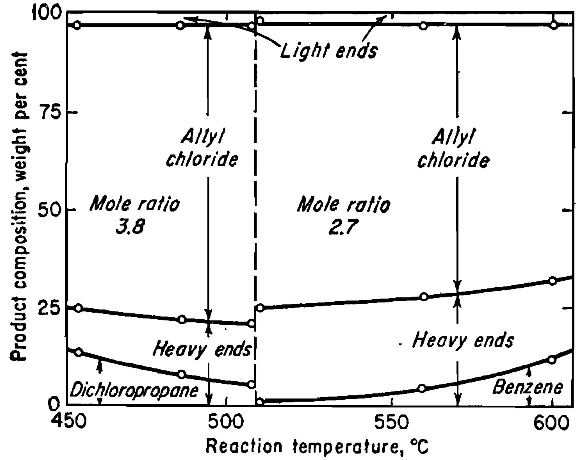

FIG. 6-12. Propylene chlorination: effect of reaction temperature on product compositions.

Thermochemistry of Allyl Chloride Manufacture. The calculated heats of reaction of allyl chloride and by-products of reaction are shown below in Table 6-9.

TABLE 6-9. CALCULATED HEATS OF REACTIONS, ALLYL CHLORIDE MANUFACTURE

Substance	Reaction	Heat of reaction, kg-cal/mole		
		ΔH_{355}	ΔH_{298}	ΔH_{273}
Allyl chloride	$CH_2:CH \cdot CH_3 + Cl_2 \rightarrow CH_2:CH \cdot CH_2Cl + HCl$	−26.7	−26.8	−26.8
2-Chloropropene	$CH_2:CH \cdot CH_3 + Cl_2 \rightarrow CH_2:CCl \cdot CH_3 + HCl$	−29	−29	−29
Isopropyl chloride	$CH_2:CH \cdot CH_3 + HCl \rightarrow CH_3 \cdot CHCl \cdot CH_3$	−16.7	−16.5	−16.4
1,3-Dichloropropene	$CH_2:CH \cdot CH_3 + 2Cl_2 \rightarrow CHCl:CH \cdot CH_2Cl + 2HCl$	−51	−51	−51
2,3-Dichloropropene	$CH_2:CH \cdot CH_3 + 2Cl_2 \rightarrow CH_2:CCl \cdot CH_2Cl + 2HCl$	−55	−55	−55
1,2-Dichloropropane	$CH_2:CH \cdot CH_3 + Cl_2 \rightarrow CH_2Cl \cdot CHCl \cdot CH_3$	−44.0	−44.1	−44.1
Heavy ends	....	−46	−46	−46

Chlorination of Acetylene. *Tetrachloroethane.* The production of tetrachloroethane by the addition chlorination of acetylene is probably best carried out by the Wacker process.[1] Here a large body of the final product, tetrachloroethane, is used as a diluent for the reacting gases; anhydrous ferric chloride is the catalyst, and the reaction is carried out under reduced pressures. The principal facilities (Fig. 6-13) are a tetrachloroethane generator which comprises a dephlegmator superimposed on the reactor (chlorinator) and a chlorine absorption tower that is integrated with a cooling system.

The generator is made of mild steel; the upper portion which is in con-

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[1] *B.I.O.S. Final Rept.* 1056, Item 22; *F.I.A.T. Final Rept.* 843.

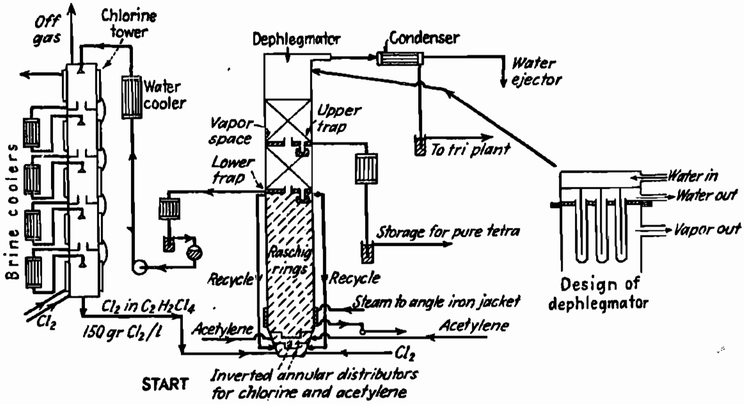

FIG. 6-13. Wacker process: manufacture of tetrachloroethane.

tact with tetrachloroethane is homogeneously lead-lined. The reaction zone is packed with earthenware rings. Two liquid traps are located in the vapor space, one just above the liquid level and the other about 2 m higher. From the lower of these traps, the tetrachloroethane required to feed the chlorine tower is withdrawn; from the upper trap, the pure product for storage is taken. At the lower part of the reactor there is an outside jacket for steam to heat the tetrachloroethane to the reaction temperature when restarting and for distilling the product when the polychloro content of the chlorinator charge reaches a maximum of 30 per cent. In the conical base of the reactor, provision is made for the separate admission of the reactants and their thorough mixing.

The dephlegmator is a series of closed tubes, each being supplied with cold water by a dip pipe. Its performance in the operations may be seen from the accompanying data:

Surface area of cooling area	50 sq m
Temperature of vapor leaving dephlegmator	40°C
Reflux rate	10 tons/hr
Product removal from upper tray	1 ton/hr
Dry acetylene feed rate	140 cu m/hr
Chlorine feed rate	284 cu m/hr
Composition of vapor condensed in final vapor cooler	10% dichloroethylene, 90% $C_2H_2Cl_4$

The exit vapors from the dephlegmator pass to a condenser and then to a stoneware water ejector that maintains a pressure of 120–130 mm Hg abs in the vapor space of the generator.

The chlorine tower is built in five jacketed sections, each separated by a liquid trap plate and packed with Raschig rings. Brine at −15°C is circulated in the jackets, and liquid is withdrawn from each plate, cooled in the external cooler, and returned to the head of the packing in the section immediately below. The function of the chlorine tower is the preparation of a dilute solution of Cl_2 in $C_2H_2Cl_4$. The tetrachloroethane is withdrawn from the bottom liquid trap of the generator, cooled by water from the operating temperature of 80–90°C to 20°C, and then to −10°C by the brine coolers. Weak chlorine is fed into the base of the tower, and a solution of 150 g per liter in tetrachloroethane is returned to the base of the reactor.

The use of high-purity chlorine containing only small amounts of dissolved impurities has been shown to be advantageous in preventing formation of undesirable by-products in this chlorination of acetylene. It is believed, however, that this absorption procedure is no longer used because the yield of $C_2H_2Cl_4$ is relatively low.

Process Operations. The chlorinator (generator) is charged with 16,000 kg of pure tetrachloroethane and about 100–150 kg of anhydrous ferric chloride. Steam is turned on the jacket and the liquid heated to 70°C. The pressure is reduced in the gas space to 130 mm Hg abs, and chlorine is admitted at the base. Acetylene is admitted when the gas space contains free chlorine and each gas rate is adjusted, the chlorine being increased first and then the acetylene, but the acetylene flow is always just less than half the chlorine until the full plant rates are reached.

The level of liquid in the vessel is observed in a sight glass which collects pure condensate from the vapor space and returns it to the vessel below the liquid level. This arrangement always ensures a constant flow of pure tetrachloroethane through the sight glass and prevents blockages. The level is kept reasonably constant by adjusting the rate of offtake of liquid from the upper plate.

Chlorination is continued until heavies (C_4 and C_5 chloro compounds) have built up to a maximum of 30 per cent in the generator liquid. When this concentration is reached, the reaction is stopped and steam is admitted to the jacket. The tetrachloroethane is distilled off and is withdrawn from the upper plate. When most of the tetrachloroethane has been recovered, the heavies are run to a batch lime-slurry treatment vessel, and after refluxing with lime slurry, the product is steam distilled and finally fractionated in batches to recover trichloroethylene and perchloroethylene. This interruption is necessary once or twice a month.

Trichloroethylene. Tetrachloroethane from the previous operations is fed with 90 per cent of the required lime slurry to the lower section of a conversion tower, the remainder of the lime slurry being delivered to the head of the middle section. Live steam is blown into the liquid at the base of the tower to maintain a temperature of 103°C. Dehydrochlorination takes place, and the trichloroethylene vapor rising in the tower is scrubbed

$$2C_2H_2Cl_4 + Ca(OH)_2 \rightarrow 2C_2HCl_3 + CaCl_2 + 2H_2O$$

with lime slurry to remove traces of acid. It is then separated from the bulk of the steam by fractionation at the top of the tower. The wet trichloroethylene vapor is condensed, freed of water in an automatic water separator, fractionally distilled, and finally stabilized by the addition of triethylamine (20 g per 1,000 kg).

Trichloroethylene from the preceding operations is used at I.G. Farbenindustrie, Höchst,[1] for the manufacture of chloroacetic acid. Unlike the chloroacetic acid processes described later, this method merely involves reaction of trichloroethylene with sulfuric acid, which acts as a hydrating agent.

$$CHCl{=}CCl_2 + 2H_2O + (H_2SO_4) \rightarrow ClCH_2COOH + 2HCl + (H_2SO_4)$$

Preparation of Monochloroacetic Acid. *Phosphorus Trichloride as Catalyst.* Monochloroacetic acid is prepared by passing chlorine through glacial acetic acid heated to 100°C, phosphorus trichloride being used as a catalyst.

The plant assembly may be arranged in the manner shown in Fig. 6-14. The acetic acid is stored in aluminum tanks of any suitable size. The acid is run into a scale tank prior to delivery to the chlorinator. The chlorinator is a large steam-jacketed enameled vessel. The top of the vessel is equipped with connections for acetic acid, chlorine, air, effluent gases, condensate,

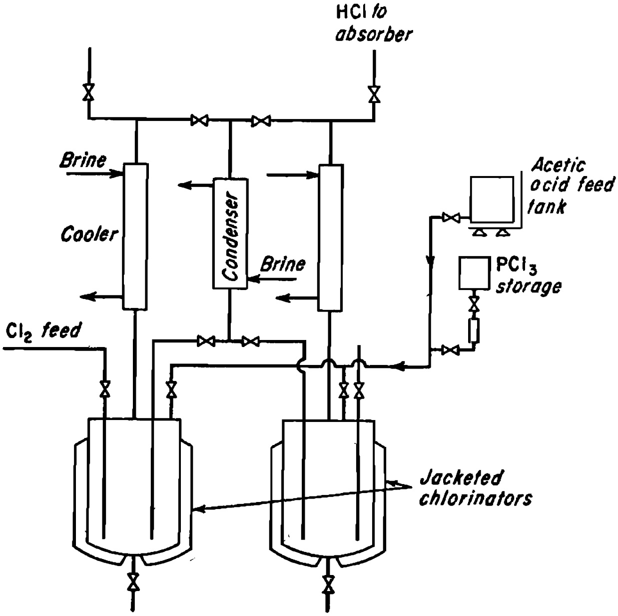

FIG. 6-14. Flow diagram, preparation of chloroacetic acid.

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[1] *B.I.O.S. Final Rept.* 929, Item 22; *C.I.O.S. Rept.* XXVI-11, Item 22.

discharge, and a thermometer well. The jacket of the chlorinator is connected to both water and steam lines. The condensing system comprises a vertical reflux cooler, through which the vapors rise, and a return condenser to complete the condensation. The noncondensable gases are trapped out while the condensate is returned to the chlorinator below the surface of the reaction mixture.

A charge consisting of 365 lb of glacial acetic acid and 12 lb of phosphorus trichloride is delivered to one of the chlorinators. Brine is shut off the jacketed reflux condenser of the adjoining finishing chlorinator and gas is run into the newly charged chlorinator to absorb HCl, acetyl chloride, and vented acetic acid. Once this absorption is complete, the chlorinator is heated to 100°C and chlorine admitted at a rapid rate, 40–60 lb per hr.

During the first part of the run, the circulation of brine through the reflux condenser system must be limited to avoid crystallizing the acetic acid. As chlorination proceeds, the quantity of acetic acid distilling off decreases, and the circulation of brine can be increased accordingly. Since the reflux condenser prevents the passage of any considerable quantity of acetic acid vapors to the return condenser, the latter may be kept at approximately 0°C to ensure the condensation of acetyl chloride.

If a high-purity monochloroacetic acid is desired, chlorination is discontinued after half a mole of chlorine is added per mole of acetic acid; but if a crystallized commercial grade is required, a full mole of chlorine is used.

The approximate composition of the two chlorinated products is shown in Table 6-10.

TABLE 6-10. APPROXIMATE COMPOSITION OF CHLORINATED ACETIC ACID

	Moles Cl_2 added per 100 moles acetic acid	
	50	100
Moles Acetic acid	46	1
Moles Monochloroacetic acid	48	86
Moles Dichloroacetic acid	1	5
Moles Residue	3	3

Chloroacetic Anhydride as Catalyst.[1] At the Gersthofen plant of I.G. Farbenindustrie, chloroacetic acid was made by the chlorination of acetic acid, using chloroacetic anhydride $CH_2Cl\cdot CO\cdot O\cdot CO\cdot CH_3$ as a catalyst. The catalyst was formed *in situ* by the action of SCl_2. The process is cyclic and may be represented diagrammatically as follows:

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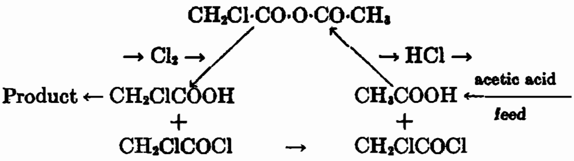
[1] *B.I.O.S. Final Rept.* 929, Item 22.



The chlorinators are 3-cu m homogeneously lead-lined steam-jacketed vessels which are charged with 2,000 liters of 98–100 per cent acetic acid from aluminum tanks and pipelines (Fig. 6-15). Then 25 liters of acetic anhydride is run in from an aluminum stock tank through a glass measuring vessel and 3–5 kg of sulfur is added. The temperature is brought up to 100°C, and gaseous chlorine is delivered through an orifice meter and silver dip pipe with distributor. About 70 hr is required for the chlorination, and the product blown to the crystallizer contains:

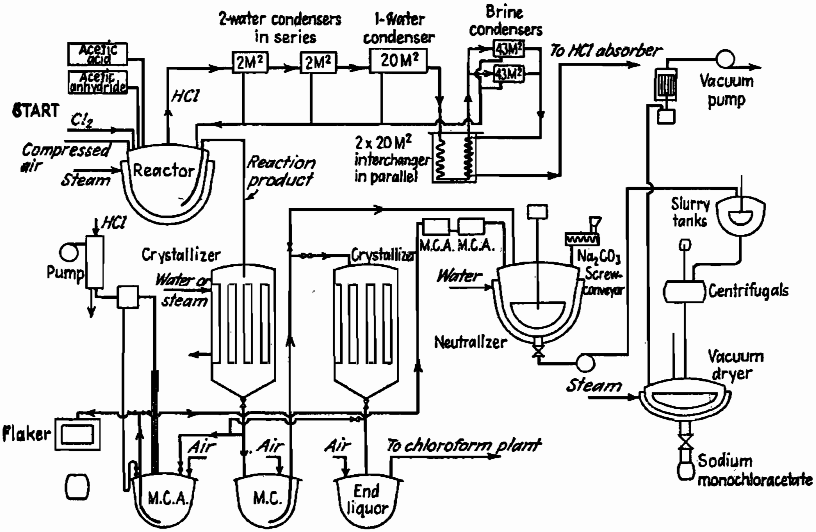


FIG. 6-15. Flow diagram, manufacture of monochloroacetic acid.

	Per Cent
Monochloroacetic acid (MCA)	93.0
Dichloroacetic acid (DCA)	6.5
Trichloroacetic acid (TCA)	0.5

The hydrogen chloride evolved during the reaction is drawn through a 9-in. lead outlet pipe, serving as an air cooler, through two small and one large water-cooled lead coolers in series, from which the condensate returns to the reactor. The residual gas travels through a brine cooler (−45°C) that permits heat exchange with gas from the final condensers. The residual hydrogen chloride goes to an absorption plant.

The chloroacetic acids in the plastic-coated vertical tube crystallizers are permitted to cool and crystallize for a 36-hr period. The mother liquor is drained off into the receivers (MC), from which it is blown to a second crystallizer. The monochloroacetic acid crystals in both crystallizers are melted and run by gravity into the MCA receivers. The end liquor contains about equal parts of mono- and dichloroacetic acids and is used for the production of chloroform (see next section).

The pure acid is delivered by air pressure from the MCA receiver, through silver pipelines to a plastic-coated, tile-lined, steam-jacketed vessel, from which it flows to a totally enclosed cast-iron drum flaker. The feed tank and flaker are both vented to a chimney through a baffle box.

The purity of the monochloroacetic acid is 99 per cent, the balance is dichloroacetic acid. The raw-material requirements per ton of product will be as follows:

Acetic acid	0.641 ton
Chlorine	0.782 ton
Sulfur	4.0 kg
HCl recovered	0.357 ton

The service charges per ton of monochloroacetic acid are:

Water	95.0 cu m
Steam	1.46 tons
Power	93.5 kwhr
Compressed air	42.0 cu m

This chlorination stage using acetic anhydride directly as a catalyst rather than forming it *in situ* by the action of sulfur dichloride lends itself excellently to a continuous chlorination process, and such commercial plants are operating in both the United States and Europe.

When sodium monochloroacetate is desired, the molten MCA from the MCA or MC receivers is delivered to plastic-coated cast-iron neutralizers (Fig. 6-15). Mother liquor from a previous charge is added, and then the equivalent sodium carbonate is run in steadily by screw feed. The resulting slurry is pumped from a bottom discharge line to holding tanks feeding a centrifugal.

Chloroform from End Liquor. The end liquors, comprising about equal parts of mono- and dichloroacetic acids, are used for the production of chloroform. The process involves noncatalytic chlorination to trichloroacetic acid and reaction thereof with milk of lime.

$$Cl_3CCOOH + CaO \xrightarrow{H_2O} CHCl_3 + CaCO_3$$

The end liquor from the monochloroacetic acid process is blown to tile-lined plastic-coated iron pots which serve to feed chlorinators that are homogeneously lead-lined and tiled. These are heated by a jacket containing oil as well as coils for steam at 20 atm. Chlorine is rotametered through a standpipe while maintaining the temperature at 130–140°C. The time cycle is 10–15 days. This operation produces 90 per cent trichloroacetic acid, which is blown from the reactor to a tank provided with a stirrer and which contains milk of lime. This is homogeneously lead-lined and double-tiled and contains sufficient $Ca(OH)_2$ as 11 per cent milk of lime to more than neutralize the acid.

The calcium trichloroacetate is digested at about 100°C. Carbon dioxide and chloroform are evolved and pass to tin water condensers (+10°C), then to a brine-cooled condenser just above 0°C, then to three $CaCl_2$ driers in series, and finally to a brine-cooled copper condenser. The condensate is separated from water, collected in stoneware jars, and distilled in a copper kettle with copper column. Chalk is added to the still, which is operated with a 5:1 reflux ratio. The chloroform vapors are condensed in a silver coil dephlegmator and collected in silver receivers.

Preparation of Chloral

Chlorination of Ethanol. Ethyl alcohol either absolute or containing water is chlorinated to form the hemiacetal of trichloroacetaldehyde from which chloral is liberated by treatment with concentrated sulfuric acid. Ferric chloride may be employed as a chlorination catalyst, but its use does not appear necessary. Five moles of hydrogen chloride is liberated for each mole of chloral produced, and the other by-products include ethyl chloride, ethylene dichloride, and ethyl ether.

Both batch and continuous processes are operated commercially for chloral manufacture, their desirability being based mainly on the size of commercial plant. Hardy[1] presents a diagram (Fig. 6-16) for a basic process for producing chloral.

Chlorination is effected by passing gaseous chlorine through ethyl alcohol in a glass-lined or ceramic tower. The reaction is exothermic, and operating temperatures are controlled by heat transfer through a jacket or internal coils and by refluxing of unreacted alcohol. The resulting product is a mixture of chloral alcoholate, excess alcohol, ethyl chloride, and minor quantities of other chlorination by-products. This mixture is pumped to a glass-lined still pot, where it is mixed with an equal volume of concentrated sulfuric acid and distilled. The sulfuric acid acts to free chloral from the alcoholate and also reacts with liberated alcohol to form ethyl ether. Upon distillation, low-boiling-point by-products, such as ethyl chloride, ethyl ether, and alcohol, are separated first, followed by the chloral "cut" which

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[1] HARDY, *Ind. Eng. Chem.*, **84** (4), 79A (1956).

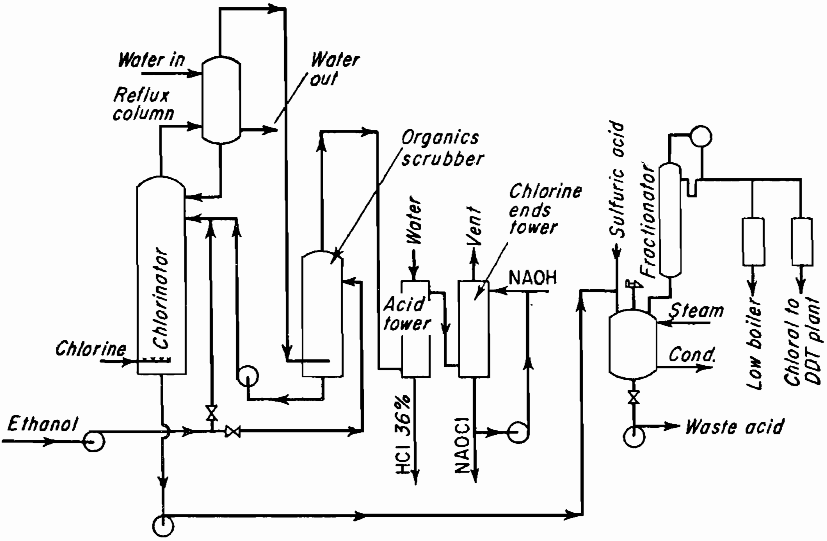


FIG. 6-16. Flow diagram, manufacture of chloral.

is taken as the fraction boiling between 93 and 98°C. Still bottoms consist largely of sulfuric acid, trichloroacetal, and resinous materials.

Hydrogen chloride gas is liberated during the chlorination step. This gas is passed through an alcohol scrubber to recover any entrained alcohol or chloral and any part of the unreacted chlorine gas. It is then absorbed in water to produce 36 per cent hydrochloric acid. Any residual chlorine leaving the acid tower is absorbed in a caustic tower to produce a small amount of by-product sodium hypochlorite.

Chlorination takes place over a period of 25–30 hr. In a batch plant equipped with a single chlorinator, two batches may be completed every 3 days.

Material requirements, by-products, and costs are given in Table 6-11.

TABLE 6-11. MATERIAL AND COST DATA: DDT MANUFACTURE

Raw material	lb/lb chloral	Cost of materials: Per lb raw material	Cost of materials: Per lb chloral
Ethyl alcohol (95%)	0.750	$0.0634	$0.0475
Chlorine	2.582	0.0300	0.0775
Sulfuric acid (as 98%)	1.735	0.0118	0.0205
			$0.1455

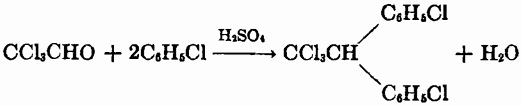
Chlorination of Acetaldehyde. In some commercial processes, acetaldehyde is chlorinated under hydrous conditions to produce chloral. Under certain conditions, this process appears to have an advantage over the chlorination of ethanol because only 3 moles of chlorine per mole of acetaldehyde is theoretically required.

$$CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl$$

One of the determining factors in the choice of starting materials is the availability of markets for the advantageous disposal of by-product hydrochloric acid. The use of acetaldehyde results in the formation of only 3 moles of hydrogen chloride per mole CCl_3CHO, while 4 moles of hydrogen chloride is liberated per mole when ethanol is employed (see discussion, p. 232).

DDT: 1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl) ethane. DDT is probably the best known of the organic insecticides that have been developed in the last twenty years. The greater part of the United States output is produced in plants with very large annual capacities, thus having very low production costs.

DDT is produced when chloral or chloral hydrate is condensed in the presence of sulfuric or halosulfonic acids with monochlorobenzene.



$$CCl_3CHO + 2C_6H_5Cl \xrightarrow{H_2SO_4} CCl_3CH\begin{matrix} \diagup C_6H_5Cl \\ \diagdown C_6H_5Cl \end{matrix} + H_2O$$

Theoretically, there are a large number of possible isomers and related products that can be obtained by this condensation. The para, para isomer, or *p,p'*-DDT, melts at 108.5–109.0°C and constitutes about 70–75 per cent of the product. The *o,p'*-DDT which melts at 74.0–74.5°C is found to the extent of 19–21 per cent. From the standpoint of insecticidal properties, the *p,p'*-DDT is the most effective.

A flow diagram of a typical plant (Fig. 6-17) is described by Hardy.[1]

Chloral and monochlorobenzene are condensed in the presence of fuming sulfuric acid at about 20°C (68°F). Water of reaction is removed by the acid, which separates from the reaction mass and is withdrawn. Excess monochlorobenzene is used to dissolve the DDT as it is formed. This solvent layer is washed with water and dried to recover the monochlorobenzene and to obtain molten DDT which is cooled and ground.

One of the major problems in the cooling and grinding of DDT is based on the crystal-phase transition at about 65°C and the tendency to supercool to a semistable mush. The most suitable procedure appears to be preliminary crystallization at 65–75°C of the molten DDT followed by

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[1] HARDY, *Ind. Eng. Chem.*, **48**, 2, 77A (1956).

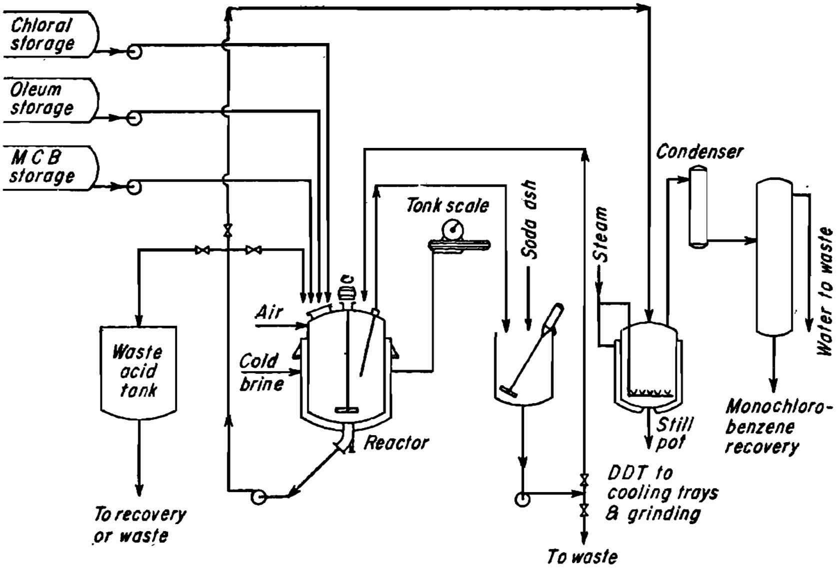


FIG. 6-17. Flow diagram of DDT plant.

mechanical manipulation while reducing the warm crystallized mass down to room temperature.

Assuming a plant to produce 10 million lb of DDT a year costing 3 million dollars to build, and depreciated at the rate of 10 per cent a year, the following figures may be developed.

	Cost per pound DDT
Raw materials	$0.130
Direct labor	0.015
Depreciation	0.030
Utilities	0.015
Maintenance	0.015
Overhead and supplies	0.015
	$0.220

No credits are indicated for muriatic acid, dichlorobenzenes, and spent sulfuric acid. These may be either an appreciable credit or debit, depending on the specific geographical economic conditions.

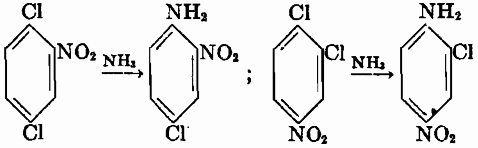
Preparation of Chlorobenzenes

The technical chlorination of benzene is carried out in iron vessels jacketed or cooled to the desired operating temperature. Ferric chloride is generally employed as the catalyst. In the chlorination of benzene, the isomeric *o*- and *p*-dichlorobenzenes are found to accompany the principal mono-chloro compound. The reaction rate of benzene to chlorobenzene is approximately 8.5 times as great as that for chlorobenzene to dichlorobenzenes.[1]

Since the market and uses for dichlorobenzenes are limited, practical considerations sometimes decree the employment of less than the required molecular quantities of chlorine. Under such conditions, some benzene remains unreacted and is subsequently recovered upon distillation of the reaction mass.

Of the two isomeric dichlorobenzenes, the more valuable crystalline para compound (mp, 53°C) is formed in the largest quantities, the ratio of para to ortho usually being greater than 2:1. In most technical operations, the chlorination is continued until a peak in monochlorobenzene is obtained. The composition of the charge will vary somewhat, depending on the temperature employed, the catalyst used, and the rate and degree of chlorination, but it will be approximately as follows: benzene, 9 per cent; monochlorobenzene, 70 per cent; *p*-dichlorobenzene, 15 per cent; and *o*-dichlorobenzene, including polychloro compounds, 6 per cent.

p-Dichlorobenzene has found considerable use as an insecticide, moth repellant, and deodorant, whereas the ortho isomer has been used principally to combat termites and as a solvent. Nitration of the dichlorobenzenes followed by amination by ammonolysis leads to the formation of useful dye intermediates. When these compounds are submitted to amination by reduction, diamino compounds are obtained.



o-Nitro-*p*-dichlorobenzene

p-Chloro-*o*-nitroaniline

1,2-Dichloro-4-nitrobenzene

o-Chloro-*p*-nitroaniline

Monochlorobenzene. The chlorination of benzene is generally carried out in tall narrow tanks, jacketed or surface-cooled (Fig. 6-18). They are provided with a reflux condenser and may have external circulation through a cooler. Chlorine is introduced through an iron distributor pipe near the base of the reactor. Dried benzene is charged to the chlorinator along with a small quantity of anhydrous ferric chloride 0.1–0.5 per cent.

Chlorine is bubbled into the charge, the rate of feed being controlled so as to keep the temperature at the desired point. With outside circulation, the temperature of the chlorinated benzene is kept at 55–60°C. When a sample shows the required density, the current of chlorine is stopped.

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[1] Bourion, *Compt. rend.*, **170**, 1309 (1920).

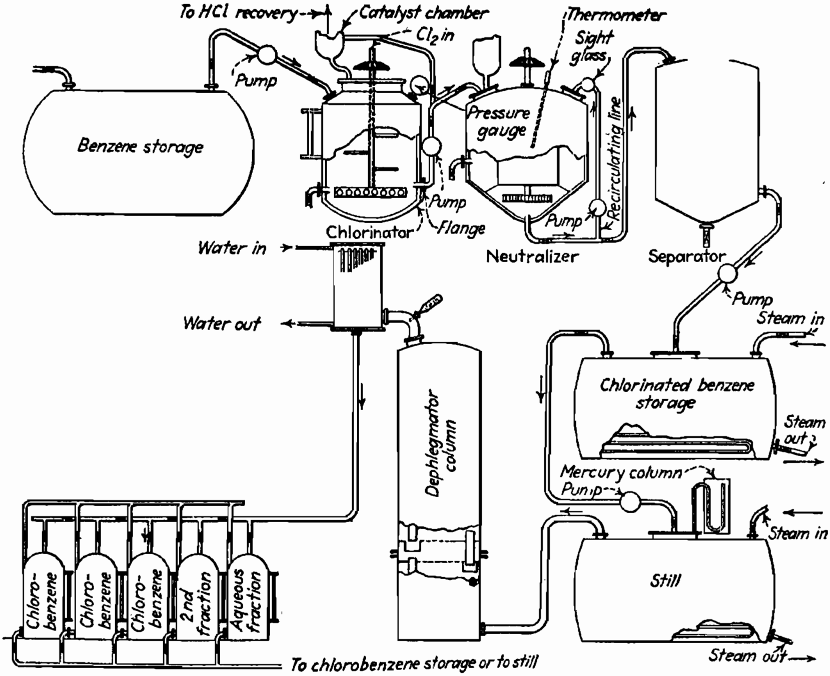

FIG. 6-18. Plant assembly: chlorination of benzene.

When all the benzene is to be chlorinated, the operation ceases when the density is 1.280 at 15°C. The time consumed is approximately 6 hr. At I.G. Farbenindustrie, Leverkusen,[1] the temperature is controlled at 25–40°C and the density of the product at 1.06–1.1 to limit the quantity of polychlorinated benzene.

The hydrogen chloride that escapes through a vent in the dephlegmating or condensing system is washed with chloro- or *o*-dichlorobenzene to remove any organic spray that has been carried away. The scrubbed gas is absorbed in a suitable absorption system.

Neutralization. The chlorinated benzene is permitted to settle and is then drawn off from a side outlet and delivered to the neutralizer. This may be a vertical jacketed steel tank equipped with a reflux or condenser and a vent. A solution of caustic soda is added to the chlorinated benzene as it enters the neutralizer to provide a distinct alkaline reaction to litmus. It is necessary to mix the charge thoroughly to ensure neutrality, and agitation with a corrosion-resistant propeller or turbine type of stirrer is preferred. The charge is kept warm by jacket steam during the neutralizing treatment.

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[1] *C.I.O.S. Rept.* XXIII-25, Item 22.

When repeated tests indicate a faintly alkaline reaction, the chlorinated benzene is delivered to a settling tank and permitted to stand for several hours. The sludge that settles out at the conical base is rich in dichlorobenzenes. The bulk of the charge is withdrawn through a side outlet and pumped to a storage tank, which is heated to prevent crystallization of the charge.

The purification system comprises a horizontal still along with a dephlegmating and condensing apparatus. The chlorinated benzene is heated by steam coils and refluxed until the system is warm. The vapors are then drawn through a tall column to the condenser by a vacuum pump. The first fraction consists of benzene and water. The second fraction (sp gr, 1.090–1.108 at 15°C) is impure chlorobenzene and is added to the batch next to be distilled. The chlorobenzene fraction (sp gr, 1.108 at 15°C) is then run into separate containers. The presence of *p*-dichlorobenzene in the distillate is indicated by a sudden increase in the density of the distillate. This point is watched closely to prevent contamination of the principal product.

The residue in the still is principally dichlorobenzenes. This may be withdrawn after each charge or mixed with subsequent batches of chlorinated benzene until a sufficient quantity of it is accumulated. The para isomer, which has a slightly lower boiling point, can be recovered in a fairly pure state by fractional distillation. The residual ortho compound is contaminated with the para isomer and polychloro derivatives, principally 1,2,4-trichlorobenzene.

Dichlorobenzenes. The dichlorobenzenes (60 per cent or more para, 40 per cent or less ortho isomers) remaining as bottoms in the distillation of monochlorobenzene are run to a cast-iron tank at 50°C and allowed to crystallize in long needles. The mother liquor, which is predominantly *o*-isomer, is filtered off at 10–12°C.

The crude crystals of para-dichlorobenzene are melted and fractionally recrystallized to high-purity material which must then be held in the solid or lump form for a number of hours to permit conversion of the needlelike crystals to the desired monoclinic form suitable for grinding and marketing.

The mother liquor which is predominately ortho-dichlorobenzene is fractionated under vacuum, giving a first fraction high in para-dichloro benzene which is returned to the crystallizer system, a main fraction of high-purity ortho-dichlorobenzene, and a polychlorobenzene fraction which is used in trichlorobenzene production.

Trichlorobenzene. Trichlorobenzene is made at I.G. Farbenindustrie, Ludwigshafen,[1] either directly from benzene or *p*-dichlorobenzene. In its preparation, 7,000 kg of benzene is chlorinated in an iron vessel, with iron filings as catalyst. The temperature is kept at 20–30°C until the specifi

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[1] *B.I.O.S. Final Rept.* 1153. Item 22.

gravity at 20°C reaches 1.22. The temperature is then raised to 55–65°C, and chlorination is continued until the density reaches 1.335 at 50°C. About 14,000 kg of chlorine is required, the chlorination cycle being 6–8 days. The reaction product is neutralized with caustic soda solution in a stirred vessel.

The crude trichlorobenzene is distilled, first at 100–120 mm (*p*-dichlorobenzene sublimes at higher vacuum), and when the setting point of the distillate begins to fall, the pressure is reduced to 20–30 mm. Intermediates with a setting point of 25°C, falling to −10°C and rising to 10°C, distill over, and these are returned to the next distillation. Trichlorobenzene then follows with a setting point rising from 10 to 17°C. The yields are:

	Kg
p-Dichlorobenzene	4,800–4,900
Intermediate fraction I	300
Trichlorobenzene	4,500–4,600
Intermediate fraction II	200
Tetrachlorobenzene	1,000–1,100

A major part of the domestic production of trichlorobenzene is derived from the inert BHC isomers in the production of γ-hexachlorocyclohexane by pyrolysis or treatment with alkalies.

BHC: Benzene Hexachloride or Hexachlorocyclohexane. Benzene is chlorinated in the liquid phase in the presence of an activation agent such as activating light, gamma rays, or elemental fluorine. A mixture of five isomers of 1,2,3,4,5,6-hexachlorocyclohexane is produced. Only the gamma isomer is insecticidally active, and it has great utility for the control of vegetable, field crop, animal, and household insects. The gamma isomer is produced in concentrations ranging from 9–30 per cent of the mixture of crude isomers. The other isomers have no insecticidal value, the delta isomer being toxic to many leafy plants.

Of all the schemes proposed for the addition chlorination of benzene, the continuous cocurrent glass-pipe chlorinator designed by Stormon[1] and modified to include external cooling by Governale and Clark[2] is the most interesting from an engineering standpoint (Fig. 6-19).

The commercial reactor consists of 13 reactor tubes in the recycle section and five tubes in the cleanup section. Each reactor tube consists of a concentric arrangement of a 2-in. Pyrex tube into which are inserted two 40-watt fluorescent lamps, a 4-in. Karbate tube enclosing the reactor section, and an 8-in. steel pipe enclosing the cooling section. Chilled water at 60°F circulates in the annular section enclosed by the steel pipe and removes the heat of reaction, which is estimated and checked calorimetrically to be around 190,000 Btu per lb mole BHC. A reaction velocity constant

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[1] Stormor. U.S. 2,499,120 (1950).

[2] GOVERNALE and CLARK, *Chem. Eng. Progr.*; 52, 281–285 (1956).

of 1.5 min^{-1} is used throughout, although a lower constant should probably apply for the cleanup section. This reactor has a chlorine conversion capacity of around 600 lb per hr and produces 14–15 per cent gamma BHC operating at temperatures in the range 90–100°F. The actual design feed concentration is around 11 weight per cent Cl_2 in order to keep the resulting BHC level below 15 weight per cent of the reactor contents.

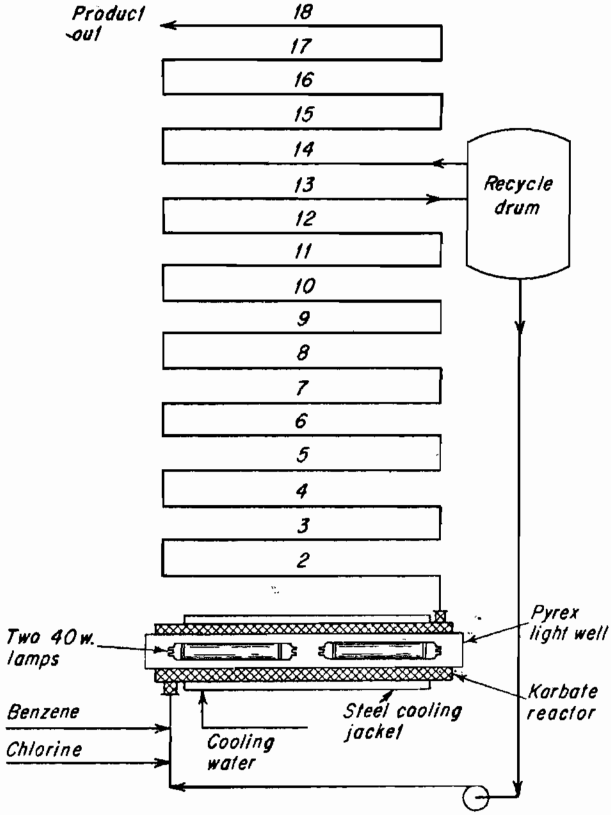

FIG. 6-19. Two-stage BHC photochemical reactor.

As pointed out in the section on photohalogenation, the use of a polar solvent can materially alter the course of a liquid-phase photochlorination. This has been indicated in experimental work by Gonze[1] and Britton et al.[2] and is claimed by Neubauer et al.[3] to give up to 30 per cent gamma isomer content in the mixture of isomers.

[1] Gonze, U.S. 2,513,092 (1950).

[2] Britton et al., U.S. 2,628,260 (1953).

[3] Neubauer et al., U.S. 2,717,238 (1955).

The product leaving the chlorinator is a mixture of 15 per cent benzene hexachloride in a solvent which may be completely removed by evaporation leaving a musty-smelling crystalline product. Most commercial producers, however, evaporate the solvent until a solution just saturate in gamma isomer exists. Under these conditions much of the alpha and beta isomers may be filtered away from the mother liquor, which can then be dried to a fortified BHC of 35–50 per cent gamma content.

A number of processes have been developed for the purification of the gamma isomer to 99+ per cent purity which is commercially marketed as Lindane, named after its original discoverer, T. Van der Linden.[1]

The waste isomers from either the fortification process or the Lindane process can be converted to trichlorobenzene either by reaction with caustic soda or other alkalies

$$C_6H_6Cl_6 + 3NaOH \rightarrow C_6H_3Cl_3 + 3NaCl + 3H_2O$$

or they can be thermally decomposed, with or without catalysts, to trichlorobenzene.

$$C_6H_6Cl_6 \xrightarrow{\Delta} C_6H_3Cl_3 + 3HCl$$

The isomers formed in either case are predominantely 1,2,4-trichlorobenzene and about 10–20 per cent of the 1,2,3-isomer. In the thermal dehydrochlorination, some disproportionation occurs with the formation of dichlorides and tetrachlorides and shifts to the stable 1,3,5-trichlorobenzene isomer can be produced in the presence of catalysts.

Chlorobromomethane. *By Bromination of Dichloromethane.* Chlorobromomethane is prepared by the bromination of dichloromethane, using aluminum filings as catalyst. The basic reactions in the process are

$$6CH_2Cl_2 + 2Al + 3Br_2 \rightarrow 6CH_2ClBr + 2AlCl_3$$

The reäction is not complete, and small amounts of by-products are obtained, thus,

$$3CH_2Cl_2 + 2Al + 3Br_2 \rightarrow 3CH_2Br_2 + 2AlCl_3$$
$$6CH_2ClBr + 2Al + 3Br_2 \rightarrow 6CH_2Br_2 + 2AlCl_3$$

To obtain good yields of chlorobromomethane (CB), it is necessary to use an excess of dichloromethane and slightly more than the calculated amount of aluminum to ensure the absence of free bromine at the close of reaction.[2]

Bromination. First, 92 kg of aluminum filings is introduced into an iron brominating vessel (item 1, Fig. 6-20), 4.5 cu m capacity, brick-lined,

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[1] Burrage and Smart, Brit. 573,693 (1945). U.S. 2,438,900 (1948); 2,553,956 (1951); 2,585,898 (1952). Kimball and Smith, U.S. 2,699,456 (1955). Smith and Sconce, U.S. 2,699,455 (1955).

[2] *F.I.A.T. Final Rept.* 972, I.G. Farbenindustrie, Höchst.

with enameled stirrers and two lead-lined iron condensers in series. Then, 500 kg of dichloromethane is run into the brominator, and 25–30 kg of bromine from flasks (2) is added while stirring. As soon as the temperature has reached 35°C, after approximately 30–50 min, 2,500 kg dichloromethane is run in from measuring vessel (3), thus cooling the charge and controlling the reaction. The temperature of the charge must not be permitted to fall below 25°C. Further additions of bromine are regulated to provide a slight reflux in the condenser. Altogether, 750 kg bromine is added over a period of 36 hr, during which period the temperature rises to 47°C. The reaction is continued for 8–10 hr after the final addition of bromine so that none of it remains unreacted.

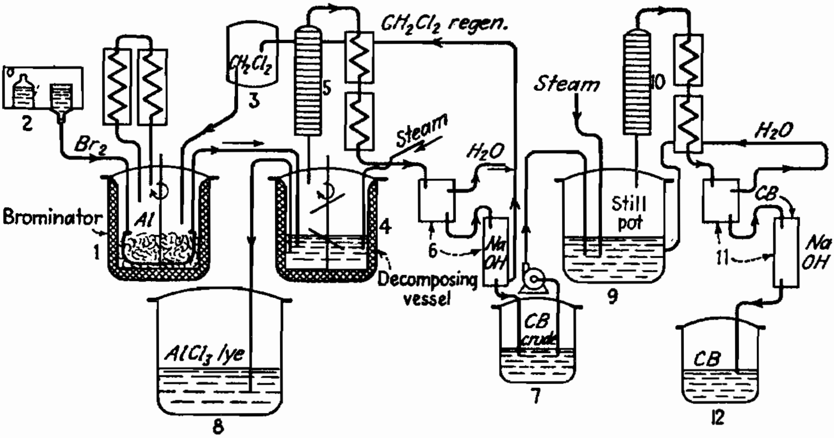

FIG. 6-20. Flow diagram, manufacture of chlorobromethane.

The reaction product is delivered by means of a standpipe into (4), an iron brick-lined decomposing vessel, 4.5 cu m, that contains 3,000 kg ice and 500 liters water. Some of the excess dichloromethane is distilled with steam by way of the plastic-coated fractionating column (5) and continuous separator (6) into vessel (3). Similarly, the crude CB is distilled to the iron storage vessel (7). The residual aluminum chloride solution is delivered to the iron receiver (8).

Purification. Three batches of crude CB are distilled together from the brick-lined vessel (9) by means of steam. Dichloromethane comes over first, and this is separated from the distilled water which is returned to the still pot. When the temperature on top of the fractionating column (10), filled with porcelain Raschig rings, reaches 53°C, CB distills over and is collected in the lead-lined iron storage vessel (12).

The yield of technical chlorobromomethane is 1,100–1,150 kg. The composition of the final product is:

	Bp, °C	Sp gr
82% chlorobromomethane	67	1.93
9% dichloromethane	40	1.32
9% dibromomethane	97	2.45

Raw materials used per ton of CB:

	Kg
Aluminum	89
Dichloromethane	890
Bromine	660
Caustic soda	5

Service requirements per ton of CB:

Electricity	350 kwhr
Water	520 cu m
Ice	2,440 kg
Steam	8 tons
Air	860 cu m

In many respects, chlorobromomethane constitutes the ideal agent for extinguishing fires. It is relatively nontoxic, has a low vapor pressure, and can be stored in ordinary vessels without pressure. It undergoes no significant change in viscosity at low temperatures and is, therefore, useful for airplanes flying at high altitudes. It has a quicker fire-extinguishing action than Freons, chloroform, or carbon tetrachloride.

Production of Ethylene Chlorohydrin. The preparation of ethylene chlorohydrin as an intermediate in the manufacture of ethylene oxide and ethylene glycol is carried out at the I.G. Farbenindustrie, Wolfen plant, in the following manner.[1] Ethylene, chlorine, and water, as indicated in

$$C_2H_4 + Cl_2 + H_2O \rightarrow ClC_2H_4OH + HCl \tag{1}$$

$$ClC_2H_4OH + Ca(OH)_2 \rightarrow 2C_2H_4O + 2H_2O + CaCl_2 \tag{2}$$

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \tag{3}$$

reaction (1), are reacted together continuously at about 2.5 atm pressure, in the reaction tower (Fig. 6-21). This is made of steel, lined with rubber and acid-resistant tile, and is packed with Raschig rings. Water enters at the lowest point, the chlorine is admitted through a distributor approximately 2 m higher, and ethylene is fed in by a blower at a point 2 m above the chlorine inlet through a distributor star.

The delivery of the three components to the reaction tower is measured by orifice meters as well as by recording meters. The reaction is exothermic, and the temperature in the reactor rises to 40–60°C, the optimum is about 50°C. The mixture of the reaction components is so regulated that

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[1] *B.I.O.S. Final Rept.* 776, Item 22.

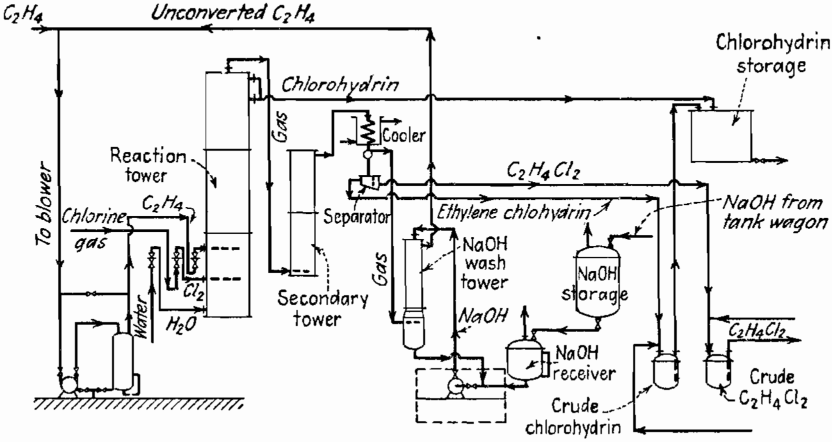

FIG. 6-21. Flow diagram, manufacture of ethylene chlorohydrin.

a 4.5–5 per cent ethylene chlorohydrin solution is obtained. In this way the chlorine is completely absorbed without circulation, while the ethylene is used in excess. The off-gases containing ethylene leave the reactor at the highest point and pass to another similar tower that has a water seal of about 2 m so that a corresponding pressure is maintained in the primary chlorinator.

The off-gases are passed to a lead cooler where some dichloroethane [reaction (3)] and chlorohydrin are condensed. These are separated and delivered to their respective enameled pressure vessels. The residual off-gases are passed through a scrubber where they are neutralized by a circulating 10 per cent sodium hydroxide solution. The unabsorbed ethylene then goes to the blower for recycling. A part of the recycled gas is continuously vented.

The ethylene chlorohydrin flows from the reaction tower through a side outlet, approximately 2 m below the top, and runs into tall tile-lined storage vessels, from which it is withdrawn for further processing. The crude chlorohydrin is obtained as a 4.5–5 per cent (by volume) solution and contains 2.2 per cent by volume of free hydrochloric acid; for this strongly corrosive solution, plastic coatings have been found to be about the best material of construction. Lead is used for pipelines carrying the gases.

In starting the plant, ethylene is circulated through the reaction tower containing water to give a saturated solution, and then chlorine is introduced. The feeds are then regulated to give a 15 per cent excess of ethylene in the tower by regulation of the blower pressure. The process is controlled by maintaining the chlorine rate constant and by regulating ethylene pressures and purges. An excess of chlorine must be avoided because of explosion hazards. On full production, each tower absorbs 270 cu m per hr of ethylene, 900 kg of chlorine, and 18 cu m of water.

On shutting down the reaction tower, the chlorine is throttled first, then the water flow is reduced, and finally, when the off-gases increase to over 50 per cent, the ethylene blowers are gradually cut off.

Freon 12: Dichlorodifluoremethane.[1] Freon 12 was made by the batch autoclave process at Höchst by I.G. Farbenindustrie from carbon tetrachloride, hydrogen fluoride, chlorine, and antimony pentachloride.

Hydrofluoric acid is transferred by means of compressed air from the underground storage tanks to a measuring vessel, where it is weighed and then blown into the autoclave (Fig. 6-22).

Carbon tetrachloride is delivered from a calibrated tank. Since the catalyst, antimony pentachloride, is an unstable compound and is not easy to handle, it is made *in situ* in the autoclave by treating antimony trichloride with chlorine dissolved in the feed carbon tetrachloride.

The charge to the autoclave consists of:

	Kg
Hydrofluoric acid 98–100%	500
Carbon tetrachloride	1,540
Antimony trichloride	200–400
Chlorine	20

An excess of hydrofluoric acid is used, the theoretical quantity being 400 kg. Chlorine is added to each batch of carbon tetrachloride in the feed tank, but the catalyst is renewed only periodically, the consumption being equivalent to 250 g per 100 kg of Freon 12 produced.

Approximately 24 hr is required to complete a batch; ½ hr for filling, 8–12 hr reaction time, 5–6 hr letting down, and 5–6 hr cooling. After charging, all the valves are closed, and steam at 130–140°C is admitted to the autoclave jacket to raise the temperature of the reaction mixture to about 100°C. After 2 hr, the pressures rises to 30 atm. gauge and is held at this point by opening the letdown valve, which allows hydrochloric acid gas and Freon to pass over into the acid absorption, drying, and liquefaction sections of the plant. The temperature of the reaction mixture varies a little, but is kept about 100°C throughout. At the start, it may fall as low as 50°C if insufficient steam is admitted to the jacket. The operation of the acid-absorption, drying, and liquefaction sections is straightforward, as noted in Fig. 6-22. A list of the plant items, their materials of construction, and notes on operating conditions is given on pp. 296 and 297.

The operation of the still is as follows: The boiler is charged with 1,200 liters of crude product per batch, and the distillation is carried out under a

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[1] *B.I.O.S. Target* 22/1 (g), Trip 1081.

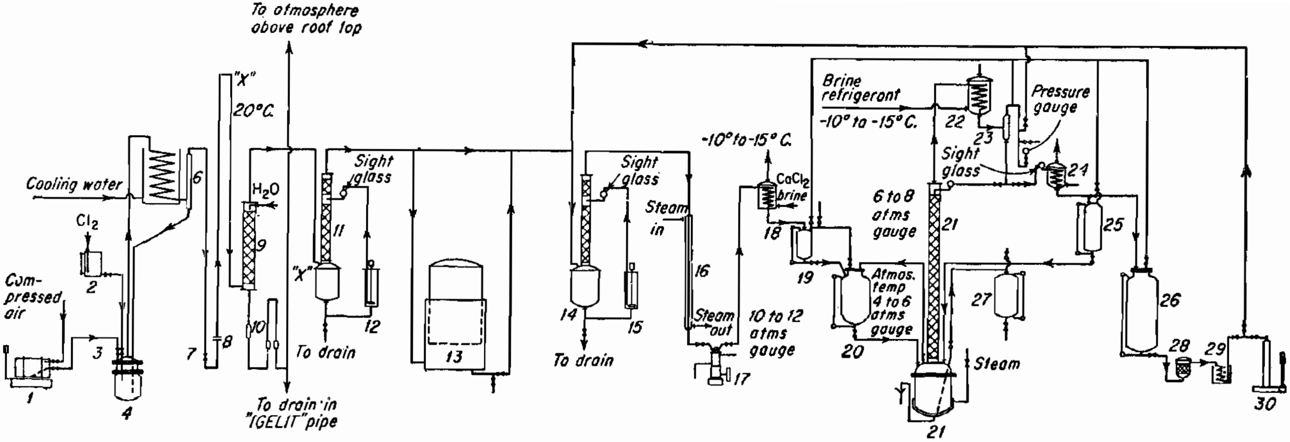

FIG. 6-22. Flow diagram of Freon plant, I.G. Farbenindustrie, Höchst Works. See pp. 296 and 297 for details.

Reaction	Acid absorption	Gas holder	Drying
Plant items: 1. 90–100% HF tank on weighing machine 2. Carbon tetrachloride measuring tank 3. HP needle valves 4. Autoclave (capacity 2,700 liters) 5. Reflux condenser 6. Separator 7. Letdown valve	8. Flowmeter 9. Acid absorption tower 10. Sight glasses 11. Caustic-wash-tower top-section spray arrestor 12. Submerged glandless circulating pump	13. Balancing gas holder, 6 cu m capacity	14. Sulfuric acid drying tower 15. Submerged centrifugal circulating pump
Constructional materials: 1. Steel 2. Steel 3. Steel 4. Autoclave of steel, lined with V_2A steel if available, if not, with MS liner 1,250 mm diam 5. Steel 6. Steel 7. Steel needle valve	8. Steel 9. All plant between the "*X*'s" is constructed of Mipolam or Igelit, the tower being packed with graphite rings 10 by 10 mm 11. Steel tower with porcelain ring packing 25 by 25 mm	All-steel construction	All-steel construction
Working Conditions: Batch process charge: 1,540 kg CCl_4 and 500 kg 98–100% HF; 200–400 kg $SbCl_3$ as catalyst. CCl_4 contains about 20 kg Cl_2, otherwise reaction does not go. Batch takes 24 hr; approx. ½ hr filling; 8 hr reaction (temp about 100°C, pressure up to 30 atm); 5–6 hr letting down; 5–6 hr to cool. Catalyst is renewed periodically and uses the equivalent of 250 g/100 kg. F12 autoclave lining lasts 200–300 charges with V_2A lining and only 100–200 with mild steel. Gases from reaction contain HCl, traces of HF, F11, and F12.	Long pipe above flowmeter allows expanding gases to warm up and prevents water getting back; wash water used only once and run to drain; caustic wash liquor initially 15% NaOH, run to drain at 6% NaOH.		Drying is with 90% H_2SO_4 which is wasted. The loss is small.

Liquefaction	Distillation and storage	Packing and dispatch
16. Heater 17. Compressor 18. Cooler 19. Batch-measuring vessel 20. Crude-product stock tank	21. Pressure still 22. Reflux condenser 23. Separator 24. Final condenser 25. Receiver for first fractions 26. CF_2Cl_2 stock tanks, three each of 8 tons capacity 27. Receiver for residues	28. Caustic-potash filter 29. Cooler 30. Containers and weighing machine
All-steel construction. Compressor, 2-stage, built by Maschinen Fabrik Surth Bei Koln. Sixty cu m/hr at 20 atm gauge when running at 275 rpm absorbing 15 hp; ordinary compressor oil used.	All-steel construction. The still kettle is 1,200 mm diam by 2,490 mm long, constructed of stainless steel with a column 350 mm bore by 8,000 mm long packed with Raschig porcelain rings 5 by 15 mm. The column is in four sections, each 2,000 mm long with perforated plates and liquid-deflecting cones at the joints of the intermediate sections.	All-steel construction
Gases are warmed to about 30°C to prevent the condensation of $CFCl_3$ (bp, 24°C) in compressor.	Still is charged with 1,200 liters/batch (1,560 kg); total evaporation 1,200 liters/hr. Offtake is, say, 100 liters/hr for 2 hr and then 200–300 liters/hr; originally temp in kettle is 25–30°C and rises to 60°C at end. Batch takes 8–12 hr to complete; yield 1,090 kg F12 per batch. First fraction is F13 with small quantities of F12 and is put back to still with next batch. Quantity about 130–260 kg per batch. Residues from still at end of distillation are returned to autoclave or distilled at ordinary pressure to give F11 for sale quantity 120–130 kg/batch. Yield of F12 = 90% on carbon tetrachloride, 80% on hydrogen fluoride.	Before filling, product is passed over KOH to ensure that there is no acidity and then cooled and packed. Containers used are 5-ton tank wagons and 90 kg-m and 2–3 kg-m cylinders (net weight of contents).

pressure of 6–8 atm gauge. The total evaporation rate is 1,200 liters per hr. When equilibrium has been reached at the top of the column, the off-take is 100 liters per hr for the first two hours and then 200–300 liters per hr. Originally, the temperature in the boiler is 25–30°C, and this rises to 60°C at the end of the batch.

The charge and yields per batch are approximately as follows:

	Kg
Charge of crude product	1,560
First runnings F-12 with a little F-13 ($CClF_3$)	130–250
F-12	1,090
Residues F-11(CCl_3F) and F-12(CCl_2F_2)	120–130

The first runnings are returned to the still with a later batch. The residues are distilled in an ordinary atmospheric-pressure still in order to produce F-11 for sale, or they can be returned to the autoclave for further fluorination.

Technically pure product is redistilled in order to ensure a maximum degree of purity and is then stocked in bulk storage tanks from which it is packed either in cylinders or tank wagons.

The yield of Freon 12 is 90 per cent of theory based on carbon tetrachloride.

Chlorination of Methane. Vapor-phase thermal chlorination of methane has been an excellent route for the preparation of methyl chloride, methylene chloride, and chloroform in this country for about thirty years, with Belle Alkali Company and Dow Chemical Company pioneering in this work. A similar process was developed at Frankfort on the Main by Farbwerke Höchst and is licensed in this country by the Lummus Company.[1]

Dry chlorine of 98 per cent purity and methane of 99 per cent purity are charged separately to a primary reactor along with recycle gas (Fig. 6-23). At above 700°F (370°C) the reaction goes to practically 100 per cent consumption of the chlorine and only partial conversion of the methane. By varying the molar ratio of chlorine and methane in the primary feed the proportion of end products can be varied over a wide range.

Two typical cases are given in the accompanying table.

	Case A	Case B
Methyl chloride, %	20	40
Methylene chloride, %	53	48
Chloroform, %	27	12

Some carbon tetrachloride is also formed, but the amount is small at low chlorine:methane mole ratios.

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[1] *Petroleum Refiner*, **32**, 125 (1953).

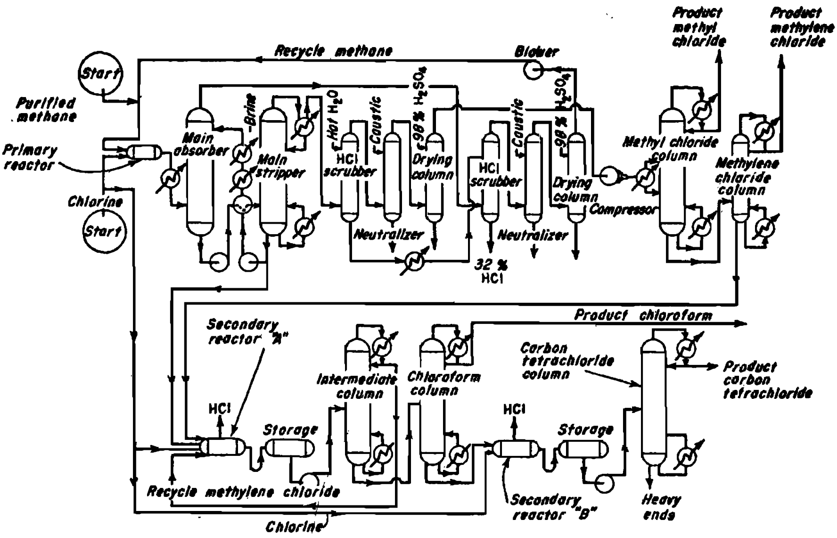

FIG. 6-23. Chlorinated methanes.

The products from the primary reactor are cooled in a tubular exchanger and are sent to the main absorber where the major proportion of chlorinated methanes is absorbed in a refrigerated mixture of chloroform and carbon tetrachloride. The stripped gas is scrubbed with dilute muriatic acid to produce a 30–32 per cent HCl solution, thus removing most of the hydrogen chloride. It is then dried. After that it is recycled to the primary reactor.

The absorber liquids are degassed by stripping off a large overhead fraction which is washed, neutralized, dried, and fed to a methyl chloride, methylene chloride fractionation column. If the desired products are chloroform and carbon tetrachloride, the entire volume of liquids may be sent to the secondary liquid-phase photoreactor where chlorine is added at reflux temperature until the chlorination is complete. The by-product hydrogen chloride is used to fortify the 30–32 per cent acid from the first HCl scrubber up to the desired commercial market-strength muriatic acid. Product from the secondary reactor is fractionated to produce solvent-grade chloroform, and the bottoms from the column are further chlorinated to carbon tetrachloride. By varying feeds and controlling cycle stocks in the three reactors, the composition of product can be varied from a peak of about 40 per cent methyl chloride down to no methyl chloride and 100 per cent carbon tetrachloride.

Vinyl Chloride. The insatiable demand for vinyl chloride resins has resulted in a number of different processes being commercialized, depending on the economics of basic raw materials. Cost and availability of ethylene, acetylene, hydrogen chloride, natural gas, and caustic soda have all been carefully weighed at each specific location, and often combinations of processes have been used.

Ethylene Dichloride Route. Ethylene and chlorine gases are reacted in liquid phase to form ethylene dichloride (see Fig. 6-24 and process description, p. 241).

$$C_2H_4 + Cl_2 \rightarrow CH_2ClCH_2Cl$$

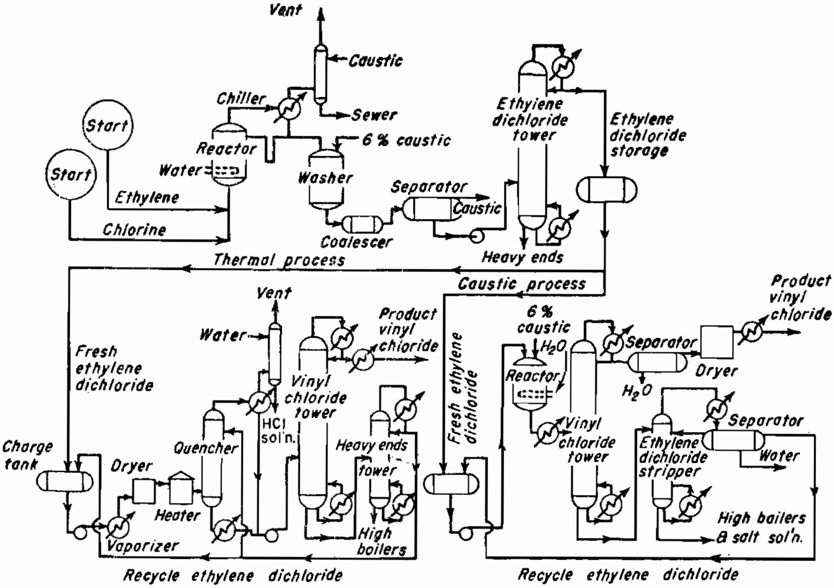

FIG. 6-24. Vinyl chloride from ethylene.

Ethylene dichloride may be reacted with alkali or it may cracked at high temperature to produce vinyl chloride.

$$CH_2ClCH_2Cl + NaOH \rightarrow NaCl + CH_2{=}CHCl + H_2O$$

or

$$CH_2ClHC_2Cl \xrightarrow{\Delta} CH_2{=}CHCl + HCl$$

Alkali Route. Ethylene dichloride is mixed with 6 per cent sodium hydroxide solution in a molar ratio of 2:1 and continuously charged to a steel reactor at 150 psig and 290°F (165°C). In a residence time of 3 min, reaction is complete and the overflow is cooled and fed to a vinyl chloride pressure fractionation column. Monomer vinyl chloride is condensed as an overhead product. The bottom stream is fed to a second column where the water–ethylene dichloride azeotrope is carried overhead and the ethylene dichloride recycled. The reaction is almost quantitative to vinyl chloride, with small amounts of ethylene glycol, acetylene, and acetaldehyde being formed.

Thermal Route. Ethylene dichloride at 50 psig is vaporized and passed through a drier to remove all traces of water. It is then fed into a stainless-steel cracking furnace of tubular design at 900–950°F (480–510°C). About 50 per cent of the ethylene dichloride is cracked, and the gases are rapidly quenched by direct contact with a circulating stream of cold ethylene dichloride. The gases from the quencher pass through a surface condenser, and the noncondensibles are scrubbed with water to produce muriatic acid.

The liquid stream from the quencher is fractionated to give monomer vinyl chloride overhead and a bottom of ethylene dichloride, which is recycled to the cracker.

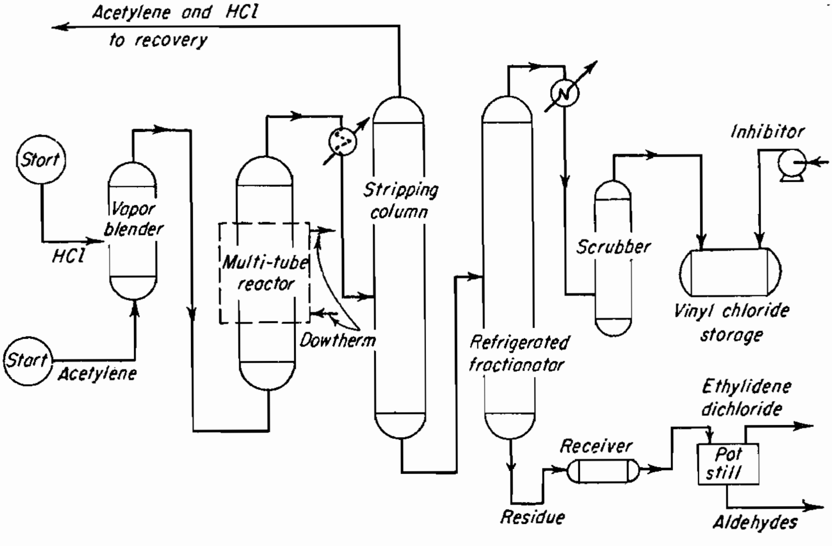

FIG. 6-25. Vinyl chloride from acetylene.

Carbon formation and deposition occur in the cracker, and it must be shut down and cleaned periodically. Increasing conversion past 50 per cent increases carbon formation and also promotes polymerization and loss of monomer.

Acetylene Route. Acetylene and hydrogen chloride combine catalytically to form vinyl chloride.[1]

$$C_2H_2 + HCl \rightarrow CH_2{=}CHCl$$

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[1] *Petroleum Refiner*, **32**, 135 (1953).

Dried hydrogen chloride and acetylene are mixed, using a 5–10 per cent excess of hydrogen chloride, and fed to a tubular reactor packed with carbon pellets impregnated with mercuric chloride (Fig. 6-25). With fresh catalyst, reactor temperature starts at 280°F (160°C) and increases slowly to 400°F (216°C) as the catalyst deteriorates. Gases from the reactor containing vinyl chloride, hydrogen chloride, acetylene, and by-product ethylidene chloride and aldehydes are cooled and fed to a stripping and fractionation system.

CHAPTER 7

SULFONATION AND SULFATION

By E. E. Gilbert and P. H. Groggins

I. INTRODUCTION

Sulfonation may be defined as any chemical process by which the sulfonic acid group $—SO_2OH$, or the corresponding salt or sulfonyl halide group (e.g., $—SO_2Cl$), is introduced into an organic compound. These groups may be situated on either a carbon or a nitrogen atom. Sulfonates of the second type (e.g., $RNHSO_2ONa$) are termed *N-sulfonates* or *sulfamates.*

Particular types of sulfonation include *sulfochlorination* (introduction of an $—SO_2Cl$ group into an alkane using sulfur dioxide and chlorine), *halosulfonation* (reaction of a halosulfonic acid—$ClSO_3H$ or FSO_3H—with an aromatic or heterocyclic compound to introduce an $—SO_2Cl$ or an $—SO_2F$ group), *sulfoxidation* (use of sulfur dioxide and oxygen to sulfonate an alkane), *sulfoalkylation, sulfoacylation,* and *sulfoarylation* (introduction of sulfoalkyl, sulfoacyl, or sulfoaryl groups).

Sulfation involves placement of the $—OSO_2OH$ group on carbon, yielding an acid sulfate ($ROSO_2OH$), or of the $—SO_4—$ group between two carbons, forming the sulfate $ROSO_2OR$. *Sulfatoalkylation* designates introduction of a sulfated alkyl group into an organic compound.

It is convenient to classify sulfonates into four main chemical types: (1) aliphatic and alicyclic, (2) aromatic, (3) heterocyclic, and (4) N-sulfonates or sulfamates. The first three types have the $—SO_2OH$ group on carbon, the chemical nature of which determines the classification. Thus, $C_6H_5OCH_2SO_2ONa$ (sodium phenoxymethanesulfonate) would be considered an aliphatic sulfonate.

For practical reasons, it is also useful to refer to three other types of sulfonates, namely, those derived from petroleum fractions, from lignin, and from fatty oils. These materials are mixtures of indeterminate or variable composition, probably comprising one or more of the main chemical types of sulfonates together with sulfates and other sulfur compounds, and are made largely by empirical procedures. All three types are commercially important.

Sulfates may be classified as *sulfated alkenes, alcohol sulfates, cyclic sulfates, sulfated carbohydrates,* and *sulfated nitrogenous polysaccharides.*

There are four general procedures for preparing sulfonates: (1) treatment of an organic compound with SO_3 or a compound thereof; (2) treatment with a compound of SO_2; (3) condensation and polymerization methods; (4) oxidation of an organic already containing sulfur in a lower state of oxidation, such as RSH. Condensation procedures refer to the reaction of organic sulfonate "building blocks" (such as $HOCH_2CH_2SO_3Na$) with other organic compounds (such as long-chain acid chlorides) to form new sulfonates with altered properties; these methods include sulfoalkylation, sulfoacylation, and sulfoarylation. For the preparation of sulfates, the first and third (i.e., sulfatoalkylation) methods only are of interest.

Sulfonating and sulfating agents are of two types—inorganic and organic. The latter type is employed in the condensation procedures.

Uses and Applications of Sulfonates and Sulfates. Millions of tons of sulfonates are manufactured annually; lignin sulfonate, obtained as a by-product of paper manufacture, constitutes the major single product. These compounds have achieved a wide variety of interesting and important uses. Most of them are employed as such in acid or salt form for applications where the strongly polar hydrophilic $—SO_2OH$ group confers needed properties on a comparatively hydrophobic nonpolar organic molecule. A few sulfonates are both marketed and used in acid form, including methane- and toluenesulfonic acids as catalysts and phenolsulfonic acid as an electroplating additive. A considerably larger group is marketed in salt form and used in acid form; such compounds include dyes, mothproofing agents, and synthetic tanning agents. In these cases, the salts are applied in acid medium, thereby liberating the free $—SO_2OH$ group which firmly attaches the organic molecule to the textile fiber or leather. The major quantity of sulfonates and sulfates is both marketed and used in salt form. This category includes detergents, emulsifying, deemulsifying, penetrating, wetting and solubilizing agents, lubricant additives, and rust inhibitors. Polymeric sulfonates include dispersing agents, elastomers, water-soluble synthetic gums and thickening agents, and ion-exchange resins which function as strong acids with complete water insolubility, an unusual combination of properties leading to many important applications.

Aromatic sulfonyl chlorides—RSO_2Cl—are useful for preparing sulfonamides (including sulfa drugs, dyes, tanning agents, plasticizers, and the sweetening agent saccharin) and sulfonate esters (insecticides).

Sulfamates include a herbicide, a sweetening agent, and a blood anticoagulant.

Sulfonates and sulfates find use as intermediates for preparing organic compounds not containing sulfur, notably phenols (prepared by caustic fusion of various sulfonates) and alcohols (made by hydrolysis of sulfated alkenes). Phenol, resorcinol, the naphthols, hydroxyanthraquinones, and 8-hydroxyquinoline are phenols so produced, while ethanol and isopropanol are examples of alcohols made from the sulfates.

A number of publications review sulfonation and sulfation primarily from the chemical standpoint regardless of product use.[2] Other treatises discuss the process as applied to the manufacture of important products such as dyes[1] and surface-active agents.[3]

II. SULFONATING AND SULFATING AGENTS AND THEIR PRINCIPAL APPLICATIONS

Agents. In the following paragraphs a survey is made of the principal sulfonating and sulfating agents, with special reference to their properties and major applications. These agents may be summarized as follows:

1. Sulfur trioxide and compounds thereof.
   - *a*. Sulfur trioxide, oleum, concentrated sulfuric acid (SO_3 plus water).
   - *b*. Chlorosulfonic acid (SO_3 plus HCl).
   - *c*. Sulfur trioxide adducts with organic compounds.
   - *d*. Sulfamic acid.
2. The sulfur dioxide group.
   - *a*. Sulfurous acid, metallic sulfites.
   - *b*. Sulfur dioxide with chlorine.
   - *c*. Sulfur dioxide with oxygen.
3. Sulfoalkylating agents.
   - *a*. Sulfomethylating agents (hydroxy- and aminomethanesulfonates).

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[1] SUTER, "The Organic Chemistry of Sulfur," John Wiley & Sons, Inc., New York, 1944; SUTER and WESTON, Direct Sulfonation of Aromatic Hydrocarbons and Their Halogen Derivatives, in "Organic Reactions," vol. III, pp. 141ff., John Wiley & Sons, Inc., New York, 1946; GILBERT, Sulfonation of Aromatic Hydrocarbons, in "The Chemistry of Petroleum Hydrocarbons," vol. III, pp. 611ff., Reinhold Publishing Corporation, New York, 1955; various articles in "Encyclopedia of Chemical Technology," The Interscience Encyclopedia, Inc., New York, including Sulfonation and Sulfation; Sulfonic Acids; Sulfur Compounds, Organic; annual reviews in the September issue of *Industrial and Engineering Chemistry* from 1948 to date (the first review goes back to 1941); "Methoden der organischen chemie (Houben-Weyl)," vol. IX, Thieme Verlag, Stuttgart, 1955.

[2] LUBS (ed.), "The Chemistry of Synthetic Dyes and Pigments," Reinhold Publishing Corporation, New York, 1955 (referred to hereafter as "Lubs"); FIERZ-DAVID and BLANGEY, "Fundamental Processes of Dye Chemistry," Interscience Publishers, Inc., New York, 1949 (referred to hereafter as "Fierz-David"); VENKATARAMAN, "The Chemistry of Synthetic Dyes," Academic Press, Inc., New York, 1952; Encyclopedia articles (*loc. cit.*), including Anthraquinone Derivatives and Naphthalene Derivatives.

[3] SCHWARTZ and PERRY, "Surface Active Agents," Interscience Publishers, Inc., New York, 1949; LINDNER, "Textilhilfsmittel und Waschrohstoffe," Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1954; Encyclopedia articles (*loc. cit.*), including Surface-active Agents.

b. Sulfoethylating agents (hydroxy-, chloro-, and methylaminoethanesulfonates; ethylenesulfonic acid).

c. Miscellaneous sulfoalkylating agents; sulfoacylation; sulfoarylation; sulfatoalkylation.

SULFUR TRIOXIDE AND COMPOUNDS THEREOF

Sulfur trioxide is theoretically the most efficient possible sulfonating and sulfating agent, since in the over-all sense only direct addition is involved according to the equations

$$R{\cdot}H + SO_3 \rightarrow RSO_3H$$
$$ROH + SO_3 \rightarrow ROSO_3H$$

Use of the compounds of sulfur trioxide, on the other hand, would at first sight appear to be considerably less efficient since the compounding material must first be reacted with sulfur trioxide to yield the compound, which is then used as the sulfonating or sulfating agent with re-formation of the compounding material. It will be noted that sulfur trioxide is thus still in effect the active reagent by the equations

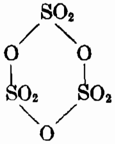
$$HX + SO_3 \rightarrow SO_3{\cdot}HX$$
$$R{\cdot}H + SO_3{\cdot}HX \rightarrow RSO_3H + HX$$

In the above, HX represents the compounding material, corresponding to water, HCl, dioxane, etc., depending upon the compound of SO_3 being used.

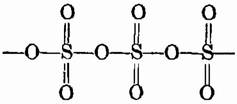
A trend toward the use of stronger (and theoretically more efficient) sulfonating and sulfating agents has in fact been noted in recent years. However, there are numerous other important factors to be considered, including product quality and side reactions—which may, and generally do, vary significantly from one reagent to another. Therefore, the various compounds of sulfur trioxide have established uses and advantages, each in its own right, resulting from a balanced evaluation of the many chemical, engineering, and economic factors involved. In the discussion to follow, an effort will be made to indicate the relative merits of different reagents for various uses.

Sulfur Trioxide—Oleum—Concentrated Sulfuric Acid. These three reagents are advantageously considered together because of their close physical relationship, and because they can in certain cases be used interchangeably. This group is of first importance, since by far the major proportion of sulfonates is produced by direct treatment of aromatic compounds with one of these reagents—especially oleum.

Properties. Sulfur trioxide polymerizes easily in a variety of ways at room temperature. The simplest polymer is the trimer (I), or γ form, which has the properties listed in Table 7-1 and is the only form of sulfur trioxide marketed as an article of commerce.



I



II

If the γ form is exposed to even a trace of moisture, it is converted to chain-type polymers with structure II, of which there are at least two forms, both of which are solids at room temperature, with neither being practical for use as a sulfonating agent.

TABLE 7-1. PHYSICAL PROPERTIES OF SULFUR TRIOXIDE (LIQUID FORM)

Boiling point, °C	44.8
Melting point, °C	16.8
Density (30°C)	1.87
Specific heat, g-cal at 25–35°C	0.77
Heat of dilution, g-cal	504
Heat of vaporization, g-cal	127.4
Viscosity, centipoises at 30°C	1.590

The fairly recent discovery that γ—SO_3 could be satisfactorily stabilized against this undesirable further polymerization by the addition of a small quantity (as low as 0.1 per cent) of various compounds—especially derivatives of boron, phosphorus, or sulfur—resulted in its commercial introduction in 1947.[1] Previously, it had been available only as "converter gas" at a contact sulfuric acid plant, or by distillation from oleum, thereby making its use for most sulfonations impractical.

TABLE 7-2. PARTIAL PRESSURES OF SO_3 OVER OLEUM (In Millimeters of Hg)

Wt % free SO_3	5	15	25	35	45	60
Wt % 100% H_2SO_4	101.13	103.38	105.62	107.87	110.13	113.50
Wt % total SO_3	82.55	84.39	86.22	88.06	89.90	92.65
40°C	. . .	. . .	. . .	22	55	217
80°C	12	37	84	209	469	
100°C	23	89	225	515		
120°C	54	194	459			
150°C	162	558				

Sulfur trioxide has a very strong affinity for water. So high is this degree of affinity, and so great is the evolution of heat in mixing the two materials, that water in its relation to SO_3 may be regarded as a basic substance.[2]

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[1] FLINT, "Encyclopedia of Chemical Technology," vol. 13, p. 501.

[2] HAMMETT and DEYRUP, *J. Am. Chem. Soc.*, **55**, 1900 (1933).

The major problem in sulfonating with SO_3 hydrates, then, comprises finding practical procedures for overcoming this affinity such that the SO_3 becomes free to react with the organic compound. The higher the water content (i.e., the more dilute the acid or oleum), the less active is the reagent for sulfonation. Likewise, it follows that one organic compound will undergo sulfonation more easily than a second, if the first has the greater affinity for SO_3.

A study of sulfonation kinetics (as discussed in a subsequent section), along with the knowledge that sulfuric acid dissociates into SO_3 and water at elevated temperatures, has led to the simple conclusion that monomeric SO_3 is the true reactive species in oleum, acid, and in SO_3 itself and that the water present in the hydrates functions only as a complexing agent and solvent. However, the physicochemical picture is less simple, since there are a number of hydrates which exist at low temperatures as definite crystalline compounds. The principal hydrates falling within the category of sulfonating agents are the following: monohydrate, $SO_3 \cdot H_2O$ or 100 per cent H_2SO_4; dihydrate, $SO_3 \cdot 2H_2O$ or 84.5 per cent H_2SO_4; and pyrosulfuric acid, $2SO_3 \cdot H_2O$ or 45 per cent oleum.

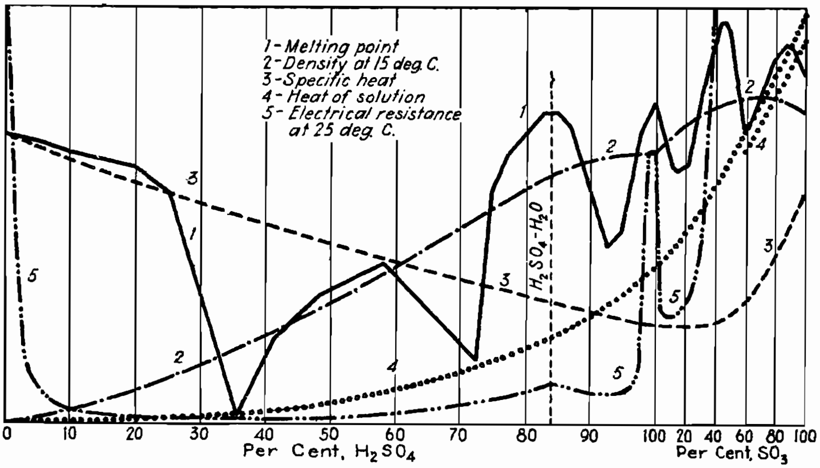

FIG. 7-1. Physical properties of SO_3 and its hydrates.

The properties[1] of these hydrates are summarized in Fig. 7-1, in which it will be noted that they correspond to peaks on the melting-point curve. Although the hydrates of SO_3 exist at low temperatures as definite crystalline compounds, with rising temperature they become increasingly less stable and finally decompose with the disengagement of either SO_3 or water;

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[1] For a complete discussion of the properties of SO_3 hydrates, see Sulfuric Acid in "Encyclopedia of Chemical Technology."

at 450°C the vapor of sulfuric acid is completely dissociated into the two components. The data of Table 7-2 clearly show how oleum dissociates with increasing temperature.

At ordinary temperatures, however, the hydrates present all the properties of simple solutions, and it is permissible to presume that between SO_3 and water there exists a consecutive series of homogeneous solutions among which are distinguished the definite hydrates mentioned above. In other words, the terms "sulfuric acid" and "oleum" are the generic names of a series of solutions of SO_3 in water, some of which are chemical hydrates of SO_3 and most of which are merely solutions of convenient strength for use in the arts.

TABLE 7-3. COMPARISON OF SULFURIC ACID AND SULFUR TRIOXIDE AS SULFONATING AGENTS

Factor	H_2SO_4	SO_3
Boiling point, °C	330 (decomposes)	44.8
Solubility in halogenated organics	Very Low	Miscible
Reaction rate	Slow	Instantaneous
Heat of reaction	Requires heat for completion	Strongly exothermic throughout
Extent of reaction	Partial	Complete
Spent acid	Substantial	None
By-product formation	Slight	Extensive in some cases
Required reactor size	Substantial	Minimum
Viscosity of reaction mixture	Low	High in some cases
Availability	Universal	Recent

From the practical standpoint, SO_3 and concentrated sulfuric acid have opposite properties as sulfonating agents, as shown in Table 7-3 for the case of aromatic hydrocarbons. Oleum, as might be expected, occupies an intermediate position; it is in fact the most widely used industrial sulfonating agent.

The advantages shown for sulfur trioxide (and correspondingly for oleums)—namely, rapid and complete reaction, minimum reactor capacity, and no requirement of heat for completing sulfonation—have become increasingly attractive industrially because of higher labor and fixed capital costs and the desire to obviate waste-acid disposal. The disadvantages (high heat of reaction with consequent decomposition or side reactions, high viscosity of the reaction mixture) can often be overcome by engineering design, choice of conditions, or use of a solvent. These factors underlie the trend toward stronger sulfonating agents.

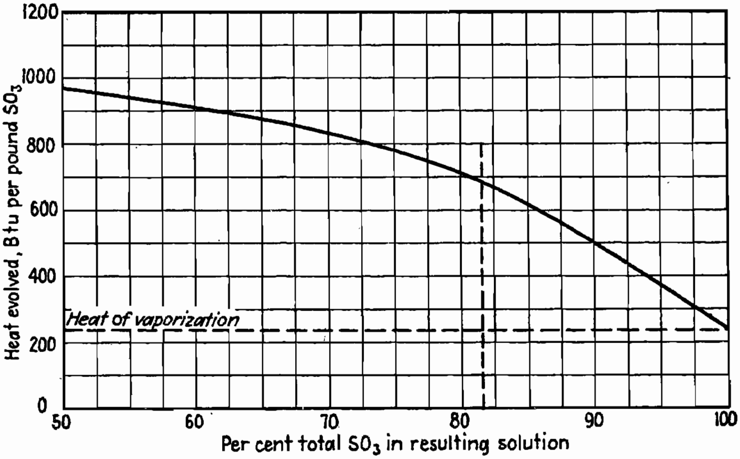

FIG. 7-2. Integral heat of mixing: sulfuric acid or oleum from SO_3 (*g*) and H_2O (*l*) at 30°C.

Sulfuric acid and oleum are often used in excess, thereby advantageously functioning as cheap, low-viscosity solvents for the product sulfonic acids which are often quite viscous in pure form. They are always used in liquid form, while sulfur trioxide, on the other hand, is usually employed as a vapor since it is easily vaporized (bp, 44.8°C) and the vapor form is considerably milder than the liquid. Liquid sulfur dioxide is an excellent sulfonation solvent for use with sulfur trioxide and with oleums, and it has been used industrially. Halogenated organic solvents (tetrachloroethylene, carbon tetrachloride, trichlorofluoromethane, etc.) are miscible with sulfur trioxide in all proportions, but not with its hydrates.

Sulfonation of Aromatic Compounds

The sulfonates of aromatic compounds, especially hydrocarbons, are of prime importance respecting both the volume and variety of products and uses.

Side Reactions during Sulfonation. A major object in choosing a suitable sulfonation reagent and process is the avoidance of undesired side reactions, the nature and extent of which will depend upon the structure of the compound being sulfonated, the sulfonating agent, and the physical conditions used. The principal side reactions encountered with aromatic compounds are sulfone formation, polysulfonation, formation of undesired isomers, and oxidation. Anhydride formation, dealkylation, and rearrangement have also been noted.

The formation of sulfone[1] proceeds according to the over-all reaction

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[1] For a more complete discussion of this and other side reactions see GILBERT, *op. cit.*, pp. 621ff.

$2RH + SO_3 \rightarrow R_2SO_2 + H_2O$. Factors favoring sulfone formation are use of strong reagents and operation in vapor rather than in liquid phase. Sulfone formation is said to be reduced by use of a solvent, addition of the organic compound to the sulfonating agent (rather than vice versa), the use of chemical "inhibitors" such as acetic acid[1] or sodium sulfate, and conducting the reaction in a comparatively large volume of the reaction product. In the benzene series, increasing substitution by number or length of alkyl groups reduces sulfone formation.

Polysulfonation is especially pronounced with polycyclic compounds. Hydrocarbons such as anthracene or phenanthrene polysulfonate so easily that the preparation of a monosulfonate always involves the formation of substantial amounts of the undesired polysubstituted compounds, even in the presence of unreacted hydrocarbon. Benzene and naphthalene are, however, easily monosulfonated without substantial disulfonation.

Oxidation is another side reaction noted especially with polycyclic hydrocarbons, or with polyalkylated benzene derivatives, especially at elevated temperatures and in the presence of catalytic materials such as mercury.

The formation of undesired sulfonate isomers can often be corrected by variations in reaction temperature or time. These factors are discussed more fully in a subsequent section. The addition of inorganic catalysts, such as mercury, can also have an important directive influence on isomer formation in some cases.

BENZENE AND ITS DERIVATIVES

Benzene. The monosulfonation of benzene is of prime commercial importance as being intermediate to one process for manufacturing phenol and to the only established process for producing resorcinol.

Benzene is especially prone to the formation of undesirable by-product sulfone with SO_3 or with oleum above about 10 per cent in strength. Acid of less than 78 per cent strength will not react because of the greater affinity of water compared to benzene for SO_3 under these conditions. Complete sulfonation of the benzene can be achieved by using excess acid to ensure a concentration greater than 78 per cent at the completion of the reaction. Details of a commercial process employing this principle are given later in this chapter. Complete utilization of the acid can, however, be attained by distilling out the water by the passage of excess benzene through the reaction mixture, thereby maintaining the acid strength above 78 per cent until it is completely consumed. This important "partial-pressure distillation procedure" is discussed in more detail in a subsequent section. The

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[1] Rueggeberg, Sauls, and Norwood, *J. Org. Chem.*, **20**, 455 (1955); Gilbert and Giolito, U.S. 2,704,295 (1955).

most efficient process, therefore, comprises reaction with 10 per cent oleum, followed by partial-pressure distillation until the acid is completely reacted.

The disulfonation of benzene is of commercial importance as being intermediate to the production of resorcinol, uses for which have steadily increased. Since the second sulfonic group is much more difficult to introduce into the benzene ring than the first, the reaction is conducted in steps, the second step under quite drastic conditions. Details of an industrial process have been outlined.[1] Monosulfonation is accomplished with monohydrate acid over a 10-hr period at a maximum temperature of 100°C, 4 hr being used for addition of the acid to the benzene at about 50°C, followed by a 6-hr digestion period during which the temperature is gradually raised to 100°C. For disulfonation, the sulfonation mixture from the monosulfonation step is mixed with 65 per cent oleum—the reaction being conducted in 6.5–7.5 hr over the range 30–85°C. The yield of desired sulfonate may be as high as 95 per cent, although it is often lower at least in part because of by-product sulfone formation. This process consumes 2.2 tons of monohydrate acid and 3.1 tons of 65 per cent oleum per ton of resorcinol produced; 6.5 tons of gypsum is formed in neutralizing the spent acid. In contrast, a theoretically perfect process would require only 1.45 tons of SO_3 and would produce no gypsum. As a result, several investigators have studied the use of stronger sulfonating agents to improve process efficiency.[2] Promising results are reported with yields of 82 per cent or better.

Toluene. Toluene resembles benzene in being well suited to the partial-pressure distillation procedure for sulfonation. This process is used industrially for producing sulfonate converted to cresols. Sulfone formation is low and the yield is maximum; these results are essential for volume production in competition with sources for cresols not employing sulfonation. Toluenesulfonate for other uses is made to some extent with SO_3. Yield loss is incurred from sulfone formation, but there are compensating processing advantages, as shown in Table 7-3.

Xylene. Pure xylene isomers are manufactured industrially in substantial quantity by selective sulfonation followed by selective desulfonation, as discussed in a subsequent section; the isomers are very difficult to separate physically. The sodium xylene sulfonates are used in steadily increasing quantity as solubilizing or "hydrotroping" agents. As in the case of toluene, the partial-pressure distillation procedure[3] and the SO_3 method are both used industrially.

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[1] Gilbert and Jones, *Ind. Eng. Chem.*, **43**, 2031 (1951).

[2] Carr and Dahlen, U.S. 1,999,955 (1935); General Chemical Division, Allied Chemical & Dye Corporation, *Tech. Service Bull.* SF-3, p. 5, 1951; Leiserson, Bost, and LeBaron, *Ind. Eng. Chem.*, **40**, 508 (1948); Swisher, Brit. 679,827 (1952).

[3] Lee, U.S. 2,556,429 (1951).

Dodecylbenzene. The sulfonation of "dodecylbenzene detergent alkylate" has become very important for the large-scale manufacture of household and industrial detergents and emulsifying agents. Hundreds of thousands of tons of this hydrocarbon are produced annually in the United States alone, nearly all being converted to the sulfonate. It is therefore by a large margin the major sulfonate in production. Dodecylbenzene is produced cheaply from abundant petroleum raw materials (tetrapropylene and benzene) and is easily sulfonated to yield a detergent of good color, odor, and performance. These advantages have appealed strongly to the numerous American manufacturers of soaps and surface-active compounds, and many of them purchase this hydrocarbon for sulfonation.

Dodecylbenzene is easily sulfonated, permitting the use of 98 per cent acid if used in requisite excess. On the other hand, it does not break down or form sulfones or disulfonates, even when treated with as strong a reagent as SO_3 vapor. Thus it becomes possible to choose any desired sulfonating agent over this broad concentration range. As long as this type of product was made in small quantities, a careful choice of the optimum reagent and reaction conditions was not especially critical. Recently, however, with greatly increased volume and competition, higher freight rates, stricter legislation on disposal of waste acid, demand for improved quality of product, and the trend toward a variety of formulations, it has become necessary to appraise with care the various factors inherent in the use of different reagents and processes. Dodecylbenzene differs from benzene or toluene in having a high boiling point which precludes completion of the sulfonation reaction by partial-pressure distillation. Consequently, a large excess of acid over the theoretical must be used to complete the reaction, and this must either be recovered in spent form or be neutralized *in toto* to yield a final detergent formulation containing much sodium sulfate.

The most common reagent for this sulfonation is 20 per cent oleum used in batch operation. Details of a typical industrial batch process using this reagent and operation on a continuous scale are discussed later. Other reagents which have been, or are being, used include: acid (98 and 100 per cent),[1] 100 per cent acid followed by 20 per cent oleum,[2] 22 per cent oleum,[3] SO_3 vapor,[4] SO_3 dissolved in SO_2,[5] and 65 per cent oleum dissolved in SO_2.[6]

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[1] Continental Oil Co., "Neolene 400, Intermediate for Synthetic Detergents," 1955; Oronite Chemical Co., "Alkane Basic Detergent Raw Material," 1955; Oronite Chemical Co., "Alkane Detergent Raw Material," 1950.

[2] *O.T.S. Rept.* PB 3,868 (Office of Technical Services, U.S. Department of Commerce).

[3] Oronite Chemical Co., *op. cit.*, 1955.

[4] Oronite Chemical Co., "Alkane Sulfonation with SO_3," 1954; GILBERT, VELDHUIS, CARLSON, and GIOLITO, *Ind. Eng. Chem.*, **45**, 2065 (1953); KIRCHER, MILLER, and GEISER, *Ind. Eng. Chem.*, **46**, 1925 (1954).

[5] Oronite Chemical Co., *op. cit.*, 1950; Morrisroe, U.S. 2,703,788 (1955).

[6] Morrisroe, *ibid.*

The SO_3 processes differ from the others in that no spent acid is formed, the active ingredient content of the sodium sulfonate is higher (95 per cent as opposed to 85–88 per cent), and the sulfonate has a better odor. Since the partial-pressure distillation process is not applicable to dodecylbenzene, the SO_3 approach is the only one entailing virtually complete utilization of all the applied sulfonating agent.

"Polydodecylbenzene." In the manufacture of dodecylbenzene, by-product alkylated benzenes of higher boiling point and molecular weight are obtained. Fractional distillation yields a mixed mono- and dialkylate (average about C-22) suitable for conversion with 20 per cent oleum or SO_3 vapor to a sulfonate useful for emulsifying agents and rust-proofing compounds. The residue, a mixed mono- and dialkylate averaging about C-25, is converted with oleum or SO_3 to a sulfonate mixture widely employed as a lubricant additive, a substantially unsulfonatable (i.e., highly solvent extracted) petroleum lubricant being customarily used as a reaction solvent. Because of steric hindrance, these polyalkylates are harder to sulfonate than the monoalkylate dodecylbenzene. The reagents are therefore used in considerable excess over theory.

Polystyrene. Another noteworthy sulfonation in the benzene hydrocarbon series is that of polystyrene. Two types of product are of interest: one, water-insoluble, produced in bead form from styrene-divinylbenzene copolymer, and used as an ion-exchange resin; the other, water-soluble, made from styrene homopolymer, and employed as a synthetic gum, as a tanning agent, or as a soil-conditioning compound. Both types of polymer are quite easy to sulfonate, thus resembling the nonpolymeric monoalkylated benzenes such as toluene. The polymeric nature of the hydrocarbons does, however, introduce certain unusual problems during sulfonation. Sulfonation of the copolymer is entirely heterogeneous. Beads of the hydrocarbon are preswollen with an organic solvent to ensure smooth and uniform penetration of the solid by the sulfonating agent;[1] otherwise, straining and cracking occur, yielding a weak and unstable resin. For the same reason the mildest possible conditions must be used in practice. To prepare the water-soluble sulfonate, the homopolymer can be sulfonated with SO_3, using a halogenated aliphatic solvent, either alone[2] or mixed[3] with SO_2. In this case it is imperative to avoid even a small degree of sulfone formation, which gives an insoluble product. It is therefore surprising that free SO_3 can be used in this process, since (like other strong sulfonating agents) it generally favors sulfone formation. As will be shown later, SO_3 complexes are also used for this sulfonation; however, they are milder reagents with less tendency to form sulfone.

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[1] WHEATON and HARRINGTON, *Ind. Eng. Chem.*, **44**, 1796 (1952).

[2] Teot and Wiggins, U.S. 2,640,820 (1953).

[3] ROTH, *Ind. Eng. Chem.*, **46**, 2435 (1954).

Miscellaneous Benzene Derivatives. The sulfonation of various nonhydrocarbon, substituted benzene derivatives with acid or oleum is of importance, especially for the preparation of dye intermediates.

Aniline and its derivatives are sulfonated by two procedures which yield different isomers.[1] Liquid-phase sulfonation at moderate temperatures (e.g., 30–80°C) with excess acid or oleum may introduce the sulfonic group meta to the amino group (as with *o*- or *p*-anisidine, or 5-aminosalicylic acid) or para (as with 2,5-dichloroaniline). Anilino-substituted anthraquinones are converted by this procedure to an important group of acid dyes;[2] monosulfonation of the anilino group predominates, but the product is an empirical mixture also containing unreacted starting material and polysulfonates. The "baking process," on the other hand, always yields the ortho or para isomer, operates in the solid phase at a higher temperature (170–280°C), and consumes nearly theoretical acid; details of this process as applied to sulfanilic acid are given on p. 383. The toluidines, xylidines, chlorinated anilines, and naphthylamines are so sulfonated. A modified baking process, operating at 150–200°C, employs an inert suspending medium such as ortho-dichlorobenzene to promote rapid sulfonation by azeotropic removal of water.[3]

Nitrobenzene, the nitrotoluenes, and nitrochlorobenzenes can be sulfonated with oleum at moderate temperatures, but violent explosions have occurred during these sulfonations. Dinitrobenzenesulfonic acids are prepared by nitration of the mononitro sulfonates since dinitro compounds decompose when sulfonated.

Phenolic compounds sulfonate very easily. Phenol reacts to the extent of 94 per cent when heated with an equimolar quantity of concentrated acid for 2 hr at 100°C. The cresols react less completely with considerable variation in isomers. These phenolic sulfonates find application for preparing tanning agents and ion-exchange resins. Chlorinated phenols are sulfonated in the preparation of dye intermediates.[4]

NAPHTHALENE AND ITS DERIVATIVES

The sulfonic acids of naphthalene, of the naphthols, and of the naphthylamines are of great importance as intermediates for azo and triphenylmethane dyes. In view of the complexity and the specialized nature of this field, it will be considered here only very briefly[5] and from the standpoint of general principles.

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[1] *O.T.S. Rept.* PB 85,687, *passim.*

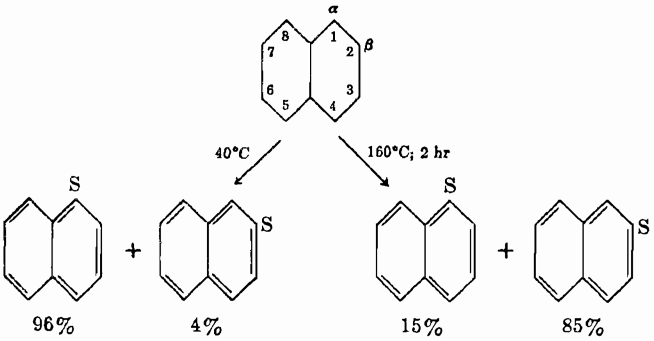
[2] LUBS, p. 394.

[3] *O.T.S. Rept.* 73,911.

[4] *O.T.S. Rept.* PB 85,172.

[5] For detailed reviews, see "Encyclopedia of Chemical Technology," Naphthalenesulfonic Acids, Naphtholsulfonic Acids, Naphthylaminesulfonic Acids; LUBS, pp. 65ff.

Naphthalene. The most important sulfonic acids of naphthalene itself (two mono-, two di-, and one tri-) are all made by direct sulfonation of the hydrocarbon with acid or oleum. Mixtures are always obtained, but satisfactory yields of desired isomers are achieved by a careful choice of acid: hydrocarbon ratio, acid concentration, and time-temperature relationship and by the use of the correct product work-up procedures. In preparing polysulfonic acids (i.e., disulfonic and higher) in the naphthalene series, including the hydroxy and amino derivatives, it is often customary to add the reagents in several steps, with gradually increasing temperature and acid concentration. A summary of the conditions used for the two monosulfonic acids of naphthalene is shown below. Details for preparing the most important 2- (or β-) sulfonate are given on p. 379.



Of special assistance in the preparation of any particular naphthalenesulfonate isomer by direct sulfonation are the orientation rules to the effect that (1) no sulfonic group can be introduced ortho, para, or peri to an existing group and (2) in disulfonation of a naphthalenemonosulfonic acid, the second group enters the unsulfonated ring. Thus, of the 10 theoretically possible disulfonic acids as prepared by any route, only 6 can be obtained by direct sulfonation; only 3 of 14 possible trisulfonic acids can be so prepared. Also helpful is the fact that low temperatures (i.e., below 50°C) and short reaction times favor alpha orientation, while higher temperatures (about 160°C) and longer times favor beta substitution. The technique of removing a sulfonic acid group from the ring by hydrolytic desulfonation is often used for naphthalene compounds; examples are the removal of by-product α-sulfonic acid from the desired beta isomer by steaming and the preparation of the 6-amino-1,3—disulfonic acid as described below. (The desulfonation reaction is discussed in more detail in a separate section.)

Naphthalene sulfonations are usually conducted on a batch scale in 250–800 gal cast-iron stirred kettles. The sulfonates so obtained are not used as such but are converted, often without actual isolation, to dye intermediates, nearly all of which contain hydroxyl or amino groups.

Naphthols. Of the four important naphtholmonosulfonic acids, only two are produced by direct sulfonation of the naphthol. 2-Naphthol-1-sulfonic acid (Armstrong's acid) is formed by treatment with 97 per cent sulfuric acid at low temperature with a short reaction time or with SO_3 using a solvent, while 2-naphthol-6-sulfonic (Schaeffer's acid) is produced at 120–125°C with 78 per cent sulfuric acid. The two major naphtholdisulfonic acids [2-naphthol-6,8-disulfonic acid (G acid) and 2-naphthol-3,6-disulfonic acid (R acid)] are formed together by direct sulfonation of 2-naphthol, using sulfuric acid followed by oleum and raising the temperature in steps from 15 to 80°C. They are isolated as the potassium and sodium salts, respectively, by differential salting out.

Naphthylamines. The naphthylamine sulfonic acids are an important group of dye intermediates. The monosulfonates, as well as many of the others, are usually made by indirect procedures, since direct sulfonation of the corresponding amines yields complex mixtures or an unduly high proportion of unwanted isomers. 1-Naphthylamine-4-sulfonic acid (naphthionic acid) is, however, prepared by the baking process (see Sulfanilic Acid, p. 383) at 180°C for 8 hr by heating either dry in an oven or suspended in *o*-dichlorobenzene solvent. Two important naphthylaminedisulfonic acids (the 6-amino and the 7-amino-1,3-disulfonic acids) are prepared together by direct treatment of 2-naphthylamine with 45 per cent oleum at 95°C. The latter acid is obtained as a direct sulfonation product, but the former is produced by the removal (with hydrolytic desulfonation) of one sulfonic acid group from a trisulfonic acid formed during the sulfonation.

Alkylated Naphthalenes. Alkylated naphthalenesulfonate textile wetting agents are manufactured by treating a mixture of naphthalene and an aliphatic alcohol (*n*-butanol or isopropanol) at room temperature with 96 per cent acid followed by 24 per cent oleum. Following addition, stirring is continued for 6 hr at 50°C.[1] In this case the acid functions both as an alkylating catalyst and a sulfonating agent. Such products can also be made by treating diamylnaphthalene with excess concentrated acid or with SO_3 vapor.[2]

ANTHRAQUINONE AND ITS DERIVATIVES

Anthraquinone sulfonates are important dye intermediates.[3] The four sulfonates of most industrial importance are as follows:

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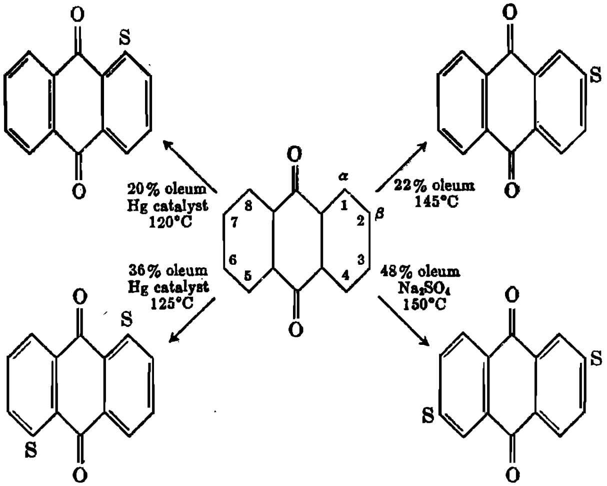
[1] *B.I.O.S. Rept.* 421, Item 22 (British Intelligence Objectives Sub-committee).

[2] GILBERT et al., *loc. cit.*

[3] "Encyclopedia of Chemical Technology," Anthraquinonesulfonic Acids; LUBS, pp. 335ff.; VENKATARAMAN, *op. cit.*, vol. 1, pp. 59ff.; FIERZ-DAVID, pp. 234ff.



The carbonyl groups in anthraquinone render sulfonation rather difficult. Anthracene sulfonates readily at room temperature with 96 per cent acid, but sulfonation of anthraquinone with this reagent begins only at about 200°C. Oleum reacts at lower temperatures and is therefore the preferred reagent. Attempts to introduce more than two sulfonic groups in any ring generally result in excessive oxidation, a side reaction noted to some extent even under practical operating conditions. The ease of introduction of a second sulfonate group (i.e., one in each ring) is close to that of the first. It is therefore necessary, when the monosulfonate is desired, to sulfonate only partially to avoid excessive yield loss by disulfonation. Thus, in preparing the 1-sulfonic acid (see details on p. 381), about 50 per cent of the starting material is recovered, whereas with the 2-sulfonic acid about 60 per cent remains unchanged;[1] some disulfonate is still formed, however. In the naphthalene series, orientation of an entering sulfonate group (i.e., whether alpha or beta) is largely determined by temperature, but with anthraquinone this is controlled almost entirely by the presence or absence of a mercury catalyst added as sulfate or oxide at 1–2 per cent by weight of the anthraquinone used. As shown in the diagram above, substitution occurs almost completely in the 1 (or alpha) position in the presence of mercury. Although mercury and its compounds are known to influence orientation in other sulfonation reactions, their use in the anthraquinone series is certainly the most striking example as well as the largest such application in actual practice. As in the naphthalene series, the desulfonation reaction is often used to produce a desired isomer.

Mono- and diamino- as well as dihydroxyanthraquinones are sulfonated

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[1] *O.T.S. Rept.* PB 85,172.

with 20 per cent oleum at 100°C or above to yield dye intermediates. In some of these sulfonations, sodium sulfate or boric acid may be added to facilitate sulfonation, and mercury sulfate may be included to direct orientation.

Heterocyclic Compounds. Many heterocyclic compounds (e.g., furan, pyrrole, indole, thiophene, cumarone, and their derivatives) decompose in the presence of acids and, therefore, cannot be sulfonated with SO_3 or its hydrates. Other heterocyclics, however, are stable and yield sulfonates of industrial interest. 3-Pyridinesulfonic acid, an intermediate in one process for producing nicotinic acid, can be prepared with difficulty by heating pyridine-SO_3 at 225–235°C in the presence of mercury sulfate or by the reaction of pyridine with 20 per cent oleum at 250–270°C, using the same catalyst. Quinoline can be sulfonated in the benzene nucleus (5 and 8 positions) with oleum at 170–180°C; caustic fusion of the 8 isomer yields 8-hydroxyquinoline, an important analytical reagent and fungicide. Carbazole is converted commercially to the 1,3,6-trisulfonate by heating with excess 95 per cent acid at 50–100°C; this sulfonate is then nitrated with displacement of all the sulfonate groups to yield a tetranitrocarbazole fungicide.[1] An intermediate for a thiazole dye is prepared by treating dehydrothio-*p*-toluidine with 20 per cent oleum to yield the 7-sulfonic acid; further sulfonation by the baking process yields a disulfonate. The sulfonates of the phthalocyanines are steadily increasing in importance as dyes. A process study[2] has shown that (1) the monosulfonic acid is formed with 40 per cent oleum below 20°C, (2) the disulfonic acid is formed at 51°C in 15 hr, and (3) above 60°C considerable trisulfonate is formed. Four sulfonate groups are the maximum attainable, corresponding to one sulfonate group for each benzene nucleus.

Petroleum Fractions. Oleum and SO_3 are employed in the manufacture of oil-soluble sulfonates from petroleum lubricating oils. These products are consumed in thousands of tons annually as rust preventives, additives for heavy-duty engine lubricants, and emulsifiers. They are obtained as a by-product from the manufacture of mineral white oils, but since World War II the demand for the sulfonates has increased so much more rapidly than that for white oil that the former are now produced per se.

Petroleum is a complex mixture of hydrocarbons of only generally known structure, the composition varying from one oil to another, depending on the crude source, boiling range, and degree and method of refining. The constituents vary greatly in ease and degree of sulfonation from highly reactive to inert, the latter comprising about 80 per cent by weight in a typical refined lubricant. The desired oil-soluble monosulfonates contain

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[1] *O.T.S. Rept.* PB 60,890.

[2] *O.T.S. Rept.* PB 85,172, vol. III, pp. 304–308.

fairly small aromatic ring systems with comparatively long side chains, such as in dinonylnaphthalene.[1] Also formed are less valuable water-soluble mono- and polysulfonates derived from larger polynuclear aromatic ring systems with shorter side chains; oxidation and sludge formation are extensive side reactions. Detailed operating conditions for lubricant sulfonation, both on a batch and a continuous basis, are given on p. 373.

Sulfonation and Sulfation of Aliphatic Compounds

Sulfur trioxide and its hydrates are generally unsuitable for sulfonating saturated aliphatic compounds. Either no reaction occurs, or oxidative decomposition takes place, yielding a complex mixture. Long-chain saturated fatty acids can, however, be smoothly sulfonated with SO_3 (liquid or vapor) to give good yields of α-sulfo acids as follows:

$$RCH_2COOH + SO_3 \rightarrow RCH(SO_2OH)COOH$$

A technical palmitic–stearic acid mixture has been sulfonated thus at 25–60°C on a commercial scale,[2] using carbon tetrachloride as sulfonation solvent.

The sulfation of alkenes or alcohols with concentrated acid is, on the other hand, an important reaction. Both types of sulfation can yield dialkyl as well as monoalkyl sulfates. Furthermore, sulfation (like sulfonation) will not reach completion if excess water is present:

$$ROH + H_2SO_4 \rightleftharpoons ROSO_3H + H_2O \qquad (1)$$
$$RCH{=}CH_2 + H_2SO_4 \rightleftharpoons RCH(CH_3)OSO_3H \qquad (2)$$
$$2ROSO_3H \rightleftharpoons (RO)_2SO_2 + H_2SO_4 \qquad (3)$$
$$RCH{=}CH_2 + H_2SO_4 \rightarrow [RCH(CH_3)O]_2SO_2 \qquad (4)$$

Thus, in sulfating ethanol with SO_3 at equimolar ratios,[3] equilibrium for reaction (3) is slowly reached at 45 per cent monosulfate, 25 per cent disulfate, and 30 per cent H_2SO_4. To obtain a good yield of monosulfate, immediate neutralization is therefore required. For maximum yield in sulfating lauryl alcohol, reaction (1) is driven to the right by using a 70 per cent excess of 100 per cent acid, followed by immediate neutralization before reaction (3) occurs. In sulfating long-chain alkenes, a 5-min. reaction time using excess acid reduces dialkyl disulfate formation by driving reaction (3) to the left.[4]

Alkenes. Oleum or SO_3 cannot be used for alkene sulfation, since SO_3 sulfonates, rather than sulfates, these compounds as follows:

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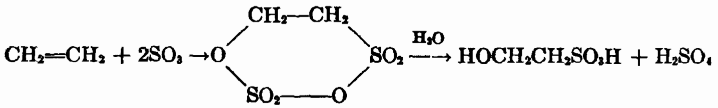
[1] Brown, *Inst. Petroleum Rev.*, **9**, 314 (1955); "The Chemistry of Petroleum Hydrocarbons," vol. III, pp. 633ff.

[2] *O.T.S. Rept.* 12,272; *O.T.S. Rept.* 30,081.

[3] Breslow, Hough, and Fairclough, *J. Am. Chem. Soc.*, **76**, 5361 (1954).

[4] Kooijman, *Intern. Congr. Pure Appl. Chem. (London)*, **11**, 499 (1947).



The sulfation of the lower alkenes derived from petroleum (ethylene, propylene, butylenes) with concentrated acid is operated on a large scale for producing the corresponding alcohols; for the case of ethanol, the reactions are as follows:

$$CH_2{=}CH_2 + HOSO_2OH \rightarrow C_2H_5OSO_2OH$$
$$2CH_2{=}CH_2 + HOSO_2OH \rightarrow C_2H_5OSO_2OC_2H_5$$
$$C_2H_5OSO_2OH + C_2H_5OSO_2OC_2H_5 + 3H_2O \rightarrow 3C_2H_5OH + 2H_2SO_4$$

Hundreds of millions of gallons of ethanol are produced annually by this procedure. Operating in competition with other methods, this process accounts for about two-thirds of all the ethanol manufactured in the United States. The success of this process has been made possible by good yields, continuous operation on a large scale, an efficient procedure for reconcentrating the spent sulfuric acid for recycle, and, of course, a cheap source of ethylene. It will be noted that both the mono- and disulfates are converted to alcohol. A detailed description of a commercial operation, using 97.5 per cent acid, is given on p. 385.

A similar process has been detailed for producing isopropanol.[1] A more dilute acid (85 per cent) is used for the propylene sulfation step, which is run at 24–27°C. Ethylene is not sulfated under these mild conditions.

Sulfation of long-chain alkenes (C_{12}–C_{18}) is operated commercially in Europe on a substantial scale for the production of detergents and wetting agents,[2] using hydrocarbons obtained either by the cracking of petroleum or from shale oil. This sulfation is carried out at 10–15°C with 90–96 per cent acid, an acid: alkene molar ratio of approximately 2:1 being used. Short contact time and efficient mixing are essential. Working-up involves tar removal (by centrifuging), breakdown of undesired dialkyl sulfates (by holding at 90°C for 8 hr with aqueous sodium carbonate), and removal of unreacted hydrocarbons (by solvent extraction). This type of detergent is not manufactured in the United States.

Alcohols and Ethers. The sulfation of these materials is important industrially. Dimethyl sulfate, used as a methylating agent, is manufactured in excellent yield and purity by continuous reaction of dimethyl ether with SO_3:

$$(CH_3)_2O + SO_3 \rightarrow (CH_3)_2SO_4$$

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[1] FAITH, KEYES, and CLARK, "Industrial Chemicals," p. 391, John Wiley & Sons, Inc., New York, 1950.

[2] INSKEEP and MUSSARD, *Ind. Eng. Chem.*, **47**, 2 (1955).

The process (described later in detail) involves simple countercurrent mixing of the two reactants in an aluminum tower, charged with reaction product, at 40°C with moderate external cooling. This procedure is apparently not adaptable to other ethers.

Long-chain alcohol sulfates, especially sodium lauryl sulfate, are important detergents and foaming agents. Although chlorosulfonic acid (*q.v.*) has long been the established reagent for this type of sulfation, SO_3 vapor and monohydrate acid have more recently come into commercial use. Oleum is unsuitable since decomposition is prohibitive.

The over-all reactions involved in these two processes are:

$$ROH + H_2SO_4 \rightleftharpoons ROSO_2OH + H_2O$$

$$ROH + SO_3 \rightarrow ROSO_2OH$$

The first procedure employs monohydrate acid in considerable excess (to drive the reaction to the right), at about 70°C, with a reaction time limited to a few seconds by immediate "quenching" of the reaction mixture either by cooling or neutralization. This "flash" method, discussed in more detail on p. 374, can be used only on a continuous basis, since the much longer holding time inherent in batch operation results in excessive decomposition of the unstable acid sulfate in the presence of free sulfuric acid. The product so obtained is high in sodium sulfate and may contain about 10 per cent of the starting alcohol in unreacted form. This high content of sodium sulfate renders such a product unsuitable for many liquid formulations, but for solid formulations which can tolerate the sulfate, it is satisfactory. The SO_3 vapor process,[1] on the other hand, can be used in batch operation since little or no free sulfuric is present during reaction. It gives a product low in inorganic sulfate and unreacted alcohol, therein resembling the behavior of chlorosulfonic acid. The SO_3 process yields no HCl, which is an advantage over the use of chlorosulfonic acid, but is more exothermic than either the chlorosulfonic or monohydrate process.

Sulfated ethylene oxide condensates of generic structure $RO(CH_2CH_2O)_xSO_2OH$, as derived from long-chain alkylated phenols or long-chain alcohols, have attained prominence as surfactants because of good detergency, foam formation, and rinsibility. Sulfamic acid (*q.v.*) has long been the established reagent for this sulfation. SO_3 vapor, passed in at about 60°C,[2] is now also being used commercially. SO_3 is a much cheaper reagent than sulfamic acid, it reacts at a lower temperature without heating and yields any desired product salt by direct neutralization. Sulfamic acid yields the ammonium salt. With SO_3 some sulfonation of the highly reactive phenoxy group occurs, while only sulfation takes place with sulfamic

[1] GILBERT et al., *loc. cit.*

[2] General Chemical Division, Allied Chemical & Dye Corporation, unpublished research data.

acid; this difference is important in some uses, but not in others. Other compounds of SO_3 (e.g., $ClSO_3H$ or oleum) are not suitable for this sulfation since ring sulfonation is excessive. Ring sulfonation is of course not a factor in sulfating the condensates from long-chain alcohols.

Fatty Oils. Concentrated sulfuric acid is widely used for the preparation of the so-called "sulfonated" fatty oils, as from castor, soybean, peanut, tallow, sperm, neat's-foot, and various fish oils, as well as from the derived esters, anilides, free acids, etc. The manufacture of these materials has increased steadily since 1875, when sulfonated castor oil (Turkey-red oil) was first introduced as a textile assistant. The chemical reactions occurring during this type of "sulfonation" are complex, but sulfation of double bonds and of hydroxyl groups predominates. Process conditions, which are entirely empirical and have varied little over the years, comprise gradual addition of excess cold concentrated acid (often 20–40 per cent of the weight of the oil) to the oil, with good agitation and cooling in a batch operation using a lead, Monel, or nickel-clad steel reaction kettle.

In American practice there are two general commercial procedures for conducting the sulfonation step—at a low reaction temperature (maximum about 35°C) with a correspondingly long reaction time or at a higher reaction temperature (maximum about 55°C) with a short reaction period. In the trade these methods are termed, respectively, "high" and "quick," the former yielding maximum sulfates and sulfonates, and the latter procedure more hydroxy acids and other secondary products. The subsequent operation involves removal of the considerable quantity of unreacted acid (known as the "washing step") and neutralization. These steps may require several days and are extremely critical, since the techniques of washing and of neutralization will determine the quality and performance of the product. A detailed process description is given on p. 386.

Sulfated Monoglycerides. The fatty monoglyceride sulfates ($RCOOCH_2$-$CHOHCH_2OSO_3Na$; where RCO may be any long-chain fatty acid radical, as in the common triglycerides such as coconut oil) have been manufactured for many years as industrial and household detergents by a simple one-step process involving mixing the triglyceride (1 mole), glycerol (2 moles), and sulfuric acid or oleum in excess. Alcoholysis occurs as well as sulfation. These sulfates are simple to manufacture and are perhaps the cheapest of the fat-based synthetic detergents, but they are chemically unstable and not easily produced with low sodium sulfate content. Consequently, they have been largely replaced by the dodecylbenzenesulfonate detergents.

CHLOROSULFONIC ACID

Chlorosulfonic acid, $ClSO_3H$, is a liquid boiling at 152°C. It dissolves readily in chloroform, carbon tetrachloride, nitrobenzene, and liquid SO_2; these solvents are sometimes used with this reagent both industrially and in the laboratory. Although this compound is a strong acid, and is therefore usually written $ClSO_3H$, its method of preparation (direct reaction of SO_3 and HCl), behavior at the boiling point (dissociation to SO_3 and HCl), and mode of reaction with organic compounds (liberation of HCl and introduction of SO_3) indicate that it is a compound of SO_3 with HCl and that the formula $SO_3 \cdot HCl$ would be more accurately descriptive. Since the HCl is evolved easily as a gas, reactions involving it go readily to completion in contrast to the use of sulfuric acid, which (as discussed in detail in the case of aromatic hydrocarbons) requires a relatively high temperature and partial-pressure distillation to obtain complete reaction by removal of water. This apparent advantage in favor of $ClSO_3H$ over sulfuric acid is, however, more than offset (1) by higher cost of the reagent per pound and a higher molecular weight (meaning more weight of reagent per pound of SO_3 introduced), (2) by undesired by-product formation of sulfonyl chlorides, and especially (3) by the highly corrosive nature of the associated HCl. The major uses for this reagent are in the preparation of aromatic sulfonyl chlorides, alcohol sulfates, and sulfamates.

Aromatic Sulfonyl Chlorides. The preparation of these compounds involves two reactions:

$$RH + ClSO_3H \rightarrow RSO_3H + HCl\uparrow \qquad \text{(Step 1)}$$
$$RSO_3H + ClSO_3H \rightleftharpoons RSO_2Cl + H_2SO_4 \qquad \text{(Step 2)}$$

Step 1 goes to completion easily since hydrogen chloride is evolved, driving the reaction toward the right. Step 2, however, is an equilibrium reaction, and a considerable excess of reagent is required to ensure a fair yield of desired sulfonyl chloride.

Although step 1 occurs easily, chlorosulfonic acid is not ordinarily used to prepare sulfonic acids by this reaction, since step 2 also occurs to some extent inevitably as an objectionable side reaction. Also, the hydrogen chloride obtained is corrosive and presents a disposal problem. In special cases, however, this reagent is used to make sulfonic acids with excellent results, notably for the preparation of certain naphthalene and anthraquinone dye intermediates and for introducing four sulfonate groups into phthalocyanine. The aromatic sulfonyl chlorides are useful intermediates for preparing sulfonamides, sulfonates, esters, and thiols. The usual preparative procedure comprises slow addition of the organic compound to a large excess (two to five times theory) of chlorosulfonic acid in a batch operation, followed by a digestion period, then drowning in ice water to precipitate the desired water-insoluble sulfonyl chloride. A detailed description of the industrial process for so preparing 4-acetylaminobenzenesulfonyl chloride, an intermediate for nearly all sulfa drugs, is given on p. 382; the organic raw material is acetanilide. The reverse order of addition (reagent to organic) yields more by-product sulfone, and in any case would not be convenient for solid organic compounds unless a solvent were also employed. Compounds so converted to the sulfonyl chlorides, beside acetanilide, include various chlorinated benzenes, toluenes, and nitrobenzenes, salicylic acid, 2-hydroxy-1-naphthoic acid (all as dye intermediates), benzene (for insecticides), and toluene (for saccharin). In the case of toluene, a low temperature (about 0°C) is used to promote preferential formation of the desired ortho isomer.

The evolution of hydrogen chloride in step 1 above can be avoided by using a mixture of chlorosulfonic acid and sulfur trioxide,[1] the quantity of sulfur trioxide being equimolar with the organic reactant. Step 1 then becomes

$$RH + SO_3 \rightarrow RSO_3H$$

This modification is used industrially, and such mixtures are commercially available for producing sulfonyl chlorides.

Alcohol Sulfates. Alcohols are sulfated with chlorosulfonic acid as follows:

$$ROH + ClSO_3H \rightarrow ROSO_2OH + HCl\uparrow$$

This process achieved prime commercial interest about 1930, when sodium lauryl sulfate was introduced as the first synthetic detergent, and large quantities of this product are still so produced. Details of this process are given in the technical section. Other alcohols sulfated industrially by this reagent include *n*-butanol, oleyl alcohol (with some attack of the double bond), sperm alcohol, cetyl alcohol, and long-chain secondary alcohols prepared via the aldol condensation. Batch operation is usually employed at a temperature in the range 10–30°C, the acid being added to the alcohol in equivalent quantity or slightly more. Solvents, including liquid SO_2, chloroform, or carbon tetrachloride, are sometimes used to facilitate this sulfation. This reagent is also used for continuous sulfation, but (as explained in detail on p. 374), there is some justification for believing that it is poorly adapted for such operation.

The use of chlorosulfonic acid with pyridine for alcohol sulfation is often mentioned in the literature, and this mixture has been used commercially. The actual reagent in this case is pyridine—SO_3 formed by the reaction

$$ClSO_3H + 2C_5H_5N \rightarrow C_5H_5N{\cdot}SO_3 + C_5H_5N{\cdot}HCl$$

The applications of this compound are discussed in a subsequent section.

Sulfamation. Chlorosulfonic acid is also used to prepare sulfamates (N-sulfonates), both in the laboratory[2] and industrially. Sodium cyclo-

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[1] GILBERT et al., *loc. cit.*

[2] AUDRIETH, SVEDA, SISLER, and BUTLER, *Chem. Revs.*, **26**, 49 (1940).

hexylsulfamate, a widely used sweetening agent, can be so produced from cyclohexylamine by the equation

$$3C_6H_{11}NH_2 + ClSO_3H \rightarrow C_6H_{11}NHSO_3H{\cdot}H_2NC_6H_{11} + C_6H_{11}NH_2{\cdot}HCl$$

Neutralization with caustic soda forms the sodium salt and liberates 2 moles of amine for recycle. Sodium di (*n*-butyl) sulfamate, a textile mercerizing assistant, is prepared likewise from di (*n*-butyl) amine.

SO_3— ORGANIC COMPLEXES

Just as sulfur trioxide reacts with inorganic materials (e.g., water, HCl) to yield compounds of varying reactivity and therefore of correspondingly varying usefulness for different sulfonation reactions, it also reacts with many organic materials to form addition compounds ("complexes" or "adducts") which have similarly varied usefulness. The most widely applied of these complexes are derived from tertiary amines (such as trimethylamine, pyridine, or dimethylaniline) and from ethers [e.g., dioxane or bis(2-chloroethyl) ether]. They can be prepared by direct mixing of the components with efficient cooling in a solvent such as chloroform or tetrachloroethylene. Amine complexes are also sometimes prepared by reacting the amine (2 moles) with chlorosulfonic acid (1 mole) (see equation in the section on chlorosulfonic acid).

The SO_3 complexes are white solids of generally low solubility in organic solvents with which they do not react. Dimethylformamide, however, is not only a good solvent for them but also dissolves an unusually large number of organic compounds; this amide also forms a complex with SO_3 which is readily soluble in excess solvent. The adducts vary widely in their chemical stability. The trimethylamine compound, one of the most stable, is a solid melting at 240°C. It can be purified by recrystallization from water and is an effective sulfating and sulfamating agent even in aqueous medium. Replacement of one methyl group in trimethylamine by phenyl yields a complex so unstable as to be hydrolyzed even by atmospheric moisture, although it can be isolated as a crystalline solid. The dioxane complex is so unstable that it must be used soon after preparation. The SO_3 adducts also vary greatly in their reactivity as sulfonating or sulfating agents. Thus, the pyridine adduct, one of the least reactive, does not sulfonate benzene or its homologues, but does react with thiophene, furan, and other heterocyclic compounds. The thioxane complex yields naphthalene-1-sulfonic acid, but not the disulfonic acid, nor does it react with benzene under the same conditions, whereas the dioxane adduct will sulfonate benzene as well as naphthalene. The dimethylformamide complex is quite reactive and is an effective sulfating agent even at 0°C. Almost any desired degree of activity can be obtained by a correct choice among the many SO_3 complexes.

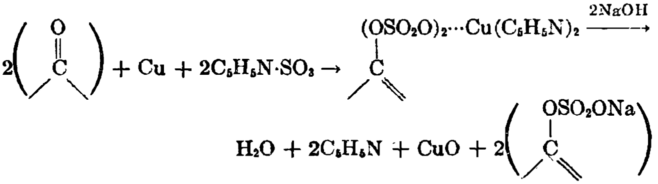
Amine Complexes. The pyridine —SO_3 complex has proved broadly applicable in the laboratory for the sulfonation of certain acid-sensitive ("acidophobic") compounds. This is in fact the preferred procedure for sulfonating five-membered heterocyclic compounds[1] including furan, pyrrole, indole, thiophene, coumarone, and many of their derivatives. Yields are generally good (70–90 per cent), and the technique is simple (heating in a sealed tube at 80–140°C in the presence or absence of a solvent such as ethylene dichloride). The same method also works well in the sulfonation of alkadienes. Butadiene, for instance, yields the 1-sulfonic acid in fair yield.[2]

The amine complexes are, however, of more interest as sulfating agents for hydroxy compounds; for pyridine-SO_3 the reactions are as follows:

$$ROH + C_5H_5N{\cdot}SO_3 \rightarrow ROSO_2OH{\cdot}C_5H_5N$$
$$ROSO_2OH{\cdot}C_5H_5N + NaOH \rightarrow ROSO_2ONa + C_5H_5N$$

Sodium oleyl sulfate, an excellent detergent, has been prepared thus industrially from oleyl alcohol. Other reagents attack the olefinic bond in oleyl alcohol and yield an inferior product. Phenols, as aqueous solutions of the sodium salts, can be sulfated with triethylamine-SO_3. These sulfates cannot be prepared with stronger sulfating agents such as SO_3, sulfuric acid, or $ClSO_3H$ since ring sulfonation always occurs preferentially. The aromatic sulfates are stable in neutral or alkaline solution and are not affected by the oxidation or reduction of other groupings in the molecule. Also, these sulfates are water-soluble, and the sulfate group is easy to introduce and remove. Consequently, sulfation has sometimes been used to block phenolic hydroxyl groups before the oxidation of various organic compounds. Selective sulfation of phenols (e.g., *o*- and *p*-phenylphenols) with triethylamine-SO_3 forms the basis for a method of separation of isomeric mixtures.[3]

Combined reduction and sulfation of vat dyes, especially anthraquinone dyes, has been increasingly used in industry since 1924 to achieve water solubility, with consequent easy application to the textile fibers. The reaction is conducted by heating the dye with a metal (copper, iron, or zinc) and pyridine-SO_3 (or other amine complexes) by the following reaction:



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[1] Gilbert and Jones, *Ind. Eng. Chem.*, **43**, 2039 (1951); **45**, 2053 (1953); Lisk, *ibid.*, **41**, 1929 (1949).

[2] Gilbert and Jones, *Ind. Eng. Chem.*, **43**, 2023 (1951).

[3] Hardy and Scalera, *J. Am. Chem. Soc.*, **74**, 5212 (1952).

Oxidation of the organic sodium sulfate in acid solution converts it to the original insoluble form of the dye, thereby fixing it on the textile fiber. This direct and widely applicable procedure is used to produce over 50 individual dyes; current manufacturing practice has been reviewed in detail.[1] A more recent variation of this procedure involves preliminary reduction of the dye in aqueous solution to the leuco (hydroxy) form, followed by sulfation in the same solution with trialkyl amine-SO_3.

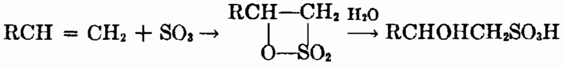
The amine-SO_3 compounds are also sulfamating agents:

$$RNH_2 + R_3N{\cdot}SO_3 \rightarrow RNHSO_3H{\cdot}NR_3$$

In the case of pyridine-SO_3, advantage has been taken of its combined ability to sulfamate and to sulfate in numerous attempts to duplicate synthetically the potent naturally occurring blood anticoagulant heparin.

Ether Complexes. The SO_3-ether complexes are considerably more reactive than the amine compounds. The dioxane and bis(2-chloroethyl) ether complexes sulfonate the benzene ring at room temperature or below and, as a result, have been found useful for converting styrene homopolymer to a water-soluble sulfonate,[2] the salts of which give viscous water solutions and are useful as thickening agents. This reaction is conducted below 15°C, using ethylene dichloride solvent. In this sulfonation it is important to avoid sulfone formation, which would make the product water-insoluble; it is also necessary to avoid an excess of sulfonating agent, since the product is so viscous as to render difficult the removal of sulfate ion.

Dioxane-SO_3 has proved useful in the laboratory for converting alkenes to sulfonates or hydroxysulfonates:[3]



$$RCH = CH_2 + SO_3 \rightarrow \begin{array}{c} RCH{-}CH_2 \\ |\quad\;| \\ O{-}SO_2 \end{array} \xrightarrow{H_2O} RCHOHCH_2SO_3H$$

Aliphatic aldehydes and ketones are easily sulfonated with this reagent on the carbon adjacent to the carbonyl group:[4]

$$RCOCH_2R' + SO_3 \rightarrow RCOCH(SO_3H)R'$$

The yields are good, mono- or disulfonic acids may be obtained depending upon the proportions used, and the reaction is widely applicable. In all these cases, ethylene dichloride may be used as reaction solvent at room temperature or below.

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[1] VENKATARAMAN, *op. cit.*, pp. 1046ff.

[2] Baer, U.S. 2,533,210; 2,533,211 (1950).

[3] SUTER, EVANS, and KIEFER, *J. Am. Chem. Soc.*, **60**, 538 (1938); BORDWELL, COLTON, and KNELL, *ibid.*, **76**, 3950 (1954).

[4] TRUCE and ALFIERI, *ibid.*, **72**, 2740 (1950); TERENT'EV and YANOVSKAYA, *Doklady Akad. Nauk S.S.S.R.*, **75**, 235 (1950).

SULFAMIC ACID

Sulfamic acid, NH_2SO_3H, is a stable, high-melting (200°C) crystalline solid with strongly acidic properties.[1] It is available commercially, being prepared by reacting urea with pyrosulfuric acid.

$$NH_2CONH_2 + H_2S_2O_7 \rightarrow 2NH_2SO_3H + CO_2\uparrow$$

In its reactions involving sulfation and sulfonation, it generally resembles the tertiary amine-SO_3 complexes. In fact, it may from this standpoint be conveniently considered as an ammonia-SO_3 complex, $NH_3{\cdot}SO_3$,[2] even though it is not so prepared, and even though the formula NH_2SO_3H more correctly denotes its role as a strongly acidic analogue of sulfuric acid. It is used industrially for the sulfation of alcohols, yielding the ammonium salt of the sulfated alcohol:

$$ROH + NH_3{\cdot}SO_3 \rightarrow ROSO_3H{\cdot}NH_3$$

This technique is employed principally for sulfating ether alcohols, such as that made by condensing dodecylphenol with 3 moles of ethylene oxide. The reaction is conducted at 125°C in an enameled kettle with a 2-hr reaction time.[3] Such sulfates are good detergents with excellent foaming power. Other sulfating agents, such as $ClSO_3H$, unlike sulfamic acid attack the easily sulfonated phenolic nucleus, yielding inferior products; SO_3 vapor, however, can be used without excessive attack, as discussed on p. 322.

Sulfamic acid, like pyridine-SO_3, can be used for preparing sulfamates, such as the widely used sweetening agent sodium cyclohexylsulfamate:[4]

$$2C_6H_{11}NH_2 + NH_3{\cdot}SO_3 \rightarrow C_6H_{11}NHSO_3H{\cdot}H_2NC_6H_{11} + NH_3\uparrow$$

Neutralization with caustic soda yields the desired sodium salt, with the liberation of cyclohexylamine for recycle.

In the laboratory, sulfamic acid has been used in special cases for sulfonation. Styrene and related compounds can be so sulfonated on the aliphatic moiety:

$$C_6H_5CH{=}CH_2 + NH_3{\cdot}SO_3 \rightarrow C_6H_5CH{=}CHSO_3H{\cdot}NH_3$$

Several ketones have been sulfonated on the carbon adjacent to the carbonyl group by heating with this reagent at 150–170°C for 3–6 hr, and phenolic ethers have been sulfonated on the ring under the same conditions.

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[1] "Encyclopedia of Chemical Technology," Sulfamic Acid.

[2] BAUMGARTEN, *Ber. deut. chem. Ges.*, **62**, 820 (1929).

[3] *O.T.S. Rept.* PB 63,822.

[4] Brit. 662,800 (1951).

THE SO_2 GROUP OF COMPOUNDS

This group of sulfonating agents is of specialized application compared to those derived from SO_3; in part this is explained by the comparatively recent discovery of two of the main categories of reaction, sulfochlorination and sulfoxidation. The SO_2 compounds are not used at all for sulfation, and only to a minor degree for sulfamation. If the lignin sulfonates are included, however, the volume of products made with these reagents far exceeds that made with the compounds of SO_3. These sulfonates are not made per se, however, but are by-products of paper manufacture.

Sulfochlorination. It was discovered by Reed in 1936[1] that an $—SO_2Cl$ group can be introduced on aliphatic carbon using a mixture of sulfur dioxide and chlorine in the presence of a chain-initiating catalyst such as actinic light:

$$RH + SO_2 + Cl_2 \xrightarrow{\text{catalyst}} RSO_2Cl + HCl$$

Further study showed that the starting material RH could be varied widely and included the lower (propane, butane, etc.) and higher alkanes (e.g., paraffin wax, polyethylene), as well as many types of substituted alkanes. This process was accorded immediate and intensive commercial development by the du Pont Company in the United States[2] and by the I.G. Farbenindustrie in Germany[3] for the production of sodium sulfonate detergents at minimum cost. The organic raw materials were, respectively, a petroleum white oil and a hydrogenated gas oil obtained by the Fischer-Tropsch process. The sulfonate detergents were formed by alkaline hydrolysis of the sulfonyl chlorides; the annual production of the German detergent Mersolate reached 80,000 tons by the end of World War II.

Side reactions noted during sulfochlorination are chlorination and polysulfonation. Expedients for minimizing them are partial conversion of the organic compound (50–70 per cent) and employment of excess SO_2 (3:1 mole ratio to chlorine). The consequent necessity for raw-material recycle, high raw-material cost (i.e., the use of unproductive chlorine), the need for specialized equipment (due to the formation of corrosive hydrogen chloride and the requirement of photochemical activation), and the necessity for a final saponification step have put this process in an unfavorable position for detergent production relative to the direct sulfonation of dodecylbenzene, the conversion of which to a detergent has none of these disadvantages. Interest still continues, however, in the use of this process

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[1] Reed, U.S. 2,046,090 (1936).

[2] Lockwood, *Chem. Inds.*, **62**, 760 (1948).

[3] Eckoldt, "Methoden der organischen Chemie (Houben-Weyl)," vol. IX, pp. 411ff., Thieme Verlag, Stuttgart, 1955.

for the preparation of long-chain sulfonyl chloride tanning agents. The sulfonyl chlorides can also be converted to many potentially useful derivatives, for example, by reducing the —SO_2Cl group to a thiol or by reacting it with amines to yield sulfonamides or with alcohols or phenols to form sulfonate esters. Another promising application of sulfochlorination involves the conversion of polyethylene to an elastomer which can be cured with various inorganic or organic agents to a synthetic rubber of outstanding abrasion resistance and durability on exposure to oxygen, ozone, heat, and weather. Chemically, the elastomer is a high-molecular-weight chlorinated polysulfonyl chloride.

Sulfoxidation. This reaction is chemically quite similar to sulfochlorination, except that acetic anhydride is added:

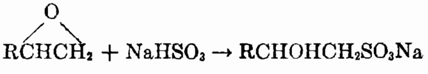
$$\mathrm{RH + SO_2 + O_2 + (CH_3CO)_2O \rightarrow RSO_2OOCOCH_3 + CH_3COOH}$$
$$\mathrm{RSO_2OOCOCH_3 + SO_2 + 2H_2O \rightarrow RSO_2OH + CH_3COOH + H_2SO_4}$$

This reaction has been studied extensively by the I.G. Farbenindustrie[1] for producing detergents from long-chain paraffins. The products closely resemble those obtainable from the same organic raw materials by sulfochlorination, but the sulfoxidation approach has the advantages of not requiring chlorine as a raw material and of not producing corrosive hydrogen chloride as a product. Further, the sulfoxidation by-products—acetic and sulfuric acids—are largely recoverable, the former being capable of recycle to the process as acetic anhydride. For various nondetergent uses such as those mentioned above which require the sulfonyl chloride group, however, the product obtained by sulfoxidation cannot be substituted for that produced by sulfochlorination. These include use as tanning agents, or elastomers, reduction to thiols, and condensation with amines, phenols, or alcohols to yield sulfonamides or sulfonate esters.

Sulfite Reactions. Metallic sulfites and bisulfites are used for this group of reactions. Sulfurous acid is sometimes employed. Most sulfite reactions are conducted by mixing the reactants in aqueous or aqueous-alcoholic solution, followed by heating as necessary.

Aliphatic Compounds. *Aldehydes and Epoxides.* These compounds react easily with bisulfite to yield 1-hydroxy- and 2-hydroxyalkylsulfonates, respectively.

$$\mathrm{RCHO + NaHSO_3 \rightarrow HOCH(R)SO_3Na}$$



$$\mathrm{\overset{O}{RCHCH_2} + NaHSO_3 \rightarrow RCHOHCH_2SO_3Na}$$

These materials are useful "building blocks," or sulfoalkylating agents, for preparing other sulfonates, as explained more fully in a subsequent section.

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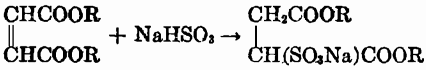
[1] GILBERT and JONES, *Ind. Eng. Chem.*, **43**, 2025 (1951).

Unsaturated Compounds. The direct addition of bisulfites to various alkenes in the presence of peroxide catalysts has been established as a general reaction:[1]

$$\mathrm{RCH{=}CH_2 + NaHSO_3 \xrightarrow{catalyst} RCH_2CH_2SO_3Na}$$

This reaction has been studied industrially[2] for the possible production of detergents from long-chain 1-olefins; apparently this process is not in manufacturing use, however.

The diesters of maleic acid add bisulfite with ease, no catalyst being required:



$$\begin{array}{l}\mathrm{CHCOOR}\\ \Vert\\ \mathrm{CHCOOR}\end{array} + \mathrm{NaHSO_3} \rightarrow \begin{array}{l}\mathrm{CH_2COOR}\\ |\\ \mathrm{CH(SO_3Na)COOR}\end{array}$$

These products are excellent industrial wetting agents and are manufactured in quantity. A detailed description of the commercial procedure is given on p. 376. A variation of this reaction involves a similar addition of bisulfite to compounds of the type RCOCH=CHCOOR′, where R is derived from a long-chain alkylated benzene and R′ from a long-chain alcohol.

The Strecker Reaction. This reaction, involving replacement of halogen on an aliphatic carbon atom by a metallic sulfonate group using a sulfite, has proved a useful tool both industrially and in the laboratory. Commercially it is employed for preparing sodium 2-chloroethanesulfonate, which is used to make other sulfonates by sulfoalkylation (as discussed in the following section):

$$\mathrm{ClCH_2CH_2Cl + Na_2SO_3 \rightarrow ClCH_2CH_2SO_3Na + NaCl}$$

A second commercial application is for the preparation of surface-active agents:

$$\mathrm{C_8H_{17}C_6H_4OCH_2CH_2OCH_2CH_2Cl + Na_2SO_3 \rightarrow}$$
$$\mathrm{C_8H_{17}C_6H_4OCH_2CH_2OCH_2CH_2SO_3Na + NaCl}$$

The detergent sodium lauryl sulfoacetate is also prepared by this procedure from lauryl chloroacetate:

$$\mathrm{C_{12}H_{25}OCOCH_2Cl + Na_2SO_3 \rightarrow C_{12}H_{25}OCOCH_2SO_3Na + NaCl}$$

The Strecker reaction has been shown to be a rapid, simple, and widely applicable procedure for preparing arylmethanesulfonates ($\mathrm{RCH_2SO_3K}$, where R is aromatic) by chloromethylation of aromatic hydrocarbons, followed by reacting with sulfite.[3]

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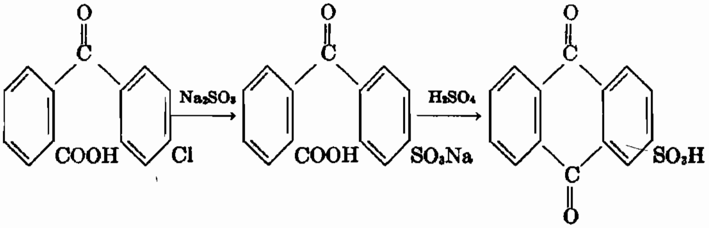
[1] Kharasch, May, and Mayo, *J. Org. Chem.*, **3,** 175 (1938).

[2] Brit. 682,207 (1952).

[3] Bunton and Halevi, *J. Chem. Soc.*, **1952,** 4541.

Aromatic Compounds. *Halogen Replacement.* Halogenated (usually chlorinated) aromatic compounds can be converted to the sulfonates by halogen replacement, using sulfites. This reaction is analogous to the Strecker reaction with aliphatic halides, as discussed above. When the ring chlorine is activated by nitro groups, as in the case of 2,4-dinitrochlorobenzene or of 2-nitrochlorobenzene-4-sulfonic acid,[1] the reaction proceeds easily by refluxing in aqueous-alcoholic solution at atmospheric pressure. Other aromatic chlorides are less reactive, and more drastic conditions are required, such as heating under pressure for 6–16 hr at 140–200°C in the presence of copper sulfate catalyst. Compounds prepared industrially in this manner include 2-sulfobenzoic acid[2] and 2-sulfobenzaldehyde;[3] direct sulfonation in these cases would yield the 3—isomers rather than the desired 2—isomers. This reaction is also useful in the anthraquinone series. 4′-Chloro-2-benzoylbenzoic acid yields the 4′-sulfo analogue, which is readily cyclized to anthraquinone-2-sulfonic acid:



The sulfonate so prepared is purer than that obtained by direct sulfonation. 1,2-Dichloroanthraquinone is separated from the 2,3—isomer by reaction of the chlorine in the 2 position of the former with sulfite; the other isomer does not react.[4]

Aromatic Nitro Compounds. Aromatic nitro compounds react in various useful ways with sulfites. Polynitro compounds of suitable orientation react easily by nitro-group replacement as follows:

$$RNO_2 + Na_2SO_3 \rightarrow RSO_3Na + NaNO_2$$

This reaction is used industrially to remove the 1,2- and 1,4-dinitrobenzene isomers from the 1,3 isomer, which does not react,[5] and to eliminate the undesired by-product 2,3,4- and 2,4,5-isomers from the explosive TNT.

Other aromatic nitro compounds yield sulfamates:

$$RNO_2 + 3NaHSO_3 \rightarrow RNHSO_3Na + 2NaHSO_4$$

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[1] FIERZ-DAVID, pp. 103–106.

[2] *O.T.S. Rept.* PB 100,937.

[3] *O.T.S. Rept.* PB 85,687.

[4] *B.I.O.S. Rept.* 987.

[5] FIERZ-DAVID, p. 111.

Such aromatic sulfamates can often be rearranged to aminosulfonates by the following general reaction:

$$C_6H_5NHSO_3Na \rightarrow H_2NC_6H_4SO_3Na$$

The aminosulfonates, as well as the intermediate sulfamates, are manufactured as dye intermediates.

Lignin Sulfonates. Millions of tons of water-soluble lignin sulfonates are produced annually as a by-product of the manufacture of paper pulp by heating wood under pressure with an aqueous solution of metallic bisulfite and sulfur dioxide ("sulfite cooking acid"). These sulfonates are used as dispersing agents and as raw materials for producing vanillin, tanning agents, and ion-exchange resins.

The structure of lignin is not known, but it appears to comprise a mixture of polymers containing aromatic rings, methoxyl groups, hydroxyl groups (both phenolic and alcoholic), and carbonyl groups. The chemical structure of the sulfonate is likewise unknown, even though it has been studied for many years. The sulfonation reaction appears to proceed in steps, yielding at least three types of sulfonates depending upon the conditions used, especially the pH of the reaction mixture. A predominant type of reaction yielding sulfonates is thought to be:

$$RC(OH)R'R'' + NaHSO_3 \rightarrow RC(SO_3Na)R'R'' + H_2O \text{ (R = substituted phenyl)}$$

Several derivatives of benzyl alcohol have been found to undergo this reaction, yielding the corresponding phenylmethanesulfonates. A similar reaction (R and R′ dialkylaminophenyl, R″ hydrogen) is used to prepare a diphenylmethanesulfonate dye intermediate.[1]

Comparison of Sulfonation Procedures Using SO_2 and SO_3. An instructive comparison can be made of the basic factors involved in sulfonating with a compound of SO_2 and with one of SO_3.

Since SO_3 is made by the oxidation of SO_2, it can be said that, if SO_2 is taken as the starting point, two major steps are involved in sulfonating with a compound of SO_3: (1) an oxidation step and (2) the sulfonation step proper.

When sulfonating with a compound of SO_2, the process likewise involves going from SO_2 to an organic sulfonate by the same two reactions of oxidation and sulfonation. The difference in the use of the two types of reagents lies in the fact that, when using a compound of SO_2, it is the organic rather than the inorganic compound which undergoes the oxidation. Also, the order of the steps may be reversed.

As illustrated by the case of the sulfonation of ethylbenzene, the two routes can yield different types of products. (In the equations below, *a* is the oxidation step, *b* the sulfonation step.)

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[1] *O.T.S. Rept.* PB 85,687.

1. Sulfonation with SO_3 (oxidation of the SO_2):

$$(a)\ SO_2 + O \rightarrow SO_3$$

$$(b)\ C_2H_5C_6H_5 + SO_3 \rightarrow C_2H_5C_6H_4SO_3H$$

2. Bisulfite addition (oxidation of the organic compound before sulfonation):

$$(a)\ C_2H_5C_6H_5 \rightarrow CH_2{=}CHC_6H_5 + H_2$$

$$(b)\ CH_2{=}CHC_6H_5 + NaHSO_3 \rightarrow C_6H_5CH_2CH_2SO_3Na$$

3. Sulfochlorination (oxidation of the organic compound with sulfonation):

$$(a \text{ and } b)\ C_6H_6CH_2CH_3 + SO_2 + Cl_2 \rightarrow C_6H_5CH_2CH_2SO_2Cl + HCl$$

4. SO_2 with $AlCl_3$ (oxidation of the organic compound after sulfonation):

$$(b)\ C_2H_5C_6H_5 + SO_2 \xrightarrow{AlCl_3} C_2H_5C_6H_4SO_2H$$

$$(a)\ C_2H_5C_6H_4SO_2H + O \rightarrow C_2H_5C_6H_4SO_2OH$$

It will be seen that two of the three procedures employing compounds of SO_2 (2 and 3) yield side-chain sulfonates which cannot be obtained using SO_3 in two steps. The third method using a compound of SO_2 (4) gives a ring sulfonate, but by a less advantageous procedure than when employing SO_3. A side-chain sulfonate can, however, be prepared using SO_3 in three steps, as follows:

5. Use of SO_3-dioxane with the alkene (oxidation of both SO_2 and the organic compound before sulfonation, followed by reduction of the product):

$$(a)\ SO_2 + O \rightarrow SO_3 \qquad C_2H_5C_6H_5 \rightarrow CH_2{=}CHC_6H_5 + H_2$$

$$(b)\ CH_2{=}CHC_6H_5 + SO_3\cdot\text{dioxane} \rightarrow HO_3SCH{=}CHC_6H_5$$

$$(c)\ HO_3SCH{=}CHC_6H_5 \xrightarrow{H_2} HO_3SCH_2CH_2C_6H_5$$

Sulfoalkylating Agents and Related Compounds

Sulfoalkylating agents are organic sulfonates containing usually one to three carbon atoms and a reactive functional group (e.g., hydroxyl, amino, chlorine, aldehyde, or olefinic unsaturation) allowing easy attachment to an organic compound of higher molecular weight (e.g., a water-insoluble dye, drug, or polymer) upon which it is desired to confer the properties of a sulfonate group, especially water solubility. These compounds may therefore be properly regarded as *organic sulfonating agents.*[1]

Sulfomethylation. Sodium hydroxymethanesulfonates ("aldehyde bisulfites") are used to sulfomethylate on reactive carbon atoms (e.g., in phenols or ketones) or on nitrogen (i.e., amines, amides, or sulfoamides) by the following reactions:

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[1] GILBERT and JONES, *Ind. Eng. Chem.*, **43**, 2029 (1951).

$$HOC_6H_5 + HOCH(R)SO_3Na \rightarrow HOC_6H_4CH(R)SO_3Na + H_2O \qquad (1)$$

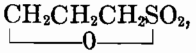
$$R'NH_2 + HOCH(R)SO_3Na \rightarrow R'NHCH(R)SO_3Na + H_2O \qquad (2)$$

Reaction (1) is applied industrially using formaldehyde-bisulfite (R = H), employing excess formaldehyde to give simultaneous resinification. By controlling the amount of formaldehyde, the resins may be made water-soluble (tanning agents) or water-insoluble (ion-exchange resins). Reaction (2) yields dye intermediates (see details of the commercial process for sulfomethylating aniline on p. 375) and pharmaceuticals (R′ representating a sulfa drug). In the latter case, sulfomethylation is an advantageously mild method for rendering these drugs desirably water-soluble; direct sulfonation procedures are not suitable since they destroy their activity. Compounds sulfomethylated on nitrogen can also be prepared alternatively by reacting a nitrogen-free compound with the reagent $H_2NCH_2SO_3Na$.

Sulfoethylation. Important industrial wetting agents (Igepon A and Igepon T) are prepared by reacting long-chain fatty acid chlorides with salts of 2-hydroxyethanesulfonic acid, $HOCH_2CH_2SO_3Na$, or N-methyltaurine, $CH_3NHCH_2CH_2SO_3Na$. Details of the industrial process for making the former are given on p. 376; the latter is prepared by the following reaction:

$$RCOCl + CH_3NHCH_2CH_2SO_3Na + NaOH \rightarrow RCON(CH_3)CH_2CH_2SO_3Na + NaCl$$

Sodium 2-chloroethanesulfonate, $ClCH_2CH_2SO_3Na$, and sodium ethylene sulfonate, $CH_2{=}CHSO_3Na$, have been used industrially and in the laboratory to solubilize starch, cellulose,[1] and other compounds by sulfoethylation.

Other Sulfoalkylating Agents. These include sodium 2-hydroxy-3-chloropropanesulfonate-1, $ClCH_2CHOHCH_2SO_3Na$, used industrially to sulfopropylate long-chain fatty acids, and propane sultone,  $\underbrace{CH_2CH_2CH_2SO_2}_{O}$, a highly reactive sulfopropylating agent made via sulfochlorination of 1-chloropropane. Other sultones react similarly. Compounds containing aldehyde groups include potassium acetaldehyde disulfonate, $OCHCH(SO_3K)_2$, from acetylene and oleum, and *n*-1-butanalsulfonate-3, $OCHCH_2CH(SO_3H)CH_3$, made from crotonaldehyde and sulfurous acid.

Sulfoarylation. This procedure is analogous to sulfoalkylation, except that an aromatic sulfonate is employed. Phenolsulfonic acid yields tanning agents or ion-exchange resins by reaction with formaldehyde, and naphthalene-2-sulfonic reacts with it, forming important dispersing agents.

Sulfatoalkylation. This procedure is analogous to sulfoalkylation, except that a sulfate rather than a sulfonate is employed. Thus, the $—NHCH_2-CH_2OSO_3H$ grouping is introduced into certain anthraquinone dyes used on synthetic fibers, and it has been converted to a detergent by reaction

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[1] GILBERT and JONES, *Ind. Eng. Chem.*, **46**, 1898 (1954).

with a long-chain fatty acid chloride.[1] The —NH$(CH_2)_4OSO_3H$ group in phthalocyanine dyes confers a desirable solubility when applying the dye but is sufficiently labile for subsequent removal so that the dye remains fixed on the fiber in insoluble form.

Sulfonation by Oxidation of Thiol Derivatives

Sulfonation procedures described in preceding sections entail the use of an inorganic or organic sulfonating agent. The oxidation of compounds already containing sulfur in a lower valence state is also an important preparative method; no sulfonating agent is employed since oxidation is the only reaction involved.

III. CHEMICAL AND PHYSICAL FACTORS IN SULFONATION AND SULFATION

When employing SO_3 or its compounds for sulfonation or sulfation, important variables determining the rate and course of the reaction are (1) concentration of SO_3 in the sulfonating agent, (2) chemical structure of the organic compound, (3) time in relation to temperature and reagent strength, (4) catalysts, and (5) solvents.

Concentration of SO_3

To carry sulfonation or sulfation to completion, it is necessary to maintain the SO_3 concentration in the sulfonating agent at a certain minimum level.

When SO_3 itself is employed, the concentration is at a maximum and the initial stage of the sulfonation is completed easily and rapidly. However, the sulfonic acid formed in the initial stage easily reacts with a second mole of SO_3 to form a complex which may be much less reactive than SO_3 itself. Thus, when reacting a hydrocarbon with SO_3 on an equimolar basis, one half of the hydrocarbon is sulfonated with SO_3 and the other half is sulfonated by the less reactive complex (see the section on Kinetics). Likewise, when sulfonating organic acids with SO_3, the initial reaction product is an acyl sulfate which is next converted to the desired sulfonate under considerably more drastic conditions. The second half of these reactions is the slower, and the rate and reaction conditions are determined by the stability of the initial complex, which varies greatly. The benzenesulfonic acid-SO_3 complex is quite reactive, while that from naphthalenedisulfonic acid is comparatively unreactive. When SO_3 is used for sulfation, the reaction appears simpler:

$$ROH + SO_3 \rightarrow ROSO_3H$$

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[1] *B.I.O.S. Rept.* 421.

When using $ClSO_3H$, these reactions go to completion quite easily since HCl is evolved and this acid forms complexes with the sulfonates less easily than SO_3:

$$RH + ClSO_3H \rightarrow RSO_3H + HCl\uparrow$$
$$ROH + ClSO_3H \rightarrow ROSO_3H + HCl\uparrow$$

However, this advantage is offset by other objections to this reagent, as discussed in a preceding section.

Hydrates of SO_3. As stated previously (p. 308), the hydrates of SO_3 (i.e., sulfuric acid and oleum) are properly regarded as solutions of SO_3 in water. The water has a great affinity for SO_3, however, and may in this system even be regarded as a base which in proportion to its concentration tends to neutralize the acidic SO_3 and prevent its reaction with the organic compound. As the concentration of water increases, the rate of sulfonation steadily decreases, since (as explained more fully on p. 351) the reaction rate is inversely proportional to the square of the water concentration. Finally, the reaction stops short of completion (using stoichiometric quantities), since the SO_3 concentration in the sulfonating agent has been reduced to an ineffective level:

$$RH + H_2SO_4 \rightarrow RSO_3H + H_2O$$
$$ROH + H_2SO_4 \rightarrow ROSO_3H + H_2O$$

Guyot[1] designated the SO_3 concentration at which reaction stops by the Greek letter π and concluded that in the preparation of benzenesulfonic acid sulfonation stopped at a π value of 64 (corresponding to $H_2SO_4 \cdot 1.5H_2O$, or 78.4 per cent H_2SO_4) regardless of temperature, agitation, or catalysts. The π value he also thought to be independent of the concentration of the starting acid. Thus, with 100 per cent acid, 60 per cent of the available SO_3 has reacted by the time the π value is reached; with 94 per cent acid, about 46 per cent of the SO_3 is utilized.

Further study by Courtot[2] led to an equation for the minimum quantity of acid required for sulfonating a gram mole of an organic compound:

$$\frac{Xa}{100} = 80 + (X - 80)\frac{\pi}{100} \qquad \text{or} \qquad X = 80\,\frac{100 - \pi}{a - \pi}$$

where X is the weight of the acid in grams and a is its SO_3 content expressed in per cent. Courtot was the first to show that sulfonic acids form addition compounds, or complexes, with SO_3 and that these render difficult the completion of the reaction by reducing the availability of SO_3 in a reactive form.

Courtot noted that different organic compounds have different π values,

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[1] Guyot, *Chimie & industrie*, **2**, 879 (1919).

[2] Courtot, *Rev. gén. mat. color.*, **33**, 177 (1929).

that polysulfonates have higher π values corresponding to the degree of sulfonation, and that the reaction temperature has an effect:

	π value	Per cent H_2SO_4
Naphthalene (monosulfonation at 60°C)	56	68.5
Naphthalene (monosulfonation at 160°C)	52	63.7
Naphthalene (trisulfonation at 160°C)	79.8	97.3
Nitrobenzene (monosulfonation)	82	100.1

Thus, the more easily a compound is sulfonated, the lower is its π value.

The concept of π has proved useful from a practical standpoint, but further study[1] has shown that the numerical value of π depends upon many other factors, including the excess of starting compound, the reaction time, and the concentration of the starting acid. It is therefore necessary to stipulate in detail the reaction conditions used for determining π in any particular case. Failure to do this may account for the divergent values of π noted in the literature even for the simplest cases, viz., benzene and naphthalene.

Procedures for Completing Sulfonation. The above considerations show that, to sulfonate an aromatic compound completely, it is necessary to maintain the acid strength above that corresponding to the π value. This can be done in several ways, as follows:

Use of Excess Acid. The organic compound will be completely sulfonated if sufficient excess acid is employed to stay above the π value even when diluted by the water formed during reaction. In practice, the excess quantity should be sufficient to effect complete sulfonation at a point above the π value, since the reaction rate becomes impractically slow as the π value is closely approached. Thus, in one method of sulfonating benzene with 100 per cent acid (see p. 369), 200 per cent of theory of acid is employed at 105°C, yielding a spent acid of about 83 per cent, which is above the π concentration. This approach to completing sulfonation is fairly simple, but requires excess acid which must be separated and discarded. It can be made more efficient by employing acid (or oleum) of maximum strength compatible with yield and product quality and by operating at maximum permissible temperature. Neither of these expedients will give complete utilization of acid, however.

Excess acid is also used to achieve maximum completion of reaction in the sulfation of alcohols. Thus, lauryl alcohol is reacted to the extent of 90 per cent by employing a 70 per cent excess of monohydrate acid.[2] Oleum gives excessive decomposition.

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[1] Spryskov, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 833 (1944).

[2] Whyte, *J. Am. Oil Chemists' Soc.*, **32**, 313 (1955).

Physical Removal of Water. It was Guyot who first observed that nearly theoretical utilization of both acid and organic compound could be achieved by partial-pressure distillation of the water from the reaction mixture by repeatedly distilling an excess of the material to be sulfonated through the reactor. In this manner the acid is maintained above π concentration until completely consumed. This procedure combines simplicity of operation with excellent utilization of both acid and organic compound and is the prevalent industrial approach for sulfonating low-boiling stable aromatic hydrocarbons such as benzene (see pp. 311 and 377), toluene (see p. 312), and the xylenes (see p. 312). In the case of naphthalene, as described in detail on p. 379, the reaction is carried rapidly to completion by the combined use of excess acid (40 per cent excess over that converted to sulfonate) and a high temperature (160–165°C) sufficient to maintain the acid well above the π concentration by distillation of water (0.95 mole per mole naphthalene sulfonated). Although some naphthalene does distill with the water, excess hydrocarbon is not employed to assist in its removal as in the case of benzene and its homologues. Attempts to obtain complete acid utilization with naphthalene have not met with success, since this approach has yielded more sulfone and a higher proportion of the undesired alpha isomer.

This procedure has been extended to aromatic amines, using orthodichlorobenzene or a similar compound as the inert azeotroping agent. Rapid and continuous removal of water occurs in the range 150–200°C, with an equimolar quantity of acid.[1] This a variant of the "baking process," described in detail on p. 383 for the case of sulfanilic acid. In the baking procedure, water is removed at high temperature by circulating air or by the use of vacuum.

Chemical Removal of Water. Sulfonation can also be completed by adding to the sulfonation mixture a material capable of reacting with the water formed, thereby removing it and allowing the reaction to go to completion. The introduction of BF_3 accomplishes this; a comparable test without BF_3 showed only 42 per cent reaction.[2] Thionyl chloride, $SOCl_2$, can also be used; in this case the water is removed by the following reaction:

$$H_2O + SOCl_2 \rightarrow 2HCl\uparrow + SO_2\uparrow$$

These chemical procedures for completing sulfonation are too costly for industrial use, but are convenient for the laboratory.

Procedures for Completing Chlorosulfonation. In the preparation of aromatic sulfonyl chlorides, the following reactions occur.

$$RH + ClSO_3H \rightarrow RSO_3H + HCl\uparrow \qquad \text{(Step 1)}$$

$$RSO_3H + ClSO_3H \rightleftharpoons RSO_2Cl + H_2SO_4 \qquad \text{(Step 2)}$$

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[1] *O.T.S. Rept.* PB 73,911, frames 4648–4660.

[2] THOMAS, ANZILOTTI, and HENNION, *Ind. Eng. Chem.*, **32**, 408 (1940).

Step 1 goes to completion easily, since hydrogen chloride is evolved. Step 2, however, is an equilibrium reaction and—just as when using SO_3 hydrates for sulfonation—special means are required to drive it to maximum completion.

Completion of step 2 by distillative removal of a reaction product—a useful technique when sulfonating with sulfuric acid—cannot be applied here because of the high boiling points. Use of excess sulfonating agent (varying from 1 to as high as 6 moles of chlorosulfonic acid per mole of organic compound) does improve the yield and is standard laboratory and industrial practice even though complete reaction is still not achieved. For example, in one commercial procedure for preparing the important sulfa drug intermediate 4-acetylaminobenzenesulfonyl chloride, as detailed on p. 382, 5.4 moles of acid is used per mole of acetanilide.

Removal of the sulfuric acid formed by chemical means has also been considered as a method for completing the chlorosulfonation reaction. In this connection, it has been found[1] that the yield of benzenesulfonyl chloride may be raised from 75 to 90 per cent by the combined use of excess acid and sodium chloride, the latter removing the sulfuric acid by forming sodium acid sulfate and hydrogen chloride. Further improvement was obtained (in terms of reduced chlorosulfonic acid requirements) by the combined use of the sodium chloride and an inert organic solvent such as carbon tetrachloride, which must be present during the reaction, rather than added later to extract the sulfonyl chloride after drowning the reaction mixture on ice. Comparative yield data are summarized in Table 7-4.

TABLE 7-4. BENZENESULFONYL CHLORIDE YIELD DATA

Method	Benzene, moles	Acid, moles	Sodium chloride, moles	Yield, %
Standard (no solvent, no NaCl)	2	6	None	76
NaCl	2	10.7	2.1	90
NaCl plus solvent	2	6	2.1	90

Chemical removal of the sulfuric acid formed has also been effected by the expedient of adding a reagent capable of reconverting it to chlorosulfonic acid, thereby not only reducing the amount of required acid but also driving the reaction to completion.[2] Carbon tetrachloride and sulfur with chlorine have been used; the over-all reaction is as follows:

$$2RH + 2ClSO_3H + S + 2Cl_2 \rightarrow 2RSO_2Cl + SO_2 + 4HCl$$

$$RH + ClSO_3H + CCl_4 \rightarrow RSO_2Cl + COCl_2 + 2HCl$$

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[1] *O.T.S. Rept.* PB 58,835.

[2] Schirm, German Patent Application D 84,646; Schirm, Ger. 757,503 (1952).

Chemical Structure

Aromatic hydrocarbons, as a class, are easily sulfonated. Substitution of the hydrocarbon ring with hydroxyl or amino groups, or with successive alkyl groups, increases the ease of sulfonation as reflected by the rate of reaction or the π value. Halogen, nitro, carbonyl, and sulfonyl groups, on the other hand, make sulfonation more difficult. It will therefore be seen that (aside from halogen which is only mildly deactivating) ortho-para directing groups facilitate ring sulfonation, while meta directing groups hinder sulfonation. Isomeric compounds show pronounced differences in ease of sulfonation. The para isomer of xylene is more difficult to react than the other two; this result is in agreement with the general rule that an entering sulfonate group tends for steric reasons to avoid entering a position adjacent to other substituents, since it is fairly bulky. Likewise, the entering sulfonate group, for the same reason, occupies preferably a position adjacent to the smaller of two groups, as in the case of 4-isopropyltoluene where substitution is almost entirely in the 2 position.[1] With the monoalkylated benzenes, the reaction rate depends upon the nature of the alkyl group, as shown in Table 7-5.[2]

TABLE 7-5. RELATIVE RATES OF SULFONATION OF ALKYLBENZENES BY SULFURIC ACID
(In Nitrobenzene Solution)

Compound	*Relative rate*
Toluene	1.00
Ethylbenzene	0.95
Isopropylbenzene	0.66
t-Butylbenzene	0.56
o-Xylene	3.50

These differences in ease of sulfonation (and correspondingly of desulfonation, as discussed in a subsequent section) have formed the basis of a chemical method for the separation of mixtures of compounds otherwise hard to separate. The sulfonation of polycyclic hydrocarbons, such as anthracene or phenanthrene, occurs so easily that polysulfonates are formed even under such mild conditions that some of the hydrocarbon remains unsulfonated. For this reason, such sulfonations have been investigated relatively little and what data exist tend to be contradictory. Sulfonates derived from anthracene are usually prepared from anthraquinone, which yields fewer by-products than the hydrocarbon, although some disulfonation does occur even with the usual industrial practice of partial sulfonation of the quinone.

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[1] LEFEVRE, *J. Chem. Soc.*, **1934**, 1501.

[2] NELSON and BROWN, Aromatic Substitution, in "The Chemistry of Petroleum Hydrocarbons," vol. III, p. 538, Reinhold Publishing Corporation, New York, 1955.

Quantitative expression of the effect of substituents in the benzene ring on the rate of sulfonation is given in Table 7-6[1] for SO_3 and in Table 7-7[2] for H_2SO_4. In both tables some degree of correlation is evident between the velocity constants and activation energies; in Table 7-6 additional correlation is shown with dipole moment function, except for nitroanisole.

TABLE 7-6. REACTION RATES: ARYL SULFONATION WITH SO_3

	Velocity constant, liters/g mole sec, k, 40°C	Activation energy, cal/g mole, E	Dipole moment functions, $f(\mu)$
Benzene	48.8 (40.8)	4,800 (5,500)	0.00
Chlorobenzene	2.4	7,720	1.56
Bromobenzene	2.1	7,840	1.53
m-Dichlorobenzene	4.36×10^{-2}	9,220	3.12
Nitrobenzene	7.85×10^{-6}	11,400	3.97
p-Nitrotoluene	9.53×10^{-4}	11,025	3.56
p-Nitroanisole	6.29	4,320	5.13

TABLE 7-7. REACTION RATES: ARYL SULFONATION WITH H_2SO_4

Compound sulfonated	Velocity constant, $k_o \times 10^6$ at 40°C	Activation energy, E	Compound sulfonated	Velocity constant, $k_o \times 10^6$ at 40°C	Activation energy, E
Naphthalene	141.3	6,100	Bromobenzene	9.5	8,850
m-Xylene	116.7	6,400	*m*-Dichlorobenzene	6.7	9,460
Toluene	78.7	6,700	*p*-Nitrotoluene	3.3	9,770
1-Nitronaphthalene	26.1	8,400	*p*-Dichlorobenzene	0.98	9,570
p-Chlorotoluene	17.1	7,440	*p*-Dibromobenzene	1.01	9,670
Benzene	15.5	7,500	1,2,4-Trichlorobenzene	0.73	9,940
Chlorobenzene	10.6	8,940	Nitrobenzene	0.24	11,060

The importance of chemical structure in determining ease of sulfonation is further illustrated in the pyridine series. These compounds as a group are very difficult to sulfonate, ordinarily requiring a mercury catalyst at over 250°C using oleum. 2,6-Di-*tert*-butylpyridine has been found, on the other hand, to sulfonate easily even at −10°C, using SO_3 dissolved[3] in SO_2. In this exceptional case, steric hindrance prevents formation of the difficultly sulfonatable addition compound with SO_3.

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[1] DRESEL and HINSHELWOOD, *J. Chem. Soc.*, **1944**, 649; WADSWORTH and HINSHELWOOD, *ibid.*, p. 469.

[2] STUBBS, WILLIAMS, and HINSHELWOOD, *J. Chem. Soc.*, **1948**, 1065.

[3] BROWN and KANNER, *J. Am. Chem. Soc.*, **75**, 3865 (1953).

A study of the sulfation of alcohols with sulfuric acid[1] has shown that primary alcohols sulfate ten times as fast as secondary.

Time-Temperature-Reagent Strength

To obtain maximum efficiency in commercial sulfonation and sulfation, the reaction time must be reduced to the minimum compatible with product quality and yield. This may be accomplished by using a stronger sulfonating agent or, in the case of any particular reagent, by raising the reaction temperature, or by using a larger proportion of the reagent.

In the section on Kinetics (p. 350), it is shown that sulfonation resembles other chemical reactions in that the rate of reaction is approximately doubled for each increase of 10°C in temperature. This method of increasing reaction rate is often limited, however, by a parallel increase in objectionable side reactions, as discussed below for a number of specific cases. Sometimes it is possible to use an elevated temperature with a short reaction time (i.e., "quenching"). In most cases, however, low temperatures with correspondingly long reaction periods tend to yield purer and lighter-colored products.

Maximum reaction rate is attainable with the strongest reagent, namely, SO_3, and its use is increasing. As a consequence of the increased production of sulfonates, there is a compelling interest in more efficient and more rapid and especially continuous processes. The use of SO_3 is subject to limitations, however, as noted in Table 7-3. It reacts virtually instantaneously with many compounds, for example, hydrocarbons or alcohols, even at low temperatures. In other cases, however, it first forms a complex with the compound being sulfonated, and rearrangement to the desired sulfonic acid requires time and heat, as with benzoic acid, benzenesulfonic acid, and pyridine.

Benzene Derivatives. In the sulfonation of toluene, reaction temperature has a pronounced effect on product isomer distribution, as shown in Table 7-8.

TABLE 7-8. EFFECT OF TEMPERATURE ON ISOMER YIELDS IN THE SULFONATION OF TOLUENE*

Isomer	25°C	50°C
Ortho	18–22	12–18
Meta	4–6	5–6
Para	74–76	78–82

* ENGLUND, ARIES, and OTHMER, *Ind. Eng. Chem.*, **45**, 189 (1953).

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[1] DENO and NEWMAN, *J. Am. Chem. Soc.*, **72**, 3852 (1950).

Consequently, in the chlorosulfonation of toluene to obtain the orthosulfonyl chloride (the intermediate for saccharin) a reaction temperature of 0–5°C is employed for maximum yield.

Product color is important in sulfonating dodecylbenzene detergent alkylate. In Table 7-9, it is shown[1] that, when 22 per cent oleum is used, it is possible to employ less sulfonating agent at a higher temperature, but a darker product is obtained.

TABLE 7-9. SULFONATION OF DODECYLBENZENE WITH 22 PER CENT OLEUM

Acid: hydrocarbon mole ratio	Temp, °C	Color*
3.25	24	2–3
2.9	29	4–5
2.6	38	5–6

* The higher the number, the darker the color.

Reaction temperature is often important in determining the ratio of mono- to polysulfonates. This is clearly illustrated in the commercial process for sulfonating 4-aminoazobenzene with a fixed quantity of oleum, as shown in Table 7-10.[2]

TABLE 7-10. SULFONATION OF 4-AMINOAZOBENZENE

Temp., °C	Time, hr	Product
0	36	Mono-
10–12	24	Half mono-, half di-
19–20	12	Di-

Naphthalene and Derivatives. The time-temperature relationship is especially important in this series from the standpoint of isomer distribution. Low temperatures (50°C and below) and/or short reaction periods favor alpha substitution, while higher temperatures (about 160°C) and/or a longer time favor beta substitution. Even when the more stable beta isomer is the final product, the less stable (but more easily formed) alpha isomer is produced first, but undergoes desulfonation and resulfonation to the beta sulfonate. The data for naphthalene are shown in Table 7-11.[3] The same considerations hold in the disulfonation of naphthalene and in the preparation of the naphthol- and naphthylaminesulfonic acids.

[1] Oronite Chemical Co., "Alkane Basic Detergent Raw Material," 1955.

[2] *O.T.S. Rept.* PB 102,210.

[3] EUWES, *Rec. trav. chim.*, **28**, 298 (1909).

TABLE 7-11. EFFECT OF TEMPERATURE ON THE SULFONATION OF NAPHTHALENE

Temp, °C	80	90	100	110.5	124	129	138.5	150	161
Alpha, %	96.5	90.0	83.0	72.6	52.4	44.4	28.4	18.3	18.4
Beta, %	3.5	10.0	17.0	27.4	47.6	55.6	71.6	81.7	81.6

In the anthraquinone series, on the other hand, time and temperature have very little influence on product orientation.

When reacting acid-sensitive organic compounds, an understanding of the effects of time and temperature is especially necessary, as has been shown for the sulfation of lauryl alcohol with monohydrate acid,[1] where a difference of 40 sec in time or of 10°C in temperature reflects a major difference in product quality.

Catalysts and Sulfonation Aids

The addition of other chemicals, usually in small amounts, can have a marked effect on some sulfonations in a variety of ways.

Changing Orientation. The addition of mercury changes the orientation in a number of aromatic sulfonation reactions. This is of great practical importance especially with anthraquinone, since in the presence of the catalyst the α-sulfonate is formed almost exclusively, while without mercury only the β-sulfonate is obtained. The α-sulfonate, in fact, was unknown until as late as **1903** when the reaction was unintentionally conducted in the presence of mercury. This catalytic effect was subsequently studied extensively, with major conclusions as follows:

1. The form of mercury employed is immaterial—the metal, sulfate, or chloride (-ous or -ic) all being equally satisfactory provided that the equivalent of 1 per cent of metal based on anthraquinone is used.

2. An organic mercurial intermediate is formed, which is the compound actually undergoing a replacement-type sulfonation, as follows:[2]

$$RH + HgSO_4 \rightarrow RHgSO_4H + SO_3 \rightarrow RSO_3H + HgSO_4$$

3. The catalytic effect functions for disulfonation, as well as for monosulfonation, thereby allowing preparation of the various α-β, α-α, or β-β anthraquinone disulfonates at will, depending on whether the mercury was present during the mono- or the disulfonation step or during both or during neither.

4. Mercury functions catalytically only when using oleum or SO_3 as the sulfonating agent. It does not function with aqueous acid, the use of which presumably inhibits one of the intermediate steps.[3]

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[1] WHYTE, *J. Am. Oil Chemists' Soc.*, **32,** 313 (1955).

[2] LAUER, *J. prakt. Chem.*, **130,** 231 (1931).

[3] SENSEMAN, *Ind. Eng. Chem.*, **13,** 1124 (1921).

5. Mercury affects the orientation of other organic compounds than anthraquinone, including: benzoic acid, phthalic anhydride, α-naphthol, nitrobenzene, benzenesulfonic acid, *o*-xylene, and chloroanthraquinones. However, the quantity of mercury needed is often high in these cases, and the change in orientation is sometimes only partial—a mixture of the "normal" and "abnormal" products being formed.

6. As mentioned below, mercury is sometimes used to increase the yield in certain difficult sulfonations, but without changing the orientation.

Facilitating Reaction. The addition of catalysts sometimes allows the use of lower reaction temperatures, improves yields, accelerates reaction, or in some cases even renders reaction possible.

In the sulfonation of pyridine with SO_3 or oleum, the addition of a small percentage of mercury raises the yield from 50 to 71 per cent.[1] Mercury is also added in converting benzenedisulfonic to the trisulfonic acid. Both of these sulfonations are run under drastic conditions.

A catalytic quantity of a copper salt is added to facilitate the reaction of 2-chlorobenzaldehyde with sodium sulfite to yield the sulfonate by replacement of the relatively inert aromatic chlorine.

An oxide of nitrogen facilitates the air oxidation of the lower alkane thiols (such as CH_3SH) to the sulfonic acid. In this case, NO_2 may be the real oxidizing agent yielding NO, which is reconverted to NO_2 by the air.

Several sulfonations using compounds of SO_2 (sulfochlorination, sulfoxidation, the addition of bisulfite to an olefinic bond) proceed by free radical chain reactions which characteristically require catalysts for initiation. Many catalysts have been proposed for these three types of sulfonation. As mentioned in the discussion of these reactions, common catalysts used are, respectively, light, acetic anhydride, and peroxides. In the second case, the acetic anhydride is not strictly a catalyst since it is used in stoichiometric amount and yields an acetate derivative intermediate.

Inhibiting Side Reactions. As stated in a preceding section, undesired by-product sulfone formation is pronounced in the mono- and disulfonation of aromatic hydrocarbons such as benzene, toluene, or xylene with SO_3 or strong oleum. The addition of acetic acid (about 5 per cent by weight of the hydrocarbon) inhibits, but does not eliminate, sulfone formation.[2] Sodium sulfate and sodium benzenesulfonate are also said to inhibit sulfone formation from benzene.[3] In sulfonating dodecylbenzene detergent alkylate with SO_3, sulfone formation does not occur as it does with benzene or toluene, but sulfonic anhydride formation does occur.[4] This objection-

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[1] McElvain and Goese, *J. Am. Chem. Soc.*, **65**, 2233 (1943).

[2] Gilbert and Giolito, U.S. 2,704,295 (1955); Rueggeberg, Sauls, and Norwood, *J. Org. Chem.*, **20**, 455 (1955).

[3] Swisher, Brit. 679,826 (1952); Molinari and Affholter, U.S. 2,578,823 (1951).

[4] Gilbert and Veldhuis, *Ind. Eng. Chem.*, **47**, 2300 (1955).

able side reaction can be eliminated by adding a small percentage of concentrated sulfuric acid to the hydrocarbon before introducing the SO_3, or the anhydride can be rapidly hydrolyzed to the product sulfonic acid by adding water.

In sulfonating hydroxyanthraquinones, boric acid is often added to block the free phenolic group by the formation of boric esters, thereby inhibiting oxidation as a destructive side reaction. Sodium sulfate is also added to such sulfonation mixtures; presumably pyrosulfate is formed, which is more moderate in its action than oleum.

Sulfonation Solvents

Many sulfonates are viscous liquids or solids. The use of reaction solvents is therefore often either essential or preferable to obtain efficient mixing, thereby ensuring uniform reaction. In many cases they function as suspending media, rather than as true solvents, since either or both of the reagents as well as the sulfonate product may be only slightly soluble.

Excess Acid. The helpful function of excess sulfuric acid as an inexpensive, low-viscosity solvent for most sulfonic acids is often overlooked because of the difficulty of recovering a product dissolved in it, or because of the disposal problem often encountered. Sulfonation of most of the hydroxyl, amino, nitro, and carboxylic derivatives of benzene, naphthalene, and anthraquinone is facilitated in this manner by the presence of excess acid. The same effect applies to anthraquinone itself, to petroleum lubricant fractions during sulfonation to mahogany and green acids, and to the sulfation of fatty oils. Chlorosulfonic acid, used in large excess for the conversion of aromatic compounds to sulfonyl chlorides by chlorosulfonation, functions in a similar manner.

Instead of allowing the sulfonating agent proper (or the spent acid from it) to function as the reaction solvent, it is sometimes customary to dissolve or suspend the organic compound (e.g., an aromatic amine) in monohydrate acid or low-strength oleum, followed by addition of the sulfonating agent (e.g., 65 per cent oleum).

Chlorinated Solvents. Ortho-dichlorobenzene or similar compounds are used in a modified form of the "baking process" for sulfonating aromatic amines, as discussed in a preceding section. They are high-boiling, relatively inert, inexpensive, and are immiscible with water, thereby facilitating removal of the latter from the reaction mixture by partial-pressure distillation.

Chlorinated aliphatic solvents used for sulfonation include methylene chloride, chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, and tetrachloroethylene. Fluorinated-chlorinated solvents find use in the laboratory. Such solvents have been employed[1] to preswell

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[1] WHEATON and HARRINGTON, *Ind. Eng. Chem.*, **44**, 1796 (1952).

beads of styrene-divinylbenzene copolymer preliminary to sulfonation with concentrated acid at 100°C to yield an ion-exchange resin. The sulfonation is heterogeneous; the function of the solvent is solely to effect swelling to facilitate penetration of the beads by the acid and removal of the excess after reaction. Styrene homopolymer, on the other hand, can be sulfonated with SO_3 in solution in carbon tetrachloride–liquid SO_2 mixture to yield a water-soluble sulfonate.[1] Chloroform and carbon tetrachloride have been used as solvents in the commercial sulfation of long-chain fatty alcohols with chlorosulfonic acid. The similar use of carbon tetrachloride in the chlorosulfonation of benzene leads to an improved yield of benzenesulfonyl chloride. It is also employed as solvent for the sulfochlorination of polyethylene with SO_2 and chlorine and for the sulfonation of saturated fatty acids in the alpha position[2] with SO_3. Tetrachloroethylene has also been used for the latter process; both solvents are miscible with SO_3. Amides of oleic acid have been sulfonated commercially with monohydrate acid at 0°C, using trichloroethylene solvent. Ethylene dichloride has been employed as solvent for sulfonating many heterocyclic compounds[3] with pyridine-SO_3; the sulfonating agent and product sulfonate are suspended rather than dissolved in this procedure.

Liquid SO_2. This material is an excellent sulfonation solvent. It is inexpensive, widely available, inert, nonflammable, miscible with sulfonating and sulfating agents, as well as with many organic compounds and product sulfonates, and can function as its own refrigerant to remove heat of reaction because of its boiling point (−10°C).[4] Objections to its use are its strong odor, a tendency to corrode the equipment used for its recovery, and the necessity of operating under pressure at temperatures above −10°C. It has been used to a limited extent commercially for sulfonating toluene and dodecylbenzene detergent alkylate and for sulfating long-chain alcohols.

Aqueous Solvents. Water or aqueous acetic acid is employed as the solvent for oxidative chlorination of thiol derivatives to the sulfonyl chlorides. The water participates in the reaction by providing oxygen, as well as functioning as a reaction medium; both the other reactants as well as the product sulfonyl chloride are relatively insoluble. The addition of acetic acid increases the solubility of the organic compounds. Water or aqueous alcohol is the usual solvent for nearly all reactions involving a sulfite reagent; this comprises the group of reactions involving addition to a

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[1] ROTH, *Ind. Eng. Chem.*, **46**, 2435 (1954).

[2] *O.T.S. Rept.* PB 30,081.

[3] TERENT'EV and GOLUBEVA, *Compt. rend. acad. sci. U.R.S.S.*, **51**, 689 (1946).

[4] LEISERSON, BOST, and LEBARON, *Ind. Eng. Chem.*, **40**, 508 (1948); ROSS, PERCY, BRANDT, GEBHART, MITCHELL, and YOLLES, *ibid.*, **34**, 924 (1942); Morrisroe, U.S. 2,703,788 (1955).

double bond (see p. 376) as well as those involving halogen replacement in either aliphatic or aromatic compounds. Sulfoalkylation reactions are also often conducted in aqueous medium (see p. 375). Although sulfations are ordinarily run under anhydrous conditions, the SO_3 complexes of aliphatic tertiary amines can be used for sulfation in aqueous medium because of their exceptional stability.

Miscellaneous Solvents. Dry nitrobenzene is employed for converting 2-naphthol to 2-naphthol-1-sulfonic acid, using chlorosulfonic acid at 0°C. Carbohydrates (such as cellulose) and related materials (e.g., alginic acid) can be sulfated with concentrated acid, using an aliphatic alcohol (for example, butanol) as the suspending medium. The alcohol presumably participates in the process, itself undergoing sulfation. Pyridine is sometimes used as the reaction medium when sulfating with pyridine-SO_3. This approach is used commercially for preparing the sulfates of leuco vat dyes;[1] alginic acid can be sulfated by this method. Dimethyformamide is a good solvent for SO_3 complexes; these materials are insoluble in most organic solvents.

Solvent Stability. It is not always essential that a prospective solvent, well suited for a particular sulfonation reaction in one or more respects, be completely inert toward the pure sulfonating agent. Several of the solvents mentioned above, for example, ortho—dichlorobenzene, nitrobenzene, chloroform, carbon tetrachloride, methylene chloride, and trichloroethylene, will react with SO_3 or its derivatives either by sulfonation or oxidation, in some cases quite easily. Reactive solvents can be employed with little loss if (1) the organic compound is much more easily sulfonated than the solvent, (2) the sulfonating agent is added to a mixture of the solvent and the compound being sulfonated, and (3) the temperature of sulfonation can be maintained below the point at which attack of the solvent becomes extensive.

IV. KINETICS, MECHANISM, AND THERMODYNAMICS

Kinetics

Aromatic sulfonation, like nitration, halogenation, alkylation, and acylation, is a typical electrophilic substitution reaction. Sulfonation, however, differs from these other reactions in two marked respects: it is reversible, and reaction temperature can, in certain cases, have an important influence on the position of the entering group, as shown on p. 344. These characteristics have tended to complicate studies of the reaction mechanism and rate of sulfonation and to render difficult the drawing of general conclusions. Other factors having the same effect are the tendency of sulfur trioxide to form a complex with the sulfonic acids and the pronounced tendency of all

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[1] Lubbs, pp. 534ff.

the reacting species to become solvated or highly hydrogen-bonded. When sulfuric acid is used as the sulfonating agent, the formation of water slows the reaction to such degree that rate studies can often be made only during the initial stages. With SO_3, the high speed of the reaction presents a problem.

Reaction-rate measurements in oleum are not complicated by the formation of water, and in the case of 4-nitrotoluene the reaction obeys the simple kinetic expression.[1]

$$\text{Rate} = k_2(\text{ArH})(\text{SO}_3)$$

In concentrated acid (92–99 per cent), on the other hand, the reaction proceeds according to the equation

$$\text{Rate} = k_2' \frac{\text{ArH}}{w^2}$$

where w indicates the water present. It is apparent from this equation that the rate of sulfonation is inversely proportional to the square of the water concentration.

Study of the sulfonation of benzene by benzene-saturated sulfuric acid over the temperature range 90–140°C, forming 0.239–15.81 moles of sulfonic acid per hour per liter of solution, has resulted in the following rate expression:[2]

$$\frac{R_L}{C_a} = 118\,(X_A - \tfrac{1}{2}X_W + \tfrac{1}{4}X_S)^{-9.230 + 5359/T}$$

where R_L = rate of benzene sulfonation (as moles of benzenesulfonic acid per hour per liter)

X_A = mole fraction H_2SO_4

X_W = mole fraction H_2O

X_S = mole fraction benzenesulfonic acid

T = absolute temperature

C_A = concentration of H_2SO_4 (moles per liter)

A rate study has also been made of the reaction of benzene with SO_3 in ethylene dichloride solvent.[3] The extreme rapidity of this reaction required the use of special technique, and since the reaction is complicated (as discussed more fully below) only the rate of the initial stage was studied. The following rate equation was obtained:

$$\frac{-dCi}{dt} = 5.11\, C_{Hi}^{\;0.57}\, C_{Si}^{\;1.24}$$

where C_{Hi} = initial concentration of benzene, gram moles per liter

C_{Si} = initial concentration of SO_3, gram moles per liter

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[1] Cowdrey and Davies, *J. Chem. Soc.*, 1949, p. 1871.

[2] Crooks and White, *Chem. Eng. Progr.*, **46**, 249 (1950).

[3] Ratcliff, *Dissertation Abstr.*, **14**, 2018 (1954).

Like other chemical reactions, a rise of 10°C in temperature about doubles the rate of sulfonation. This has been demonstrated, for example, with 4-nitrotoluene using oleum or sulfuric acid,[1] for the conversion of naphthalene-1,5-disodiumsulfonate to the 1,3,5-trisulfonyl chloride using chlorosulfonic acid over the range 10–100°C,[2] and for the sulfonation of 4-aminoazobenzene discussed in a previous section.

Mechanism of Reaction

The mechanism of aromatic sulfonation has been studied extensively. It is not surprising, considering the technical difficulties mentioned above, that divergent conclusions have been reached by various investigators and that in aqueous sulfuric acid as many as four different reactive species have been proposed as the true sulfonating agent: (1) $H_3SO_4^+$, (2) SO_3 or a solvate, (3) HSO_3^+ or a solvate, and (4) S_2O_6 (dimeric SO_3). All these reagents require the retardation of the rate of sulfonation with increasing water concentration. It has been pointed out, however,[3] that the degree of expected retardation is markedly different for each species and that monomeric SO_3 is the only one agreeing with the Cowdrey equation given above where the rate varies as the inverse square of the water concentration. It also appears possible that monomeric SO_3 can be the active sulfonating agent in oleum. Earlier work had indicated that, with SO_3 as the sulfonating agent, it reacted as the dimer S_2O_6. However, if it is assumed that sulfonation proceeds in two steps (see below), with 1 mole of monomeric SO_3 participating in each step, the data obtained are equally consistent with monomeric SO_3 as the reactive species. It is concluded, therefore, that monomeric SO_3 is probably the active agent when using sulfuric acid, oleum, or SO_3 itself.

A study of the equimolar reaction of SO_3 with toluene[4] has suggested the following sequence:

$$RH + 2SO_3 \rightarrow RSO_3SO_3H \tag{1}$$

$$RSO_3SO_6H + RH \rightarrow R_2SO_2 + H_2SO_4 \tag{2}$$

$$RSO_3SO_3H + RH \rightarrow 2RSO_3H \tag{3}$$

This mechanism requires that about half of the hydrocarbon be sulfonated with SO_3, the other half with pyrosulfonate by reaction (3). Reactions (2) and (3) occur concurrently, with (2) yielding undesired by-product sulfone, which is formed in some quantity when using SO_3. Reaction (1) probably actually proceeds in two steps, as stated above (see also the equations in the paragraph below).

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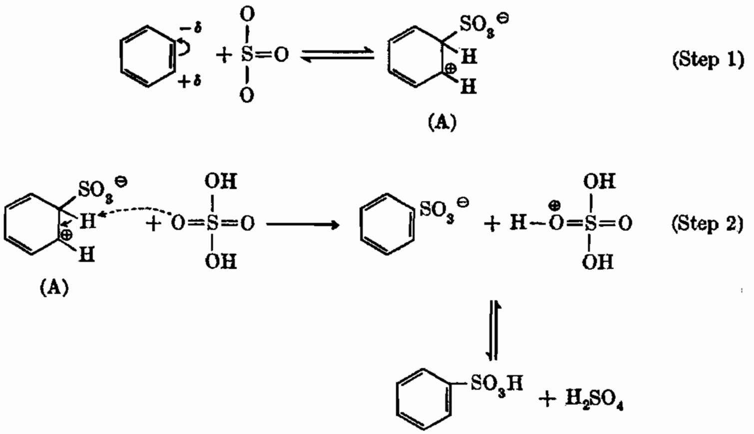
[1] Martinsen, *Z. physik. Chem.*, **62**, 713 (1908).

[2] Spryskov and Apar'eva, *J. Gen. Chem.* (*U.S.S.R.*), **19**, 1576 (1949).

[3] Ingold, "Structure and Mechanism in Organic Chemistry," pp. 299ff., Cornell University Press, Ithaca, N.Y., 1953; Nelson and Brown, Aromatic Substitution Theory and Mechanism, in "The Chemistry of Petroleum Hydrocarbons," vol. III, pp. 537ff., Reinhold Publishing Corporation, New York, 1955.

[4] Rueggeberg, Sauls, and Norwood, *J. Org. Chem.*, **20**, 455 (1955).

Aromatic substitution reactions, including sulfonation, are conceived as proceeding in two steps, the first involving reagent attack and the second proton removal. The process may be schematized as follows,[1] for the sulfonation of benzene with sulfuric acid with monomeric SO_3 as the active reagent:



Here, sulfuric acid is shown as receiving the proton from (A); other reagents, such as SO_3, could function likewise.

Although the mechanism of sulfonation is conceived as generally similar to those of nitration and halogenation, there is an important difference. The intermediate compound (A) above is electrically neutral and, therefore, more stable than the analogous intermediates involved in nitration and halogenation, which bear positive charges. Consequently, step 2 of sulfonation is much slower than the analogous second steps in the other substitution reactions and, in fact, is involved in rate determination, as has been shown by isotopic studies. This unusual stability of intermediate (A) is also consistent with the characteristically reversible nature of the sulfonation reaction.

The peculiar temperature sensitivity of sulfonation respecting variation in the ratio of isomers formed has been discussed in the light of the above reaction mechanism.[2] It is known from experiment that low temperatures and/or short reaction times (i.e., nonequilibrium conditions) favor formation of the sterically strained isomers. This has been noted, for example, with toluene (more ortho isomer at low temperature) and with naphthalene (more 1 isomer at low temperature). In intermediate (A) above, the entering sulfonate group is out of the plane of the ring, while in the final product

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[1] Alexander, "Principles of Ionic Organic Reactions," p. 252, John Wiley & Sons, Inc., New York, 1950.

[2] Nelson and Brown, *op. cit.*, pp. 500ff.

the two groups are in the same plane. Since the sulfonate group is large, compound (A) will not be in a condition of strain, whereas the final product is under strain. Under equilibrium conditions for step 2, therefore, there will be a tendency to favor in the final product those isomers with less strain (e.g., the para isomer of toluene or the 2 isomer of naphthalene). However, under nonequilibrium conditions, the degree of strain in the final product will have no effect on isomer distribution since this will have been determined in step 1 during the formation of compound (A) where steric effects are less important. Since a higher temperature tends to promote reversibility (as explained in discussing the desulfonation reaction), this condition also encourages formation of the less strained product.

The mechanism and kinetics of the sulfation of the lower alcohols with sulfuric acid have been studied.[1] The reaction proceeds by a bimolecular displacement mechanism like that of the acid-catalyzed esterification of alcohols with carboxylic acids; no oxygen-alkyl fission occurs. Neopentyl alcohol sulfates at a rate comparable to other secondary alcohols; these results indicate that within the groups of primary and secondary alcohols steric effects are minor. However, primary alcohols sulfate at a rate ten times that of secondary alcohols. The experimentally determined rate law is

$$\frac{d(\mathrm{ROSO_3H})}{dt} = k(\mathrm{ROH})\ (\mathrm{H_2SO}\ )\ (\mathrm{H^+}\ \text{activity})$$

Even under the most favorable conditions at equimolar ratios of acid and alcohol, the sulfation reaction is only 65 per cent complete by the equation:

$$\mathrm{ROH} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{ROSO_3H} + \mathrm{H_2O}$$

To obtain commercial yields of lauryl sulfate by this procedure, the reaction is driven to the right by using an excess (e.g., 170 per cent of theory) of strong (i.e., 100 per cent) acid.[2]

It has been suggested[3] that the mechanism of sulfation of lauryl alcohol differs from that of the lower alcohols in that, in batch sulfation of the former by adding $\mathrm{ClSO_3H}$, the reaction proceeds in two steps as follows:

$$\mathrm{2ROH} + \mathrm{ClSO_3H} \rightarrow \mathrm{(RO)_2SO_2} + \mathrm{HCl} + \mathrm{H_2O}$$
$$\mathrm{(RO)_2SO_2} + \mathrm{ClSO_3H} + \mathrm{H_2O} \rightarrow \mathrm{2ROSO_3H} + \mathrm{HCl}$$

Thermodynamics

A knowledge of heat effects encountered in sulfonation or sulfation processes is of great importance for determining optimum equipment design. Depending on the reaction involved and upon how it is conducted, the net

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[1] Deno and Newman, *J. Am. Chem. Soc.*, **72**, 3852 (1950).

[2] Whyte, *J. Am. Oil Chemists' Soc.*, **32**, 313 (1955).

[3] *Ibid.*

effect may vary widely from highly exothermic over a short period of time to endothermic over a long period. Some reactions are exothermic in the initial phase and endothermic in the final stage.

With SO_3 or its compounds, it is convenient to calculate the net heat effect in any particular sulfonation or sulfation by using SO_3 vapor as a reference point. There are two reasons for this: (1) more heat is evolved in sulfonation with this reagent than with any other of the group, and (2) all the compounds of SO_3 used as sulfonating agents can be made from it by direct (or, in the case of sulfamic acid, indirect) exothermic reaction with the material (e.g., water, HCl, trimethylamine) forming the compound. Using these two factors, the following equation may be employed to derive the net heat evolved in any particular sulfonation or sulfation:

$$\Delta H_C = \Delta H_V - \Delta H_D$$

where ΔH_C = heat of sulfonation with compound of SO_3 being used as sulfonating agent

ΔH_V = heat of sulfonation with SO_3 vapor (exothermic)

ΔH_D = heat of dissociation of sulfonating agent into SO_3 vapor and compounding reagent (endothermic)

Values for ΔH_V and ΔH_D are usually easily determined by direct experiment, or in some cases they may already be available in the chemical literature. The value of ΔH_D is equal but opposite in sign to the heat of reaction of SO_3 vapor with the compounding reagent. It will be seen that ΔH_C will be exothermic or endothermic, depending on the relative magnitudes of ΔH_V and ΔH_D.

When using liquid SO_3 as the sulfonating agent, ΔH_D is equal to the heat of vaporization, 224 Btu per lb SO_3 vaporized (Fig. 7-2, p. 310). It is interesting to note that although less heat is evolved in sulfonation with the liquid form of SO_3 (see Table 7-12), the vapor form is actually the milder.[1] The reason for this apparent anomaly is that SO_3 reacts so quickly that, in spite of efforts to disperse the liquid into fine droplets, local "hot spots" occur. The vapor form, on the other hand, is much more widely distributed and therefore reacts more smoothly, even though the total heat evolved is higher. Liquid SO_3 can be used to sulfonate organic compounds of high stability, however.

When employing compounds of SO_3, the above equation is applicable, provided that the sulfonating agent is completely consumed, as for example, in preparing benzenesulfonic acid by the partial-pressure distillation method or in sulfating alcohols with $ClSO_3H$ or with SO_3 complexes. In these cases, the exothermic effect of the reaction of the organic compound with SO_3 is at least in part counterbalanced by the endothermic effect of breaking the

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[1] GILBERT, VELDHUIS, CARLSON, and GIOLITO, *Ind. Eng. Chem.*, **45**, 2065 (1953).

bond between SO_3 and the reagent reacted with it to form the sulfonating agent. In the extreme case of trimethylamine-SO_3 the value for ΔH_D, per pound of SO_3, is about 1010 Btu,[1] which is even higher than the heat of sulfation of lauryl alcohol with SO_3 vapor on the same basis, 820 Btu.[2] (It should be noted that, when sulfating with amine-SO_3 compounds, the exothermic factor ΔH_N—the heat of neutralization by the amine of the acid sulfate formed—must be added as a third term to the right-hand side of the equation.) For compounds of SO_3 with water (i.e., oleum or acid), the value of ΔH_D for any strength reagent from 61.2 per cent acid to SO_3 vapor can be read from Fig. 7-2. Then, by using the above equation, the heat of sulfonation of an organic compound for any other strength of acid or oleum can be obtained, provided that either ΔH_V or one value of ΔH_C is available for that organic compound.

In many cases when sulfonating with acid or oleum, however, the reagent is used in considerable excess and is only partially consumed. The term ΔH_D is then a net figure, obtained from Fig. 7-2, by taking the difference between the respective heat values for the acid used (ΔH_{DU}) and the acid formed (i.e., the spent acid) ΔH_{DF}:

$$\Delta H_D = \Delta H_{DU} - \Delta H_{DF}$$

In the specific case of the sulfonation of dodecylbenzene detergent alkylate using 1.25 lb 20 per cent oleum per 1.00 lb hydrocarbon as operated commercially (see p. 378), the calculations are as follows, all values being expressed on the basis of 1 lb SO_3 reacted:

$$2.94 \text{ lb hydrocarbon} + 3.71 \text{ lb } 20\% \text{ oleum} \rightarrow 3.95 \text{ lb } RSO_3H + 2.70 \text{ lb } 97.8\% \text{ acid}$$

$\Delta H_V = 905$ Btu[3]
ΔH_{DU} (3.71 lb 20% oleum) $= 1905$ Btu (Fig. 7-2)
ΔH_{DF} (2.70 lb 97.8% acid) $= 1540$ Btu (Fig. 7-2)
$\Delta H_D = 1905 - 1540 = 365$ Btu
$\Delta H_C = 905 - 365 = 540$ Btu
Experimental data: 542 ± 24; 502;[4] 515[5]

It will be noted that the calculated and observed values agree. Similar calculations can be made for any other strength acid or oleum. Of theoretical interest is the fact that over-all exothermic and endothermic effects would exactly balance if 73.5 per cent acid were completely consumed during the sulfonation by a partial-pressure distillation process; this pro-

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[1] General Chemical Division, Allied Chemical & Dye Corporation, unpublished research data.

[2] *Ibid.*

[3] GILBERT, et al., *loc. cit.*

[4] *Ibid.*

[5] Continental Oil Co., "Neolene 400, Intermediate for Synthetic Detergents," 1955.

cedure is not, however, of practical interest for sulfonating detergent alkylates. Data are summarized in Table 7-12.

TABLE 7-12. HEAT EFFECTS IN SULFONATING DETERGENT ALKYLATE

Reagent	Reagent*		Spent acid*		Heat evolved, Btu*
	Lb	Strength, %	Lb	Strength, %	
SO_3 vapor	1.00	...	....	....	905
SO_3 liquid†	1.00	...	....	....	681
Oleum (20%)	3.71	...	2.70	97.8	540
Acid	5.40	98	4.39	92	430
Acid†	1.67	73.5	0	...	0

* Basis 1.0 lb SO_3 reacted; strength expressed on sulfuric acid basis.

† Theoretical interest only.

A similar calculation can be made for the sulfation of lauryl alcohol[1] with excess monohydrate acid, the data being given on the basis of 1 lb SO_3 reacted:

2.50 lb alcohol + 2.33 lb 100% acid → 3.50 lb $ROSO_3H$ + 1.33 lb 83.1% acid

ΔH_V = approx 820 Btu[2]

ΔH_{DU} (2.33 lb 100% acid) = 1290 Btu (Fig. 7-2)

ΔH_{DF} (1.33 lb 83.1% acid) = 765 Btu (Fig. 7-2)

$\Delta H_D = 1290 - 765 = 525$ Btu

$\Delta H_C = 820 - 525 = 295$ Btu

Experimental data: approx 375 Btu[3]

Agreement is considered fair since some of the data are approximate, including that used to write the above equation.

Calculations of the above type are basic to the design of pilot-plant and commercial equipment for optimum thermal and productive efficiency. It should be noted, however, that a knowledge of how the heat requirement is distributed is fully as important as knowing the total heat effect. It is never safe to assume, for example, that evolution of heat from an exothermic reaction will be directly proportional to the amount of sulfonating agent added. A notable example is the sulfation of lauryl alcohol with chlorosulfonic acid, as discussed on p. 374. In this case, 60 per cent of the heat of reaction has been evolved by the time only 20 per cent of the acid has been added. Since the factors determining heat distribution may be complex, it is often necessary to obtain such data by actual experiment for each particular reaction.

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[1] WHYTE, *loc. cit.*

[2] General Chemical Division, Allied Chemical & Dye Corporation, unpublished research data.

[3] *Ibid.*

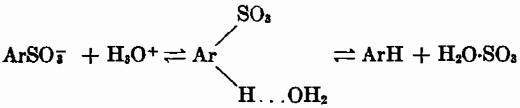
V. THE DESULFONATION REACTION

General Considerations. Aromatic sulfonates are hydrolytically desulfonated by heating in aqueous acid medium by the following over-all reaction:

$$RSO_3H + HOH \rightarrow R{\cdot}H + H_2SO_4$$

This reaction, which is the reverse of sulfonation, generally proceeds rapidly and in good yield, especially in the presence of an added mineral acid (sulfuric, phosphoric, hydrochloric, hydrobromic), which accelerates the reaction catalytically. It is important both theoretically and practically.[1]

Although the equation given above indicates the desulfonation reaction as a simple hydrolysis, a kinetic study[2] has shown that it cannot strictly be so considered in that the anion (rather than the sulfonic acid) is the reactive species. From desulfonation studies of hydroxy-, alkyl-, and nitroaminobenzenes conducted in 90 per cent acetic acid in the presence of mineral acid catalysts (HBr, H_2SO_4), it was shown that the reaction velocity is independent of sulfonic acid concentration, conforms to a first-order equation and is proportional to the hydrogen-ion activity of the solution, but is independent of the nature of the inorganic anion. (Others have indicated,[3] however, that the nature of the catalyst anion is important, with activity decreasing markedly in the order HCl, H_2SO_4, H_3PO_4.) The reversible relation between sulfonation and desulfonation is summarized as



$$ArSO_3^- + H_3O^+ \rightleftharpoons Ar\begin{matrix} \diagup SO_3 \\ \diagdown H\ldots OH_2 \end{matrix} \rightleftharpoons ArH + H_2O{\cdot}SO_3$$

It had been earlier observed[4] that for each 10°C rise in temperature the reaction velocity of hydrolysis increases 2.5–3.5 times and that a similar increase in rate was observed at any given temperature for one molar increase in the concentration of the mixed acid in the solution.

If aqueous solutions of the sulfonic acids are heated in sealed tubes, with or without added acid catalysts, only partial hydrolysis may occur gradually over a long period of time at a suitably low temperature. If, however, the aqueous acid is heated in an open vessel using good agitation, with passage of a current of steam, it is found that substantially complete hydrolysis occurs rapidly (e.g., an hour or less) and at a temperature characteristic of

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[1] For an excellent review of the desulfonation reaction up to 1943, see SUTER, "The Organic Chemistry of Sulfur," pp. 387ff.

[2] BADDELEY, HOLT, and KENNER, *Nature*, **154**, 361 (1944).

[3] SPRYSKOV and OVSYANKINA, *J. Gen. Chem.* (*U.S.S.R.*), **21**, 1508 (1951).

[4] CRAFTS, *J. Am. Chem. Soc.*, **23**, 248 (1901).

each compound. Volatile organic compounds are thus steam distilled from the reaction mixture as rapidly as formed by cleavage. The reaction is, however, also applicable to nonvolatile compounds which remain in the reactor until cleavage is complete. Desulfonation temperatures for a number of benzene derivatives are given in Table 7-13.[1]

TABLE 7-13. DESULFONATION OF BENZENE DERIVATIVES

Substituent	Decomposition temp., °C	Acid medium	Substituent	Decomposition temp., °C	Acid medium
None	227	H_3PO_4	3-Cl	182	H_3PO_4
2-CH_3	188	H_3PO_4	4-Cl	200	H_3PO_4
3-CH_3	155	H_3PO_4	2,4-$(Cl)_2$	155	H_3PO_4
4-CH_3	186	H_3PO_4	4-Br	217	H_3PO_4
2,4-$(CH_3)_2$	137	H_3PO_4	4-OH	123	H_2SO_4
3,4-$(CH_3)_2$	175	H_3PO_4	4-OH-3-CH_3	133	H_2SO_4
2,4,6-$(CH_3)_3$	80	HCl	4-OH-2-CH_3	116	H_2SO_4
Pentamethyl	25	H_2SO_4	4-OH-2,3-$(CH_3)_2$	115	H_2SO_4

It will be noted that increased ring methylation generally lowers the desulfonation temperature for both hydrocarbon and phenolic sulfonates. It will also be seen that isomeric compounds react at different temperatures.

The desulfonation reaction has seen practical application for a variety of uses both in the laboratory and in commercial manufacture.

Separation of Isomers. Sulfonation, followed by desulfonation, has been used to separate mixtures of aromatic compounds not easily separable by distillation. Either or both steps can be selective. Hydrocarbons isolated pure by this method include meta-xylene (on a substantial commercial scale),[2] 1-methyl-3-ethylbenzene,[3] 3,5-dimethyl-1-ethylbenzene,[4] three meta-dibutylbenzene isomers,[5] trimethylbenzenes,[6] and dimethylnaphthalene isomers in coal tar.[7] This procedure has also been used to isolate 3-chlorotoluene,[8] 2,5-dichlorotoluene,[9] trichlorotoluene,[10] and trichloro-

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[1] VESELY and STOJANOVA, *Collection Czechoslov. Chem. Communs.*, **9**, 465 (1937); CRAFTS, *Ber. deut. Chem. Ges.*, **34**, 1360 (1901); JACOBSEN, *ibid.*, 20, 900 (1887); BRÜCKNER, *Z. anal. Chem.*, **75**, 289 (1928).

[2] *Chem. Inds. Week*, **68** (11), 17 (1951); Hetzner and Miller, U.S. 2,511,711 (1950); LOFGREN, *Svensk. Kem. Tidskr.*, **60**, 281 (1948); MAIR, TERMINI, WILLINGHAM, and ROSSINI, *J. Research Natl. Bur. Standards*, **37**, 229 (1946).

[3] MAIR et al., *loc. cit.*

[4] Elwell, U.S. 2,541,959 (1951).

[5] WOODS and PLAPINGER, *J. Am. Chem. Soc.*, **73**, 5603 (1951).

[6] SMITH and CASS, *J. Am. Chem. Soc.*, **54**, 1614 (1932).

[7] KRUBER and OBERKOBUSCH, *Chem. Ber.*, **84**, 826 (1951).

[8] Miller, U.S. 2,523,707 (1950).

[9] *O.T.S. Rept.* PB 17,658.

[10] BRIMELOW, JONES, and METCALFE, *J. Chem. Soc.*, **1951**, 1208.

benzene isomers.[1] Cresol and xylenol isomers in coal tar have been separated in this manner.[2]

Use in Analysis. The desulfonation reaction has proved an indispensable practical tool[3] in studying the chemical structures of commercial sulfonated petroleum fractions from the lubricating oil range, both water-soluble ("green acids") and oil-soluble ("mahogany acids"). Aqueous hydrolysis yielded the parent hydrocarbon molecules, which were then analyzed by standard procedures. This approach has also been used for analyzing and determining the constituent fractions of coal tar, including both phenols and hydrocarbons.

Raw Material and Waste Recovery. In the manufacture of the insecticide DDT, oleum is employed as the condensing agent; this results in sulfonation of some of the raw material chlorobenzene as a side reaction. Passing steam into the spent acid results in the decomposition of the sulfonate, permits the recovery of chlorobenzene, and at the same time partially purifies the acid. In the industrial sulfonation of naphthalene in the 2 position intermediate to the preparation of 2-naphthol, a sulfonate mixture of 85 per cent 2 isomer and 15 per cent 1 isomer is obtained and 1-sulfonate is removed by steaming at 160–165°C to effect cleavage, the 2 isomer being stable (see p. 380). Similarly, mixtures of by-product anthraquinone disulfonate isomers (mainly 1,7; also some 1,6; 1,5; and 1,8) are recovered by removing all sulfo groups in the 1 position yielding anthraquinone and its 2-sulfonate.[4] This is effected by prolonged heating in dilute sulfuric acid at 180–200°C. Desulfonation is undoubtedly a main reaction occurring during the steaming (at 250°F or higher) of the sulfuric acid sludges obtained commercially in the refining of various petroleum products.[5] The aqueous acid can then be concentrated for reuse, and the hydrocarbon layer can be burned as fuel.

Use in Synthesis. Sulfonation-desulfonation is a useful tool for preparing ortho isomer derivatives of benzene. The sulfonic group is introduced to block the 4 position opposite a methyl, hydroxyl, or acetylamino group; then a chlorine or alkyl group is introduced ortho to the methyl or hydroxyl group. Finally, the sulfonic group is removed; for the case of 2-chlorotoluene, the reaction is as follows:

$$C_6H_5CH_3 \xrightarrow{H_2SO_4} CH_3\ (1)\ C_6H_4SO_3H\ (4) \xrightarrow{Cl_2} CH_3\ (1)\ Cl\ (2)\ C_6H_3(SO_3H)\ (4) \xrightarrow{H_2O}$$
$$\rightarrow CH_3\ (1)\ Cl\ (2)\ C_6H_4 + H_2SO_4$$

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[1] Kolka, U.S. 2,725,407 (1955); Merritt, U.S. 2,725,408 (1955).

[2] Brückner, *Z. anal. Chem.*, 75, 289 (1928).

[3] Sperling, *Ind. Eng. Chem.*, **40**, 890 (1948).

[4] Fierz-David, p. 235.

[5] Oliver and Spangler, in "The Science of Petroleum," p. 2764, Oxford University Press, New York, 1938; Squire, Pigeon, and Jones, *J. Inst. Petroleum*, **38**, 12 (1952).

Other compounds prepared by this scheme include 2,6-dichloroaniline, 2-chlorophenol,[1] 2-*sec*-butylphenol,[2] and 2-cyclohexylphenol.[3] In the last two cases, the sulfonate group is not removed by steaming, but is displaced chemically by an entering nitro group in the preparation of herbicides. The dye intermediates 3-chloro-6-nitroaniline and 2,6-dinitroaniline are likewise prepared by using the sulfonic group to block the 4 position during nitration.

The desulfonation reaction is of special importance in the naphthalene series. During monosulfonation, the following simultaneous reactions occur:

$$C_{10}H_8 + H_2SO_4 \rightleftharpoons 1\text{-}C_{10}H_7SO_3H + H_2O \qquad (1)$$

$$C_{10}H_8 + H_2SO_4 \rightleftharpoons 2\text{-}C_{10}H_7SO_3H + H_2O \qquad (2)$$

Reaction (1) reaches equilibrium much more rapidly than reaction (2). The 1-sulfonate, produced by reaction (1), is the main product at 100°C after a few hours. However, after 57 days at the same temperature, the 2 isomer, produced by reaction (2), is the major product. Thus, the 1 isomer, although the first to be formed, is more easily desulfonated, and the 2-sulfonate, being less easily desulfonated, is finally the major product, provided that sufficient time is allowed to achieve equilibrium. This difference between the two isomers has been explained on the basis that the 1 position is adjacent to the adjoining benzene nucleus which withdraws electrons and weakens the sulfur-to-carbon bond, while such does not apply to the 2 position which therefore yields a more stable sulfonate. The same desulfonation-resulfonation mechanism for the formation of naphthalene-2-sulfonates also applies in the disulfonation of naphthalene itself, as well as to the sulfonation of naphthalene derivatives.

In addition to its importance in the mechanism of formation of naphthalene-2-sulfonates, the desulfonation reaction has preparative utility in producing the dye intermediate 6-aminonaphthalene-1,3-disulfonic acid from the 1,3,5-trisulfonate. This is accomplished by refluxing at 125°C for 4 hr in dilute sulfuric acid.

In the anthraquinone series, the 1-monosulfonate can be desulfonated by heating in 80 per cent acid at 180°C; the 2 isomer is more stable.[4] As stated above, acid hydrolysis of a mixture comprising largely the 1,6- and 1,7-disulfonate isomers results in removal of the groups in the 1 position, yielding the 2-monosulfonate, together with some anthraquinone. On the other hand, the 2,6-disulfonate loses one group, while the 2,7 isomer is

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[1] HUSTON and BALLARD, "Organic Syntheses," Collective vol. II, p. 97, John Wiley & Sons, Inc., New York, 1943.

[2] Barker and Pound, Brit. 650,906 (1951).

[3] Prescott, U.S. 2,112,543 (1938).

[4] "Encyclopedia of Chemical Technology," vol. I, p. 950.

stable; in these two cases both groups are situated in the 2, or relatively stable, position;[1] yet only one of the groups is removed.

Sulfonate groups situated ortho to a hydroxyl or amino group in anthraquinone are quite labile and can be removed by heating with sulfuric acid. This reaction is of some importance for preparing several anthraquinone dye intermediates[2] and can be used to remove one or two sulfonate groups.

VI. WORKING-UP PROCEDURES

The working-up of a sulfonation or sulfation reaction mixture may be, and often is, more involved and time-consuming than the reaction proper. The presence of excess acid or unreacted starting material, or the occurrence of side reactions (polysulfonation, formation of isomers or sulfones), is a major reason for requiring separation and purification steps.

Some commercial sulfonations and sulfations employ nearly stoichiometric quantities of reagents and yield products which can be neutralized and used directly as is, or with minor purification. These include benzene, toluene, and xylenesulfonic acids as prepared by the partial-pressure distillation method; dodecylbenzene sulfonated with SO_3; long-chain alcohol sulfates prepared with $ClSO_3H$, SO_3, or NH_2SO_3H; some sulfonated aromatic amines as prepared by the "baking" process; and products from certain sulfoalkylation or sulfite reactions (see technical section for detailed examples). In other cases, even when excess acid is present, it is neutralized with the sulfonate since sodium sulfate is desired or allowable in the final product. Examples include dodecylbenzene sulfonated with oleum and lauryl alcohol sulfated with concentrated acid. In most cases, however, separation or purification is necessary. The three most common procedures may be summarized as follows:

Dilution with Water. This method often applies when using excess acid or oleum and yields the free sulfonic acid. Its use is based on the knowledge that *many sulfonic acids are relatively insoluble in sulfuric acid of intermediate strength* (i.e., about 50–80 per cent) obtainable by suitable dilution of the reaction mixture with water, even though they are soluble in the stronger acid (above about 80 per cent) remaining after sulfonation, or in more dilute acid (below about 50 per cent). This principle is applied industrially and in the laboratory to the isolation of hydrocarbon sulfonic acids such as those made from dodecylbenzene (see details on p. 378), toluene,[3] mesitylene,[4] 1,2,4-trimethylbenzene,[5] alkylated naphthalenes,[6] and petroleum

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[1] *Ibid.*

[2] LUBS, p. 355; FIERZ-DAVID, pp. 455, 459, 463.

[3] *O.T.S. Rept.* PB 91,355, frame 112.

[4] SMITH and CASS, *J. Am. Chem. Soc.*, **54**, 1606 (1932).

[5] *B.I.O.S. Final Rept.* 1153, Item 22, p. 65.

[6] *B.I.O.S. Final Rept.* 421, Item 22, p. 19.

lubricants ("green acids"). The disulfonic acids of anthraquinone are isolated by this method.[1] This procedure also works well with sulfonated aromatic amines, such as those derived from the anisidines,[2] 4-chloroaniline,[3] 2,5-dichloroaniline,[4] or 5-aminosalicylic acid,[5] but only when the amino and sulfonic groups are present in 1:1 ratio. Sulfonated fatty oils, such as neat's-foot or cod, and butyl ricinoleate can also be separated by dilution with chilled water.[6] When preparing aromatic sulfonyl chlorides by chlorosulfonation, water dilution is the standard procedure for separating the water-insoluble chlorides (see details on p. 383). This method is also used to remove water-insoluble by-product sulfones formed when sulfonating toluene or xylene industrially with SO_3 or with strong oleum.

Salting-out. This method yields the sulfonate salt by the addition of aqueous NaCl [less often Na_2SO_4, KCl, or $(NH_4)_2SO_4$] to the acid reaction mixture:

$$RSO_3H + NaCl \rightleftharpoons RSO_3Na\downarrow + HCl$$

The desired sulfonate salt is usually only slightly soluble in the dilute acid medium and often crystallizes from it in good yield. Although the reaction is of the equilibrium type, it is driven to the right by use of the correct proportions of brine and water and by cooling. This "brining-out" procedure is used commercially to isolate many sulfonate dye intermediates, including those from nitrobenzene, the nitrotoluenes, the nitrochlorobenzenes, naphthalene (see details on p. 379), naphthols, and anthraquinone (the monosulfonates; see details on p. 381). It can also be used for certain sulfonated fatty oils (shark and sperm[7]), sodium sulfate being employed. For a number of *m*-nitrobenzene and *m*-nitronaphthalenesulfonic acids, ferrous sulfate may be advantageously substituted for NaCl since the iron salts are very insoluble in 20 per cent sulfuric acid.

Salting-out is also employed to obtain efficient separation of highly water-soluble sulfonate salts from neutral solutions, as in the sulfomethylation of aniline or in the sulfonation of naphthalene.

Neutralization with Lime. This procedure involves treatment of the diluted reaction mixture with $Ca(OH)_2$ (milk of lime) or $CaCO_3$ (finely powdered chalk, limestone, or marble) to convert excess sulfuric acid to insoluble calcium sulfate (which is filtered) and the sulfonic acid to the calcium sulfonate (which appears in the filtrate). Treatment of the filtrate

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[1] FIERZ-DAVID, p. 235.

[2] *B.I.O.S. Final Rept.* 1153, Item 22, pp. 179, 180.

[3] *Ibid.*, p. 184.

[4] *Ibid.*, p. 185.

[5] *Ibid.*, p. 247.

[6] *O.T.S. Rept.* PB 99,921.

[7] *B.I.O.S. Final Rept.* 1151, Item 22, p. 7.

with sodium carbonate or sulfate yields insoluble calcium carbonate or sulfate (which is filtered); the filtrate comprises the desired sodium sulfonate. This method is considerably more laborious than the other two, but is generally applicable in the isolation of any sulfonate yielding a soluble calcium salt. It has been used industrially for purifying benzenesulfonic acid[1] and benzenedisulfonic acid.[2] When the latter is used to make resorcinol, 6.5 tons of by-product calcium sulfate is formed per ton of resorcinol.

The above three isolation procedures can usually be conducted in such a way as to effect simultaneous purification from undesired by-product isomers. Thus, with the first method (dilution with water) the pure para isomer of toluenesulfonic acid is obtained since the ortho isomer is soluble; likewise, the 1,5- and 1,8-disulfonates of anthraquinone are separated by taking advantage of different solubilities in sulfuric acid. When the second procedure is applied to the isolation of anthraquinone-1-sulfonate as the potassium salt, filtration at 85°C ensures removal of the 1,5-disulfonate in the aqueous filtrate. Metallic sulfonates are frequently purified further by recrystallization from water, often with the addition of brine to ensure a good yield by salting-out.

Use of Solvents. Organic solvents are sometimes used commercially to purify sulfonates or sulfates. Alcohols (methanol, ethanol, isopropanol) are employed to desalt and purify sodium dodecylbenzenesulfonate, sulfated monoglycerides, sulfated long-chain alkenes, and petroleum sulfonates. Sodium sulfate is insoluble, while the sulfonate dissolves in the alcohol. In the last two cases, separation of unreacted hydrocarbon is also effected, yielding a purer product; further removal of the hydrocarbon is often achieved by extraction of the alcoholic sulfonate solution with petroleum naphtha solvent. This purification scheme has also been used commercially to produce dodecylbenzenesulfonate detergents of low residual hydrocarbon content.[3]

VII. INDUSTRIAL EQUIPMENT AND TECHNIQUES

Materials of Construction

Cast iron is resistant to the action of sulfuric acid in the range 75–100 per cent in strength over a fairly wide temperature range and has been a standard material of construction for sulfonation kettles for many years, especially for numerous dye intermediates and for hydrocarbons such as benzene, toluene, or naphthalene.[4] However, it has poor tensile strength

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[1] *O.T.S. Rept.* PB 110,409.

[2] Gilbert and Jones, *Ind. Eng. Chem.*, **43**, 2031 (1951).

[3] Nevison, U.S. 2,655,530 (1953).

[4] Fierz-David, p. 362; *O.T.S. Rept.* PB 85,687.

and is corroded by oleum or SO_3. The latter objection may often be overcome in oleum sulfonations by adding the acid slowly to the material being sulfonated such that the acid concentration remains below the highly corrosive level. Improved corrosion resistance results from the addition of silicon to cast iron (e.g., Duriron), but such alloys are also of poor strength. Enameled cast iron is often employed because it is more resistant to corrosion.

The use of lined steel vessels combines low cost and high strength with good corrosion resistance. Commonly used linings include glass, enamel, and various metals such as lead, nickel, and numerous types of stainless steels. Glass-lined kettles are commonly used for the batch sulfonation of detergent alkylate or for the sulfation of lauryl alcohol with chlorosulfonic acid. Type 316 is one of the most widely used stainless steels, usually in massive form rather than as a lining.

Corrosion rates may in some cases be governed by side reactions. Thus, SO_2 can be highly corrosive, especially in the presence of moisture. Hydrogen chloride evolved when using chlorosulfonic acid is also very reactive and requires special attention. It must also be borne in mind that auxiliary steps, such as purification, neutralization, drying, etc., will impose entirely different corrosion conditions from those encountered during the sulfonation step proper. A survey study,[1] covering 39 commercial metals and alloys, gives corrosion data, obtained in most cases under plant conditions, for the sulfonation of numerous fatty oils, aromatic hydrocarbons, phenol and pyridine with acid or oleum and for reactions involving chlorosulfonic acid and aqueous meta-bisulfite. Corrosion during work-up of product sulfonates is also considered in some cases.

Commercial Sulfonation Methods

There are two general types of industrial sulfonation procedures—batch (or discontinuous) and continuous. Although batch methods were formerly used almost exclusively, and in fact still predominate, interest in continuous operation has increased sharply since about 1945, paralleling the rapidly growing production of phenol, synthetic detergents, lubricant additives, and synthetic alcohols (ethanol and isopropanol), all of which involve either sulfonation or sulfation as intermediate steps. Continuous operation is practical only where the reaction rate is high and where the volume of production is large and relatively steady. It usually entails higher process development costs and more specialized equipment. These disadvantages are far outweighed by improved process control, better product quality, and substantially lower production cost. Batch equipment is, on the other hand, simpler and more versatile, but operation on a batch scale is considerably less efficient.

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[1] FRIEND, *J. Am. Oil Chemists' Soc.*, **25**, 353 (1948).

Batch Processing. Batch sulfonations are conducted in reaction kettles or autoclaves of standard types, varying in capacity from 30–2,500 gal. Two closely related design features are of major importance: heat transfer and agitation. These factors usually require careful consideration since many sulfonation reaction mixtures are viscous, which can result in inefficient heat exchange leading to poor product quality and/or reduced productivity. Batch reactors are generally used for the four general types of sulfonation procedures discussed in the introduction; special equipment is required for a few reactions, however.

A typical batch sulfonation kettle is illustrated in Fig. 7-3. Two common types of agitators are shown on the same shaft: propeller and turbine. These are used for reaction mixtures of low or moderate viscosity. For more viscous products, a close-fitting anchor agitator equipped with supplemental vertical arms is suitable, especially if the blades have knife edges on the leading sides.

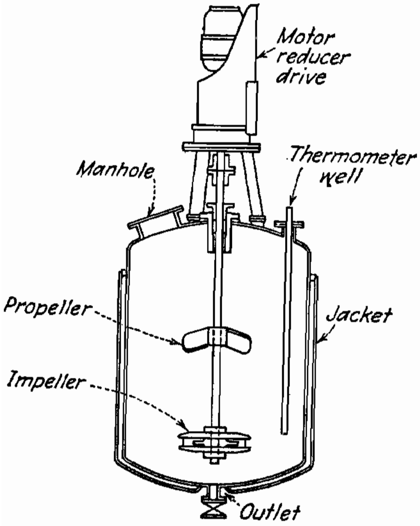

FIG. 7-3. Batch sulfonation kettle.

Logical variations in this simple type of batch equipment are made to suit the particular reaction being used. For preparing benzene and naphthalene dye intermediates, the kettles may be cast iron, or modified cast iron of 100–800 gal capacity, equipped for heating as high as 200°C or above. In the case of dodecylbenzene detergent alkylate, the reactor may be glass-lined, or 316 stainless steel, of 2,500-gal capacity with a jacket or external cooling coils. Similar sulfonations of alkylated benzenes or naphthalenes with oleum can be run in a conical lead-lined kettle, equipped with both jacket and cooling coil.[1] For reactions involving aqueous or aqueous-alcoholic sodium bisulfite (such as reaction with ethylene oxide or addition to a maleate ester; see p. 376), the kettle may be lined with lead or enamel, capable of withstanding moderate pressure (e.g., 2 atm), and jacketed for cooling or heating in the range 30–100°C. For sulfite reactions involving the replacement of tightly bound aromatic chlorine (as for 2-sulfobenzaldehyde), an autoclave operating at 140–200°C under a pressure of 4 atm or more is required. In the aqueous oxidative chlorination of bis(*o*-nitrophenyl)disulfide to the sulfonyl chloride, prolonged exposure to warm

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[1] *B.I.O.S. Rept.* 421, Item 22.

aqueous HCl and chlorine requires the use of a lead-lined kettle equipped with a rubber-coated agitator. Sulfonations by sulfoalkylation, sulfoarylation, or other condensation reactions are likewise conducted in batches in conventional equipment. Many of these reactions, including the preparation of ion-exchange resins, tanning agents, and the surface-active agent Igepon T, are operated in aqueous solution at temperatures ranging from room temperature up to about 100°C. Sulfomethylation has been run in a 2,000-gal brick-lined vat equipped with propeller agitator and coils or jacket for heating to 80°C (see p. 375). In the preparation of Igepon A, as discussed in detail on p. 376, the reactor is lead-lined (to resist HCl) and agitation is performed by a heavy-duty mixer since the reaction mixture is first a viscous liquid, then a crumbly solid, and finally waxy flakes comprising the final product. Conventional batch equipment is also used for sulfonating fatty oils (see p. 386). Here efficient cooling is important since most of these sulfonations are run below room temperature and some as low as 0°C. Jacketed enameled kettles are used for sulfations using chlorosulfonic acid.

Some batch sulfonations are, however, not readily conducted in conventional equipment. In Fig. 7-4 is shown a ball-mill sulfonator, operable under vacuum with hot-air heating, which is used with solid, doughy, or viscous masses not easily handled in an ordinary reaction kettle. This type of apparatus is used in the "baking process" for sulfonating aromatic amines; this operation is considerably facilitated by the use of vacuum to remove the water formed during reaction. Sulfochlorination likewise requires special equipment since the reaction is catalyzed by light and since the apparatus must withstand the combined corrosive action of hydrogen chloride, sulfur dioxide, and chlorine. Plastic-coated steel towers are suitable; illumination is provided by mercury-vapor lamps inserted in trans-

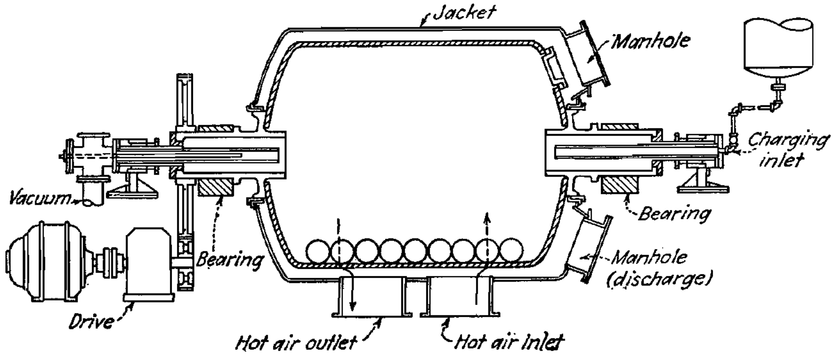

FIG. 7-4. Ball-mill sulfonator.

verse quartz tubes located in the lower section of the tower. Coiled glass piping can also be employed for this reaction, using an external light for catalysis and a water spray for cooling.

Heating and Cooling. Although direct gas fire is sometimes used for heating, as, for example, in preparing various naphthalenesulfonate dye intermediates,[1] steam is most commonly employed. For temperatures up to about 175°C, as in sulfonating naphthalene, steam under pressure is used with a jacket capable of withstanding at least 10 atm. With steam or hot water at higher temperatures, and therefore at correspondingly higher pressures, it is necessary to use coils since jackets capable of withstanding the higher pressures would be considerably more clumsy and expensive. There are several types of coil construction. One type has the coil mounted externally on copper supports (for efficient heat exchange) such that it can be easily removed for repair. Heating with hot oil or with chemicals (e.g., Dowtherm) is sometimes used to achieve temperatures above 200°C. The heat-transfer agent is usually heated in a separate boiler and pumped to the jacket of the reactor at an automatically controlled rate. This procedure has the advantage over steam that considerably lower jacket pressures are involved, but compares poorly with it in respect to heat conduction.

Cooling is required in some sulfonations, notably for fatty oils (at 0–30°C) and for long-chain alkylated benzenes and naphthalenes (20–85°C). For the fatty oils, cooling with brine is employed; for the other compounds, river water may be sufficient. In both cases, temperature control is often maintained in the plant by the inefficient expedient of adding the acid slowly over a period of several hours. Cooling may be effected by spraying water on the outside surface of a reaction kettle. Circulation of the reaction mixture through an external heat exchanger is used for dodecylbenzene detergent alkylate, thereby desirably avoiding insertion of a cooling coil into the reactor and giving more efficient heat exchange than is possible through the walls of a glass-lined kettle. The external cooler may be of the shell-and-tube type, or in the case of more viscous materials, it may comprise a scraping-blade heat exchanger (e.g., a Votator),[2] which is especially designed for heat removal from viscous materials at 7–10 times the efficiency of the usual cooling jacket or coil. External heat exchangers are also used in sulfonating benzene[3] and in sulfating the lower alkenes.

VIII. TRANSITION FROM BATCH TO CONTINUOUS PROCESSING

For most sulfonates, batch processing has always been, and probably will continue to be, the standard preparative procedure. This is especially true

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[1] *B.I.O.S. Rept.* 1152, Item 22.

[2] GERHART and POPOVAC, *J. Am. Oil Chemists' Soc.*, **31**, 200 (1954).

[3] KENYON and BOEHMER, *Ind. Eng. Chem.*, **42**, 1446 (1950).

of the many dye intermediates derived from benzene, naphthalene, anthraquinone, and phthalocyanine which are prepared in relatively small amounts by involved procedures from expensive raw materials. One of the simplest of these intermediates, naphthalene-2-sulfonic acid, produced in by far the largest quantity, was, however, considered for continuous processing,[1] but this approach has apparently not as yet been adopted for commercial use. The sulfonated fatty oils have also been studied from this standpoint, but the batch method predominates because of the great variety of products made, the variability in raw materials, and the time-consuming and empirical nature of the working-up steps (see p. 323). Several successful continuous processes have, however, been developed. It is most instructive to follow the evolution of continuous processes from the batch procedures they have partially replaced. This is done in the following paragraphs for six important sulfonations.

Dimethyl Ether. The specialty methylating agent, dimethyl sulfate, was originally made in batches in two steps:

$$CH_3OH + SO_3 \rightarrow CH_3OSO_3H \qquad (1)$$

$$2CH_3OSO_3H \xrightarrow{\text{distill}} (CH_3O)_2SO_2 + H_2SO_4 \qquad (2)$$

Over-all yield was fair, but the final product required a second distillation to achieve reasonable purity, spent acid was obtained as a by-product, and the operation as a whole was laborious.

It has long been known that dimethyl ether and SO_3 form dimethyl sulfate as follows:

$$(CH_3)_2O + SO_3 \rightarrow (CH_3O)_2SO_2$$

This reaction is ideally suited to continuous operation, being immediate, quantitative, smoothly exothermic, and operable in a simple tower using the liquid product sulfate as the reaction medium (see details on p. 384). The crude reaction mixture is sufficiently pure for most uses, but distillation gives a product purer than that obtainable by the batch procedure. In addition, the reaction of dimethyl ether with SO_3 is less exothermic than the first step [reaction (1)] of the batch process and, therefore, requires less cooling. When dimethyl ether became cheaply available as a by-product of synthetic methanol production, this process for making dimethyl sulfate was soon exploited. It is interesting to note, however, that this continuous process was adopted not so much because of a large demand for the product, but because it was ideally suited for technical reasons. It yielded a purer product with no spent acid, and the raw materials were cheaply available.

Benzene. The simplest but least efficient industrial process for sulfonating benzene may be outlined as follows, as operated on a batch basis.[1] Monohydrate acid (8,360 lb) is charged to a jacketed cast-iron sulfonation

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[1] *O.T.S. Rept.* PB 14,998.

kettle, and with agitation at 80 rpm and jacket cooling, benzene is added on the surface of the acid at such a rate that the temperature rises to 60°C over a period of 1 hr, then to 75–83°C, which temperature range is not exceeded during the addition of the rest of the benzene, which requires 4 hr in all. The reaction is then completed by jacket heating to 105–108°C over a period of 1 hr and by maintaining this temperature for 4 hr more under reflux. The total quantity of benzene added is 3,300 lb, which is 49.5 per cent of theory for the amount of acid. The spent acid is 83 per cent in strength, which is above the π concentration of 78.4 per cent, below which benzene will not react (see p. 338). The excess acid is laboriously removed by neutralization as calcium sulfate.

As the demand for phenol continued to increase, and with the development of competitive methods for making phenol out of benzene via chlorobenzene, cumene, and other methods (see Chap. 13), pressure increased for process improvement and for operation on a continuous basis. Low-strength oleum (5–10 per cent) was substituted for sulfuric acid, thereby necessitating the removal of less water. The oleum strength chosen was the maximum compatible with the production of a product low in sulfone content. The greatest improvement, however, consisted in converting the batch process to continuous operation by simply operating several batch reactors in series, using the *cascade* principle. In an American plant,[1] six 2,000-gal mechanically agitated cast-iron reactors are used. The benzene and oleum are continuously metered into the first kettle, which is cooled both by a jacket and by an external shell-and-tube heat exchanger. The product overflows into the second kettle, which is cooled by a jacket and a cooling coil. The four following kettles are jacket-heated, presumably at progressively higher temperatures. The final mixture of benzenesulfonic acid and sulfuric acid (presumably of a strength fairly close to the π concentration of 78.4 per cent) flows continuously from the sixth reactor. Neutralization of this reaction product with caustic soda yields a mixture of sodium benzenesulfonate and sodium sulfate. Since the latter is fairly insoluble in an aqueous solution of the former, it can easily be recovered by filtration and marketed as a credit for the process.

In many cases, it is not possible, because of unfavorable market conditions, to obtain credit from by-product sodium sulfate. It is therefore necessary to use the *partial-pressure distillation process,* which entails substantially quantitative utilization of both hydrocarbon and acid by repeatedly distilling excess benzene through the acid to remove water azeotropically. This basic improvement was made by Guyot as a result of the great demand for phenol during World War I, and this principle is still used to produce much of the benzenesulfonic acid made in the United States for conversion to phenol. In its original form, the process operated on a

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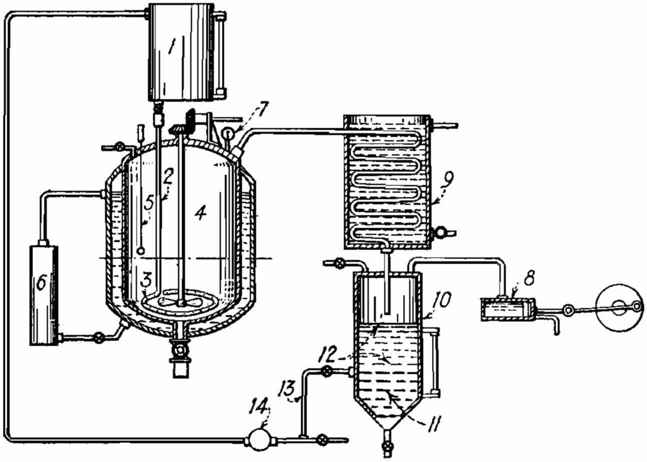
[1] KENYON AND BOEHMER, *Ind. Eng. Chem.*, **42**, 1446 (1950).

batch basis, starting with acid of 90–92 per cent strength and requiring a 14-hr reaction time with recycle of 6–8 moles of benzene per mole reacted. Equipment used in this process is shown in Fig. 7-5.



1 Benzene supply
2 Benzene feed line
3 Perforated distributor for benzene
4 Sulfonator
5 Thermometer
6 Oil-heating mechanism
7 Pressure gauge
8 Vacuum pump
9 Cooling coil
10 Condensed-liquor tank
11, 12 Water and benzene layers, respectively
13 Recovered-benzene return line
14 Circulating pump

FIG. 7-5. Batch equipment for sulfonating benzene by partial-pressure distillation.

The partial-pressure distillation procedure can, like the original "incomplete" sulfonation method described above, be made continuous by application of the cascade principle. Process details are given on p. 377.

Direct continuous reaction of SO_3 with benzene, highly successful in the case of dimethyl ether as described above, is not practical because of high sulfone formation. Indirect continuous reaction with SO_3 by a procedure stated to yield no sulfone has, however, been achieved by the method developed by Dennis and Bull. This process is based upon an observation made by the former that, in the presence of sulfuric acid, benzene will dissolve 2–3 per cent of its own volume of benzenesulfonic acid. This process is also designed to operate in continuous countercurrent flow in a cascade system, benzene being introduced at the bottom and a benzene solution of the sulfonic acid overflowing from the top. Concentrated sulfuric acid is added continuously at the top, and spent sulfuric acid (77 per cent) is removed at the bottom of the reactor. The spent acid may be fortified to original strength with SO_3 for reuse, and the benzene is recycled after the product sulfonic acid has been extracted from it with water. This procedure is, in theory, the most efficient possible, since benzenesulfonic acid is, in effect, produced from SO_3 and benzene—no water being removed as in the Guyot process. However, the heavy benzene recycle requirement (20–30 parts per part reacted) has proved an obstacle to widespread commercial acceptance of this process, although it is used in the United States.[1] Further study of the Dennis-Bull procedure[2] has shown that the reactor efficiency can be increased tenfold and the benzene recycle requirement reduced to 10–20 parts per part reacted, if the SO_3 is introduced directly into the reactor (thereby maintaining the acid at 100 per cent strength) and if the reaction is operated under pressure.

Dodecylbenzene Detergent Alkylate. The production of this sulfonate has risen, in the decade 1946-1956, from a comparatively small figure to hundreds of thousands of tons per year. It is not surprising, therefore, that with this large output there should be a correspondingly great interest in developing continuous processes. Those in manufacturing use to date for producing the preferred "high-active" product are, in the over-all sense, semicontinuous, being adaptations, employing the cascade principle, of the batch process using 20 per cent oleum, described in detail on p. 378. In outline,[3] this involves continuous intimate mixing of oleum and the hydrocarbon, either in a centrifugal pump or other similar device or in a stream of circulating reaction product, followed by immediate cooling in an efficient heat exchanger. A jacketed batch reaction kettle can also be employed as a combined continuous reactor and cooler. Such a plant[4] might comprise a 55-gal sulfonation vessel, a 102-sq ft external heat exchanger, and a 135-gal digestion kettle. The hydrocarbon is fed continuously (233 lb per hr) to the sulfonation vessel. The sulfonation product is recirculated through the heat exchanger by a centrifugal pump. Oleum (252 lb per hr of 22 per cent strength) is charged at the pump inlet. The reaction product is continuously bled off to the digester. The sulfonator and digester are both maintained at about 30°C. The "acid mix" is next diluted with water, employing cooling, to make possible subsequent layer separation; this can be done continuously. Stratification is usually a batchwise operation (as described on p. 378); it can also be done continuously with a centrifuge, but this approach has been limited in practice by corrosion. Further study of this process has indicated that the total cycle can, under unspecified conditions, be reduced from 10–13 hr over-all for batch operation to 13 min for continuous operation—8 min for reaction and 5 min for separation.[5]

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[1] *Petroleum Processing*, **9**, 238–241 (1954).

[2] PLANOVSKII and KAGAN, *Prom. Org. Khim.*, **7**, 296 (1940).

[3] KIRCHER, MILLER, and GEISER, *Ind. Eng. Chem.*, **46**, 1925 (1954); LINDNER, "Textilhilfsmittel and Waschrohstoffe," pp. 448ff.; Crouch, U.S. 2,628,200 (1953); Ross, U.S. 2,693,479 (1954); HUBER, BAKER, and SCHMIDT, *J. Am. Oil Chemists' Soc.*, **33**, 57 (1956).

[4] Oronite Chemical Co., "Alkane Basic Detergent Raw Material," 1955.

[5] *Chem. Week*, **77**, 66 (July 2, 1955).

Dodecylbenzene differs from benzene in that the former can be sulfonated satisfactorily with SO_3 vapor. It has been found that this process can be operated continuously on a "once-through" basis, using a scraping-blade heat exchanger (e.g., a Votator) as the reactor.[1] No acid-separation step is required, the sulfonic acid from the reactor being neutralized directly to a "high-active" salt. Because of its high boiling point and instability at elevated temperatures, dodecylbenzene cannot be sulfonated by the partial-pressure distillation procedure as described above for benzene.

Petroleum Lubricant Raffinates. As stated previously, the sulfonation of these materials resembles that of dodecylbenzene regarding process details and reagents used (SO_3 or oleum), but differs in that petroleum oils are only partially sulfonatable and in that the reaction is often done in stages for better sulfonate yield and lower acid consumption.

A typical batch process might comprise addition of 20 per cent oleum (about 20 per cent by weight of the oil) to the oil in a sulfonation kettle with a reaction time of 1–3 hr, maintaining a temperature range of 40–70°C by cooling. Upon standing, an upper oil layer separates, containing the desired sulfonate, while the lower layer comprises spent acid, sludge, and water-soluble polysulfonates. A single treatment of this type removes about 80 per cent of the sulfonatable aromatics for a sulfonate yield of about 5–10 per cent of the weight of the starting oil. When multiple treats are employed, the sulfonate is extracted from the oil after each treat for optimum yield.

Continuous processes are widely employed for lubricant sulfonation; they are logical adaptations of the batch procedure described above. The sulfonation step proper is conducted in a manner generally similar to that used for dodecylbenzene (efficient mixing at a controlled temperature) at about the same or slightly higher temperature (40–70°C), using the same types of reagents (oleum or SO_3 vapor). Reactor mixers typifying those used industrially include a scraping-blade heat exchanger (e.g., a Votator) functioning as a combined reactor and cooler with a 3-min retention period,[2] a horizontal reactor equipped with rotating paddles operating at a 3-sec residence time with SO_3 vapor,[3] and a 12-plate orifice mixer with 20 per cent oleum. A process employing the third has been described in some detail.[4] Six treats are employed in a white oil-sulfonate process using 45–55 per cent by weight of 20 per cent oleum at 50°C, with an optimum 10-min reaction time from mixing to layer separation in each treat. Most of the reaction occurs in a tank adjusted for continuous overflow to a centrifuge

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[1] General Chemical Division, Allied Chemical & Dye Corporation, unpublished research data.

[2] Wilson, U.S. 2,543,885 (1951).

[3] Lipkin and Reif, U.S. 2,680,716 (1954).

[4] Brown, *Inst. Petroleum Rev.*, **9**, 314 (1955).

which continuously effects layer separation; sludge is separated after each treat, and sulfonate is extracted after each group of three treats. Sulfonate extraction with alcoholic caustic soda is also run continuously. This part of the process is, however, somewhat more involved and is therefore less easily adaptable to continuous processing. It is accordingly operated in batches by some producers of petroleum sulfonates.

Lauryl Alcohol. Industrial sulfation of lauryl alcohol has for many years been conducted in batches, using chlorosulfonic acid, with or without a solvent, as described in detail on p. 384. Recently, SO_3 vapor has been used.

As the demand for lauryl sulfate steadily increased because of its excellent detergent and foaming properties, serious consideration was given to continuous processes. Several of those proposed[1] are based on the use of chlorosulfonic acid, and this type of continuous operation, employing a reaction solvent, is used commercially.

Continuous sulfation with chlorosulfonic acid has been appraised unfavorably[2] because of an unbalanced pattern of heat evolution (60 per cent evolved by the time only 20 per cent of the acid has been added) and gas evolution (most of the HCl is evolved during the latter half of reaction, with some foaming). These factors tend to result in a slow over-all reaction, since heat removal is a limiting rate factor in the initial stage and gas evolution (with foaming) in the final stage. This disparity has been attributed to a unique reaction mechanism.[3] Both effects may, however, result largely from the fact that HCl has a considerable exothermic solubility in lauryl alcohol, which would result in low gas evolution and high heat evolution during the first half and compensatingly high gas evolution with heat absorption (cooling) during the second half. Use of a reaction solvent, actually employed commercially in continuous operation as stated above, may reduce the solubility of HCl in the reaction mixture, thereby enabling more rapid reaction by promoting more balanced patterns of both heat and gas evolution.

"Flash" sulfation of lauryl alcohol with excess 99 per cent acid, using a reaction time of 60 sec or less followed by immediate "quenching" or neutralization, has been considered preferable for continuous operation to the use of chlorosulfonic acid.[3] The alcohol and acid are mixed and passed through a reaction coil where no attempt is made to control the temperature by cooling. Immediate quenching is not only desirable for fast throughput, but is necessary to avoid side reactions. It should be noted that this process, although admirably suited to continuous operation, yields a product high in sodium sulfate and in unreacted lauryl alcohol, whereas that

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[1] LINDNER, *op. cit.*, pp. 581ff.

[2] WHYTE, *J. Am. Oil Chemists' Soc.*, **32**, 313 (1955).

[3] *Ibid.*

prepared with chlorosulfonic acid contains a small percentage of sodium sulfate and less unreacted alcohol. The "flash" process with sulfuric acid is therefore not suitable for producing a product satisfactory for all formulations, while the material made with chlorosulfonic is more widely useful. A somewhat similar process,[1] operated on a pilot-plant scale, involves simultaneous feed of the alcohol and monohydrate acid to a disc rotating at 800 rpm. The reaction mixture is thus thrown centrifugally onto the cooled walls of a surrounding container. It is interesting to note that both processes operate at about 70–75°C, using monohydrate (or 99 per cent) acid in excess (170–190 per cent of theory), and that both procedures require immediate "quenching" of the reaction, in one case by cooling, in the other by neutralization. It is also noteworthy that this type of process presents an unusual case of one which can be operated only in a continuous manner, since batch operation with excess acid leads to prohibitive decomposition of the sulfate formed.

Ethylene and Propylene. Sulfation of the lower alkenes, intermediate to production of the alcohols, is well suited to continuous operation. Production is large (many hundred million gallons), and the reaction proceeds rapidly by countercurrent absorption in a tower operating under pressure. This process has always been operated continuously, except briefly during early development. Further details are given in the next section.

IX. TECHNICAL PREPARATION OF SULFONATES AND SULFATES

Detailed descriptions of 13 typical commercial processes are presented in this section. It will be noted that many of the principles employed are discussed more generally in preceding sections of this chapter.

Aliphatic Sulfonates

Sulfomethylation of Aniline.[2] Aniline is reacted with aqueous sodium hydroxymethanesulfonate (formaldehyde-bisulfite):

$$C_6H_5NH_2 + HOCH_2SO_3Na \rightarrow C_6H_5NHCH_2SO_3Na + H_2O$$

Aqueous sodium bisulfite (1,642 lb sodium bisulfite 100 per cent—15.7 lb moles—in 40 per cent aqueous solution) is charged to a 2,000-gal brick-lined vat, equipped with a blade agitator and copper coil for heating and cooling. Formaldehyde (1,698 lb of 28 per cent aqueous—15.9 lb moles) is then added with agitation, followed by heating for ½ hr at 70°C. After cooling to 25°C, the aniline is added and the temperature held for 3 hr at 25–30°C, followed by heating at 35°C for an additional hour. The solution

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[1] *B.I.O.S. Rept.* 1151, Item 22.

[2] *B.I.O.S. Final Rept.* 1153, Item 22, p. 82.

is then tested for completeness of reaction by determining whether diazotization occurs with sodium nitrite, and heating is continued until no aniline remains. Sodium sulfate (1,080 lb) and 165 gal of mother liquor from previous batches are next added to salt out the desired sulfonate, which is highly water-soluble. The solid product is filtered and washed with aqueous sodium sulfate containing 24.3 per cent by weight (anhydrous basis) of the sulfate. The yield is 92–93 per cent of theory.

This general procedure is applicable to other types of compounds containing —NH_2 groups.

Addition of Sodium Bisulfite to a Maleic Acid Ester.[1] This reaction proceeds as follows, R being 2-ethylhexyl:

$$ROCOCH{=}CHCOOR + NaSO_3H \rightarrow ROCOCH_2CH(SO_3Na)COOR$$

Di-(2-ethylhexyl) maleate (11,800 lb crude) and 95 per cent ethanol (9,530 lb) are charged to an enameled jacketed kettle provided with moderate agitation and distillation take-off. Aqueous sodium hydroxide (27 per cent) is then added (until the mixture is weakly alkaline to litmus) to neutralize toluenesulfonic acid catalyst in the crude ester. Aqueous sodium bisulfite (3,600 lb—100 per cent—as 22.5 per cent solution) is next added, and the mixture is heated to 100°C with slow agitation. It is held at this temperature for 12 hr, the pressure showing 24 psig. The mixture is cooled to 60°C to reduce the pressure to atmospheric, and the distillation take-off is connected for removal of the alcohol solvent, which begins at 80°C. Distillation of the alcohol is continued for 7 hr to a temperature of 91°C for removal of about 75 per cent of the alcohol. The solution is then cooled to room temperature for packaging without further processing. The yield is nearly quantitative.

The maleate ester raw material is easily made from 2-ethylhexanol and maleic anhydride. The product sulfonate, being a highly effective textile wetting agent and simple to manufacture, is produced widely. Similar sulfonates can be prepared from other maleate esters.

Sulfoethylation of Oleic Acid (Igepon A).[2] Oleoyl chloride is heated with sodium 2-hydroxyethanesulfonate:

$$C_{17}H_{33}COCl + HOCH_2CH_2SO_3Na \rightarrow C_{17}H_{33}COOCH_2CH_2SO_3Na + HCl\uparrow$$

Solid sodium 2-hydroxyethanesulfonate (408 lb of 98 per cent purity—2.70 moles) is shoveled into a homogenous lead-lined condensation kettle, 500 gal capacity, equipped with an efficient heavy-duty stirrer, a jacket for heating and cooling, and a take-off for HCl gas. The manhole is closed, and heating and stirring are begun while oleoyl chloride (695 lb of 95 per cent purity—2.16 lb moles) is run in. The mixture is stirred about 15 min after

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[1] *O.T.S. Rept.* PB 3,867, p. 32; Jaeger, U.S. 2,028,091 (1936).

[2] *O.T.S. Rept.* PB 3,868, p. 20.

reaching 100°C, when the reaction becomes vigorous and HCl is evolved copiously and removed through the take-off pipe. Stirring is continued as the temperature rises to about 110°C. The reaction mixture, originally a thick liquid, becomes a crumbly solid and finally disintegrates into waxy flakes, which upon stirring with cooling to 90°C become a gritty powder. Solid sodium carbonate is stirred into the product to neutralize residual HCl, and the batch is discharged to containers. The yield is 97 per cent of theory.

Aromatic Sulfonates

The Monosulfonation of Benzene. Benzene can be monosulfonated efficiently, and on a continuous basis, by the partial-pressure distillation method. A typical operating procedure, based on the flow diagram shown in Fig. 7-6, is as follows:[1]

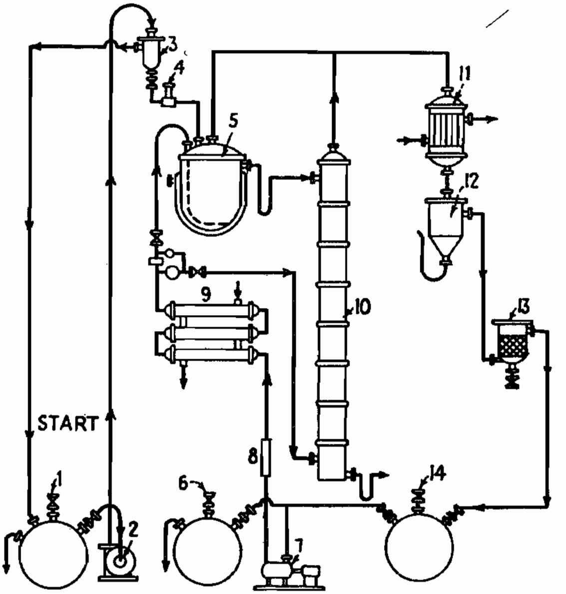

Fig. 7-6. Flow diagram: continuous partial-pressure sulfonation of benzene.

Sulfuric acid is continuously pumped from storage tank (1) by means of pump (2) through pressure regulator (3) and meter (4) to the sulfonator (5). Liquid benzene from storage tank (6 or 14) is continuously fed by pump (7) through meter (8) to the direct vaporizer superheater (9), and thence to the sulfonator (5) and the sulfonation tower (10). In the sulfonator, sulfuric acid reacts with benzene, and the reaction mass containing 30 per

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[1] Planovskii and Kagan, *Khim. Prom.*, **1944** (9), 5–10.

cent unreacted sulfuric acid flows out continuously to the top of the sulfonation tower (10), which is arranged like a plate column. The reaction mass flows downward through the tower while further reacting with a countercurrent stream of benzene vapor. The exit benzene-water vapors are continuously discharged from the top of tower (10) to condenser (11) and stratified in separator (12), and the benzene is returned through neutralizing drier (13) to benzene storage (14), while the benzenesulfonic acid, containing 2.5–3.5 per cent of sulfone and 3–4 per cent of sulfuric acid, is continuously drawn off at the bottom of the tower.

Under optimum conditions, the reaction time for this process has been calculated at 1.5 hr at 180°C, using a seven-stage reactor and employing 10 moles of benzene per mole of sulfuric acid. In contrast, the same process operated in batches (see pp. 311 and 371) at 160–180°C would require 14 hr and 6–8 moles of benzene per mole reacted. Thus, the continuous method increases by nearly ten times the capacity of the batch method. It is further estimated that the ratio of benzene used to benzene reacted could be reduced as low as 3:1 by doubling the time of reaction. The efficiency of the process can be further increased by using 10 per cent oleum instead of sulfuric acid, thereby reducing the required water removal without substantially raising by-product sulfone formation. This type of process has been used commercially in the United States.[1]

The Sulfonation of Dodecylbenzene.[2] Dodecylbenzene (detergent alkylate) is reacted with 20 per cent oleum:

$$C_{12}H_{25}C_6H_5 + SO_3 \xrightarrow{H_2SO_4} C_{12}H_{25}C_6H_4SO_3H$$

The hydrocarbon (11,000 lb—1,500 gal) is pumped into the glass-lined sulfonation kettle, 2,500-gal capacity, equipped with 10-hp turbo-type mixer, and external heat exchanger of about 1,000 sq ft of cooling capacity. Circulation of the alkylate through the external heat exchanger is begun. The mixer is turned on, and 20 per cent oleum (13,750 lb) is added as fast as possible, not exceeding a temperature of 30°C, which usually requires 1.5–2 hr. Following addition, the batch is digested for about 2 hr at about 30°C to complete reaction. At this point the spent acid has a strength of 98.2 per cent and is mixed with the sulfonic acid. To effect layer separation, water (2,660 lb) is added with full agitation and cooling at not over 60°C to yield a spent acid of approximately 78 per cent. Layer separation occurs upon standing for about 4 hr at 60°C; the lower layer, comprising 10,800 lb 78 per cent acid, is removed. The upper sulfonic acid layer is

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[1] *Southern Power and Ind.*, **62** (10), 94–99 (1944).

[2] Oronite Chemical Co., "Alkane Basic Detergent Raw Material," 1955; SNELL, ALLEN, and SANDLER, *World Petroleum Congr., Proc., 3rd Congr., Hague*, 1951, Sec V, pp. 109–118; Continental Oil Co., "Neolene 400, Intermediate for Synthetic Detergents," 1955; KIRCHER, MILLER, and GEISER, *Ind. Eng. Chem.*, **46**, 1925 (1954).

neutralized by addition to aqueous caustic soda (3,006 lb as 20 per cent solution) at not over 55°C at a final pH of 7.5–8 to yield a sodium salt slurry which can be processed further as appropriate, depending upon the final formulation required. Approximately 99 per cent of the hydrocarbon charged is sulfonated; product loss by solution in the spent acid is small.

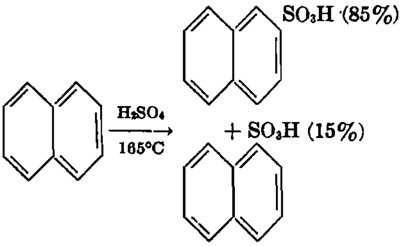
A discussion of the heat evolved in this important sulfonation was presented earlier in this chapter. The merits of other sulfonating agents employed in this process (98 per cent acid, 100 per cent acid, 22 per cent oleum, and sulfur trioxide) have previously been reviewed. Operation on a semicontinuous basis is discussed in the previous section. Much additional detailed information is available in the references cited on auxiliary equipment used, alternate materials of construction, physical properties of the starting materials, intermediates, and final products, energy requirements, etc. The quantity of added diluting water can also be varied; spent acid more dilute than 78 per cent separates more rapidly, but is much more corrosive. A cost analysis[1] for this process is given in Table 7-14.

TABLE 7-14. ESTIMATED COST* OF MANUFACTURING DETERGENT SLURRY

Raw materials (alkylate, oleum, caustic soda)	$101.50
Utilities (water, steam, power)	2.18
Labor, supervision, maintenance	8.85
Depreciation, overhead	3.38
Total	$115.91

* Per 1,000 lb sodium sulfonate (100 per cent), in a plant producing 15,000 lb sulfonate per day. No credit is taken for spent acid.

Naphthalene (β-Sulfonation).[2] The hydrocarbon is reacted with sulfuric acid; in addition to the desired isomer, about 15 per cent of the alpha isomer is also formed:



Naphthalene (3,350 lb—26.2 lb moles) is charged to a cast-iron sulfonation kettle, 1,500-gal capacity, equipped with propeller or anchor agitator,

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[1] Based on data supplied by Walter L. Hardy of Foster D. Snell, Inc.; see also HARDY, *Ind. Eng. Chem.*, **47**, 79A (1955).

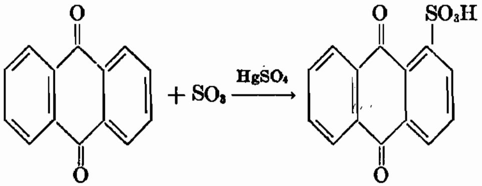
[2] SHREVE, *Color Trade J. and Textile Chem.*, **14**, 42 (1924); *B.I.O.S. Final Rept.* 1152, Item 22, p. 8.

and heated either directly with generator gas or by high-pressure (100 lb) jacket steam. It is melted by heating to 90–110°C. Sulfuric acid (3,350 lb of 96 per cent strength—32.8 lb moles) is then added with agitation, the temperature being allowed to rise to about 160°C. The batch is held at 160–165°C for about 2 hr to complete reaction, during which time water (approx. 400 lb—22.2 lb moles) and naphthalene (approx. 350 lb—2.7 lb moles) distill off and are collected by condensation. The reaction product contains mainly monosulfonic acids (85 per cent beta and 15 per cent alpha), plus some sulfone, free sulfuric acid, disulfonic acids, and tar. The undesired α-sulfonate is now removed by blowing dry steam into the charge to effect hydrolytic desulfonation (see discussion on p. 361), the liberated naphthalene being distilled and recovered. It is essential to employ dry steam to avoid foaming and to maintain a temperature in the range 160–165°C to ensure rapid reaction. About 16 per cent, or 540 lb of the original naphthalene employed, is recovered, leaving the β-sulfonate contaminated with only about 0.1 per cent alpha isomer.

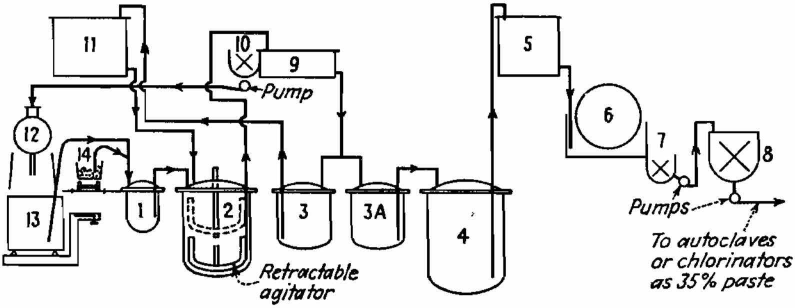
The "hydrolyzed" sulfonation mixture is discharged into the water with good agitation, and the resulting solution is run into the brine to form the sodium sulfonate salt. The slurry so obtained is agitated for 10 hr as it cools to 30°C; this yields an easily filterable precipitate. The filtration is accomplished by pumping or blowing the sodium sulfonate suspension into a pressure filter containing wooden plate filters and rubber-coated frames. The shell of the filter is coated with tar to minimize corrosion. The filtrate is permitted to stand and more salt added if necessary, and then it is refiltered to collect any additional sulfonate that has crystallized out. The second crop of sodium sulfonate is not so pure as the first. The filter cakes are washed with a minimum of water, and these washings are employed to advantage as part of the liquor in the sulfonation dilution tank. The filter cake of sodium sulfonate containing about 70 per cent water is pressed hydraulically to a water content of about 30 per cent. The press cakes are dried to a moisture content of about 5 per cent, disintegrated, and delivered to the caustic fusion kettles for conversion to β-naphthol. The yield is about 90 per cent of theory on the basis of naphthalene consumed.

Several factors ensure rapid and complete sulfonation in this process: (1) use of about 25 per cent excess acid, corresponding to about 40 per cent excess over that actually converted to sulfonate; (2) distillation of a quantity of water (22.2 moles) only slightly less than the amount of naphthalene (23.5 moles) sulfonated; and (3) use of an elevated reaction temperature. At this temperature, water will distill from dilute acid until it has increased to 68 per cent in concentration, which is above the π concentration (64 per cent) required to sulfonate naphthalene at this temperature. As in every important sulfonation, several modified procedures have been suggested to reduce the acid factor more closely to theoretical, including the use of excess naphthalene or operation under vacuum. Continuous operation has also been studied. None of these expedients has been adopted commercially. Variations in the working-up procedure have, however, sometimes proved advantageous.

Anthraquinone-1-sulfonate (Potassium Salt).[1] The quinone is sulfonated with 20 per cent oleum in the presence of mercury sulfate catalyst. To ensure maximum yield, only 40 per cent of the starting material is reacted.



The equipment used for this sulfonation is shown in Fig. 7-7. Oleum (4,620 lb of 20 per cent strength) is charged to the sulfonator, followed by the mercuric sulfate (33 lb) which is dissolved by agitating at 50–60°C for 30 min. The anthraquinone (4,580 lb: 2,420 lb new and 2,210 lb recovered material assaying 98 per cent) is then added, and the charge heated to 120°C in 1½ hr, and then held at 120°C for 3 hr to sulfonate about 40–50 per cent of the anthraquinone. The sulfonation mass is next blown to a 15,000-liter acidproof brick-lined crystallizing tank (2), which is equipped with a large heavy-duty anchor-type agitator which can be raised and lowered. Wash water from the residue filter (11) is run slowly into the hot agitated sulfona-



1 Cast-iron agitated sulfonator, 2,500 liters
2 Anthraquinone crystallizer
3 Filtrate receivers
4 Precipitator for α-K-salt, 20,000 liters
5 Storage for rotary filter
6 Rotary filter, 6 sq m
7 Neutral mixer, 2,000 liters
8 Storage mixer for 35 per cent K-salt slurry, 13,000 liters
9 Stone filter for recovered anthraquinone
10 Mixer for recovered anthraquinone
11 Wash-water storage for use in (2), 10,000 liters
12 Venuleth for drying recovered anthraquinone
13 Storage bin for recovered anthraquinone
14 New anthraquinone

FIG. 7-7. Flow diagram: manufacture of potassium anthraquinone sulfonate.

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[1] *F.I.A.T. Final Rept.* 1313, vol. II, p. 52 (Field Information Agency Technical).

tion mass in the bottom of the tank until it becomes too thick to agitate. The agitator is raised until it just clears the surface of the charge. The addition of wash water is then resumed, until sufficient has accumulated on the surface of the batch to be picked up by the agitator and worked into the thick mass from above, and is continued while lowering the agitator as rapidly as mixing will permit, until finally the agitator has reached the bottom of the mass and separation of the crystalline anthraquinone is complete. The crystallizer is then filled to capacity with wash liquor, the temperature of the slurry being maintained at 80°C with open steam heating. The slurry is next blown to three large brick-lined open filters (9), where the unsulfonated anthraquinone is filtered, washed free of acid, and returned for subsequent sulfonation.

To precipitate the desired potassium sulfonate, the filtrate [collected in receivers (3 and 3A), together with strong wash liquor] is transferred to the 20,000-liter rubber-lined precipitation tank (4) and the concentrated KCl solution is added. The temperature is maintained at 85°C to keep the by-product 1,5-disulfonate in solution. The precipitated potassium sulfonate is isolated by continuous filtration on a rubber-covered rotary filter (5 and 6), where it is washed with 5 per cent potassium chloride solution and discharged at approximately 45 per cent solids content into a horizontal trough mixer (7), from which it is pumped to one of two 13,000-liter brick-lined paste storage tanks (8). The paste content is adjusted to 35 per cent solids and brought to neutrality with a small amount of soda ash solution, after which it is pumped either to an autoclave for conversion to 1-aminoanthraquinone or to the chlorinators for conversion to 1-chloroanthraquinone.

The yield is 6,050 lb 35 per cent paste, or 2,120 lb 100 per cent sulfonate. Of 4,580 lb anthraquinone charged, 41 per cent (1,880 lb) is converted. The yield of sulfonate is therefore 72 per cent of theory. Capacity is three batches per day.

Preparation of the *2-sulfonate isomer* is similar,[1] except that no mercury is used and a higher temperature (145°C) is employed with 22 per cent oleum. In both processes, partial conversion minimizes yield loss from disulfonation and oxidation, but entails wasteful use of sulfonating agent since, for every pound of anthraquinone reacted, 2.1 lb oleum (equivalent as SO_3) is used contrasted to 0.38 lb theoretical. When mercury is used, the anthraquinone is first mercurated, followed by displacement of the mercury by the sulfonate group.

The Chlorosulfonation of Acetanilide.[2] Acetanilide is reacted with chlorosulfonic acid to yield the sulfonyl chloride, which is used as an intermediate for nearly all sulfa drugs.

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[1] *Ibid.*

[2] *O.T.S. Rept.* 91, 355, frame 27.

$$CH_3CONHC_6H_5 + ClSO_3H \rightarrow CH_3CONHC_6H_4SO_3H + HCl\uparrow$$
$$CH_3CONHC_6H_4SO_3H + ClSO_3H \rightleftharpoons CH_3CONHC_6H_4SO_2Cl + H_2SO_4$$

Chlorosulfonic acid (5,060 lb—43.5 lb moles) is charged to a cast-iron, wrought-iron, or enameled kettle, equipped with agitator, facilities for cooling and heating, and take-off for HCl gas. Acetanilide (1,100 lb—8.1 lb moles) is added slowly with cooling and agitation at a maximum temperature of 30°C. After addition, the batch is slowly warmed to 55°C over a 2-hr period, at which temperature it is held for 1–2 hr to complete reaction. The reaction mixture is then cooled to 20°C and fed in a thin stream into 1,500 gal water in a wooden vat equipped with an agitator and cooled with brine to maintain about 0°C. This process requires 13–14 hr. The precipitated solid product is filtered and washed with brine-cooled water to neutrality to Congo paper. The yield is 3,300 lb moist cake (79 per cent of theory). A large excess of acid is used to ensure a good yield by driving the second (equilibrium) reaction to the right. Much heat is evolved in decomposing this excess acid, and the working-up procedure is therefore quite prolonged since a low temperature must be maintained to avoid decomposing the product.

Sulfanilic Acid from Aniline.[1] Aniline sulfate is converted to sulfanilic acid by "baking":

$$H_2NC_6H_5{\cdot}H_2SO_4 \rightarrow H_2NC_6H_4SO_3H + H_2O$$

Aniline sulfate is first prepared in a cast-iron kettle equipped with a reflux condenser and 25-rpm propeller agitator. Sulfuric acid (3,520 lb 92 per cent acid—33.0 lb moles 100 per cent acid) is charged to the kettle. The aniline (3,030 lb—32.5 lb moles) is then added through an orifice with agitation as the temperature rises to 150°C, aniline and water being refluxed in the condenser. Two hours after addition of the aniline, the reaction is complete.

The warm paste acid sulfate is placed on trays, 12 trays to a truck. Eleven trucks are required (132 trays). One truck is placed in the "baking oven" (a funnel-type air-circulation truck drier) every 75 min; the total baking time is therefore 12½ hr. Upon removal from the oven, the truck is held in the cooling compartment for 1¼ hr. Hot air enters opposite the charging end of the oven at 260–280°C through slotted distributor vanes. The air is heated by a gas burner which is supplied with fresh air, then mixed in a chamber with recirculated air and exhausted by a circulating fan. Excess air is vented through the roof. Air pressure is 10 mm (water) in the duct before entering the chamber. The product so obtained is at least 97 per cent pure (not over 0.3 per cent aniline) and can be used as such. The yield is 5,620 lb, which is 98 per cent of theory.

Another process description,[1] employing milder conditions (8 hr at

[1] *F.I.A.T. Final Rept.* 1313, vol. I, p. 255.

190°C), yields a crude sulfonate of 90 per cent purity (3 per cent aniline), which is further purified by reprecipitation from the sodium salt. The baking step is sometimes facilitated by operating *in vacuo*. A modified version of this process, involving azeotropic removal of water with an inert solvent (ortho-dichlorobenzene), is often used.

Sulfates

The Sulfation of Dimethyl Ether with SO_3.[1] The two materials are reacted directly, as follows:

$$(CH_3)_2O + SO_3 \rightarrow (CH_3)_2SO_4$$

The vaporized ether is reacted continuously with equivalent liquid SO_3, using the reaction product dimethyl sulfate as solvent medium. The reactor comprises an aluminum tower, 8 in. inside diameter and 12 ft high, equipped with a water jacket for moderate cooling, top inlet for liquid SO_3, bottom inlet (with gas-dispersion disc for gaseous dimethyl ether, and take-off near the bottom for the continuous removal of liquid product. The tower is filled with dimethyl sulfate. Liquid SO_3 is metered in continuously at the top of the tower at a rate of 58.4 lb per hr, while equivalent dimethyl ether (33.6 lb per hr) is admitted at the bottom in finely divided gaseous form (bp, −24°C) through the dispersion disc. Reaction product is withdrawn continuously. The reaction is mildly exothermic, a temperature of 45–47°C being maintained by water cooling as necessary. Operation is fully continuous. The crude product is 96–97 per cent pure dimethyl sulfate, the remainder being H_2SO_4 and methyl acid sulfate. It can be used for many purposes without purification. One vacuum distillation over sodium sulfate gives a water-white stable product of 99 per cent purity. The yield is nearly quantitative.

This process is close to ideal in all respects, since the reaction is clean, quantitative, rapid, and mildly exothermic. Comparison with the earlier batch process is made on p. 369. This procedure is stated not to work with diethyl and other ethers.

The Sulfation of Lauryl Alcohol with $ClSO_3H$.[2] The reaction is as follows:

$$C_{12}H_{25}OH + ClSO_3H \rightarrow C_{12}H_{25}OSO_3H + HCl\uparrow$$

The lauryl alcohol (600 lb) is charged to a jacketed enameled kettle, equipped with agitator and take-off for HCl gas. The acid (374 lb) is then added gradually with stirring and cooling such that the temperature does not exceed about 30°C. The reaction mixture is next run on to ice (440 lb) and water (220 lb), the temperature not exceeding 45–50°C, and is neu-

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[1] *O.T.S. Rept.* PB 75,463.

[2] *B.I.O.S. Final Rept.* 1151, Item 22, p. 6.

tralized with caustic soda to weak alkalinity. The resulting solution of sodium lauryl sulfate can be spray dried to a powder or worked up in various other ways, depending upon the final formulation desired. The yield is nearly quantitative.

Although the equation given above shows pure lauryl alcohol, the technical material actually used corresponds more closely to a C-13 to C-14 alcohol, using the sulfating agent in some excess over theory. In this process optimum batch size is about 450 lb, maximum about 660 lb. With higher-molecular-weight alcohols, which are solids at room temperature, higher sulfation temperatures are used—up to 45°C. Chloroform (25–35 per cent by weight on the alcohol) is sometimes used as solvent in this type of sulfation. A similar process has been described for the sulfation of *n*-butanol, using stoichiometric $ClSO_3H$ at 10–20°C.[1] The neutralization procedure cited above is not the usual one, which comprises the addition of the acid reaction product to the caustic solution rather than vice versa.

Ethanol from Ethylene.[2] Ethylene is absorbed in 97.5 per cent sulfuric acid. The ethyl sulfates formed are hydrolyzed to ethanol, the spent acid being recycled after reconcentration to the initial strength.

$$CH_2{=}CH_2 + HOSO_2OH \rightarrow C_2H_5OSO_2OH$$
$$2CH_2{=}CH_2 + HOSO_2OH \rightarrow C_2H_5OSO_2OC_2H_5$$
$$C_2H_5OSO_2OH + C_2H_5OSO_2OC_2H_5 + 3H_2O \rightarrow 3C_2H_5OH + 2H_2SO_4$$

The equipment, shown in Fig. 7-8, comprises an absorption tower for operating under several atmospheres pressure and is equipped with an external heat exchanger. The process operates fully continuously. An ethylene-rich gas, obtained from petroleum cracking and free of sulfur compounds and higher olefins, is absorbed in 97.5 per cent acid in the tower reactor under conditions of temperature and pressure ensuring maximum absorption in one pass. The reaction is exothermic, cooling being effected by circulation through an external heat exchanger. The liquid product from the absorbing tower, containing ethyl hydrogen sulfate and diethyl sulfate, is bled off continuously. The sulfate mixture is pumped to a water-hydrolysis chamber and then to a column in which it is further hydrolyzed and stripped of alcohol and by-product ethyl ether. The mixed vapors of alcohol, ether, and water, after being scrubbed with caustic soda, are condensed and sent to a crude-alcohol storage tank.

An important and costly portion of this plant is the system for recovery of the spent acid, which flows in dilute form from the base of the alcohol stripping column. Reconcentration of the dilute acid is accomplished in three steps, the first bringing the strength up to 70 per cent in an acid reboiler (see Fig. 7-8), the evaporated steam being returned to the stripping

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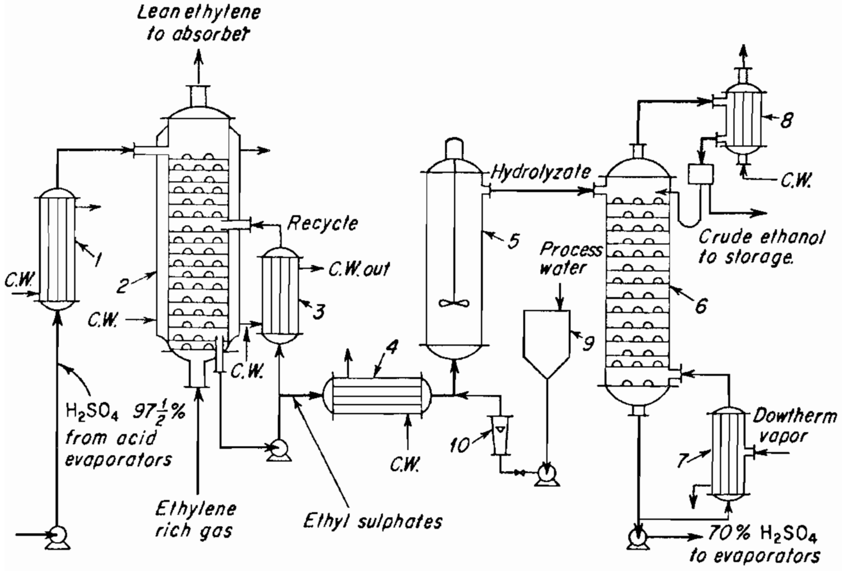
[1] *O.T.S. Rept.* PB 32,537.

[2] "Encyclopedia of Chemical Technology," vol. I, p. 280.



1 Concentrated acid cooler
2 Ethylene acid absorber
3 Ethyl sulfate recycle cooler
4 Ethyl sulfates cooler
5 Hydrolyzer
6 Ethanol stripper
7 Dowtherm stripper reboiler
8 Stripper condenser
9 Process water head tank
10 Rotameter

FIG. 7-8. Flow diagram: continuous ethanol-from-ethylene process.

column. A two-stage vacuum system next takes the acid first to 89 per cent strength under 25 psia, and finally to 97.5 per cent concentration under 0.4 psia, the acid temperature never exceeding 370°F. The yield is about 95 per cent of theory based on ethylene; about 8 lb of acid is consumed (i.e., nonrecoverable) per 100 lb alcohol.

This process is ordinarily operated in close conjunction with a petroleum refinery as a source for ethylene. Propylene is converted to isopropanol by essentially the same process, but under milder conditions. The corrosive nature of this process and the difficulty of acid recovery have led to successful development of commercial procedures for the direct catalytic hydration of ethylene under nonacidic conditions.

Fatty Oils[1]

"High" Sulfonation of Cod Oil. The oil (4,300 lb) is charged to a steel kettle equipped with agitator, provision for cooling, and bottom product outlet. Sulfuric acid (1,180 lb of 93–94 per cent strength, equivalent to 27.5 per cent on the weight of the oil) is next added as fast as possible, with agitation and cooling such that the temperature does not exceed 35°C; this

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[1] SUNDERLAND, *Soap*, **11** (11), 61–64 (1935).

requires 3–4 hr. The batch is then agitated 5–6 hr longer, or until a sample is soluble in distilled water without opalescence. The reaction mixture is now run into aqueous sodium sulfate (1,380 gal of 8 per cent solution) previously charged to a lead-lined wooden tank, and the mixture is agitated 5–10 min with warming to 40°C. The lower aqueous layer is separated, and the organic layer is made nearly neutral to methyl orange, using aqueous caustic soda. After standing overnight, the aqueous layer is again withdrawn, and final adjustment of pH in the oil layer is made with alkali.

This procedure is also applicable to other oils, including castor, cottonseed, and sperm. It is sometimes referred to as "double" sulfonation.

"Quick" Sulfonation of Oleic Acid. Oleic acid (800 lb of 10°C titer) is charged to the reactor. Sulfuric acid (180 lb of 93 per cent strength, equivalent to 22.5 per cent on the weight of the oleic acid) is added in 10 min, with strong agitation. The temperature rises from 26°C (room temperature) to 52°C by the end of acid addition, using cooling water at 10°C. The mixture is agitated for an additional 50 min and then run into aqueous sodium sulfate (200 gal of 20 per cent solution). The desired organic layer separates in 1 hr. It is neutralized with 132 lb of 28 per cent aqueous sodium hydroxide to yield the finished product.

This method is also used with castor, corn, neat's-foot, and cod oils. For further discussion of the sulfonation of fatty oils, see p. 323.

CHAPTER 8

AMINATION BY AMMONOLYSIS

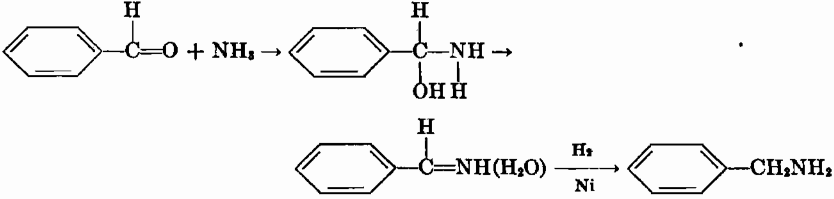
By P. H. Groggins and W. V. Wirth

I. GENERAL DISCUSSION

Classification of Reactions

Amination by ammonolysis is the process of forming amines by the action of ammonia. By extension, the use of primary and secondary amines as aminating agents (*aminolysis*) is also included. Such a broadening of the definition permits a comprehensive and integrated presentation of the subject and is fully justified in the light of the similarity of underlying principles and manufacturing practices as well as the industrial utility of the secondary and tertiary amines thus formed. Consideration is also given to *hydroammonolysis* with ammonia-hydrogen mixtures in the presence of a hydrogenation catalyst. This technique permits the direct preparation of amines from carbonyl compounds, which with ammonia alone would result in the preponderant formation of nitriles or aldimines.

$$R{\cdot}CHO + NH_3 \rightarrow R{\cdot}CN(H_2O + H_2) \xrightarrow[Ni]{H_2} R{\cdot}CH_2{\cdot}NH_2$$



Considering the behavior of ammonia, the ammonolytic reactions may involve:

1. *Double decomposition,* in which the NH_3 molecule is split into $—NH_2$ and —H fragments, the former becoming part of the newly formed amine, while the latter unites with the radical —Cl, $—SO_3H$, $—NO_2$, etc., that is substituted.

2. *Dehydration,* in which water and amines result from the ammonolysis of either alcohols or phenols and from the hydroammonolysis of carbonyl compounds.

3. *Simple addition,* in which both fragments of the NH_3 molecule enter the new compound as in the preparation of alkanolamines from alkylene oxides, aminonitriles from unsaturated nitriles, and ureas and thioureas from isocyanates and isothiocyanates.

4. *Multiple activity,* in which nascent or recycled amines compete with ammonia as a coreactant, resulting in the formation of secondary and tertiary amines by aminolysis.

Based on the preceding, as well as on known characteristics of ammonolytic reactions, it appears reasonable to discuss the subject under the following broad classifications:

1. Replacement of aryl and alkyl halogens.
2. Replacement of aryl $—SO_3H$ and alkyl $—OSO_3H$.
3. Conversion of alcohols and functionally substituted alcohols.
4. Hydroammonolysis of carbonyl compounds.
5. Addition reactions.
6. Reaction of ammonia with hydrocarbons.
7. Miscellaneous reactions, such as conversion of phenols, replacement of aryl nitro groups, and polymerization with formaldehyde.

II. AMINATING AGENTS

The aminating agent may be NH_3 employed as liquid ammonia, as a solution in water or an organic solvent, or as a gas in a vapor-phase reaction or ammonia evolved from solid compounds such as urea or ammonium salts. In each case, it is reasonable to believe that ammonolysis is actually brought about by NH_3. In selecting the particular aminating agent, consideration would be given to the temperature and pressure conditions normally required for a given type of compound, the type of catalyst that might be effective, the stability and solubility of the compound to be aminated, the avoidance of side reaction such as hydrolysis, and the formation or suppression of secondary amines. Some of the properties of the aminating agents will now be briefly reviewed.

Liquid Ammonia. The properties of liquid ammonia are compared with those of water in Table 8-1.

Liquid ammonia resembles water in its general physical and chemical properties, as is apparent in the values of Table 8-1. It can also be seen, from the boiling point, for example, that the technique of ammonolysis may be different, depending on whether liquid ammonia or aqueous ammonia is used as the aminating agent.

Both ammonia and water are associated liquids. The degree of association of ammonia from molecular-weight determinations (24.5) suggests an equilibrium mixture:

$$(NH_3)_2(60\%) \rightleftharpoons 2NH_3(40\%)$$

TABLE 8-1. PROPERTIES OF AMMONIA AND WATER

Properties	Liquid ammonia	Water
Melting point	−77.7°C	0°C
Boiling point	−33.35°C	100°C
Specific heat, g-cal at bp	1.07	1.01
Specific gravity at 20°C	0.607	0.9982
Critical temperature	131°C	365°C
Critical pressure, atm	112	195
Surface tension, dynes/cm	22.0 at 20°C	72.8 at 20°C
Dielectric constant	22.7 at −50°C	81.1 at 18°C
Mobility of K ion, cm/sec/volt	0.0176 at −33°C	0.0067 at 20°C

They form compounds with salts, are good solvents, and, although virtual nonconductors themselves, effect the ionization of electrolytes. The ionizing power of liquid ammonia is due largely to the high speed at which the ions of dissolved electrolytes move in this solvent.

Liquid ammonia may be introduced into reaction systems, and ammonolysis then carried out at temperatures higher then the critical temperature. These are really examples of the use of gaseous ammonia as the aminating agent or of ammonia dissolved in one of the reactants or in an inert organic solvent.

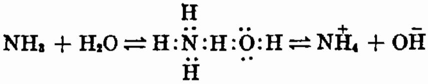
Aqueous Ammonia. For liquid-phase reactions, aqueous ammonia will continue to be the aminating agent used in the greatest amount and in the greatest number of cases. It has the advantage of greater convenience in handling and general applicability, and it readily dissolves sulfonic acids, for example, as well as catalysts such as copper salts or reduction inhibitors, such as $KClO_3$, used in the amination of chloroanthraquinone. Disadvantages may be the limited solubility of chloro compounds and the occurrence of hydrolysis along with ammonolysis.

TABLE 8-2. SOLUBILITY OF AMMONIA IN WATER AT 760 MM

Temperature, °C	0	10	20	30	40	50	60	70	80	90
G NH_3/100 g of solution, %	47.4	40.7	34.1	29.0	25.3	22.1	19.3	16.2	13.3	10.2

Aqueous ammonia might be employed under a variety of conditions, since the solubility of ammonia in water is influenced by both temperature and pressure. In practice, however, ammonolysis with aqueous ammonia usually refers to the use of 25—50 per cent aqueous ammonia under pressure at temperatures greater than 100°C. Table 8-2 illustrates the solubility of NH_3 in water as a function of temperature at 1 atm pressure.

Ammonolysis with aqueous ammonia should be interpreted as being brought about by NH_3, not by NH_4OH. As water is only a very weak acid, the ammonia addition product is very unstable, and ammonium hydroxide exists in aqueous ammonia as a weak base present in small amount. To account for the weakness of ammonium hydroxide, it has been assumed that a hydrogen atom acts as a bond:



$$NH_3 + H_2O \rightleftharpoons H:\underset{\displaystyle H}{\overset{\displaystyle H}{\ddot{N}}}:H:\underset{..}{\ddot{O}}:H \rightleftharpoons \overset{+}{N}H_4 + O\overset{-}{H}$$

The presence of hydroxyl ions from the dissociation of ammonium hydroxide, alkyl or arylammonium hydroxide, or water is responsible for the simultaneous formation of hydroxy compounds in certain reactions. Thus, in the amination of chlorobenzene and chloroanthraquinones by this unit process, phenol and hydroxyanthraquinones, respectively, are found accompanying the amino compounds in the reaction product:

$$C_6H_5Cl \xrightarrow{NH_3\text{ aq.}} C_6H_5NH_2 + \text{some } C_6H_5OH + NH_4Cl$$

In the preparation of aniline, the concomitant formation of phenol is not always objectionable; the situation is entirely different in the preparation of compounds such as 2-aminoanthraquinone and other solid amines which cannot be purified by inexpensive physical or chemical means.

Secondary and tertiary amines are almost always formed during the ammonolysis of halogeno and hydroxy compounds, the quantity depending on the specific reactants, the reactivity of the amine, the NH_3 ratio, and other conditions employed. Their further formation is inhibited either by reintroduction of these products[1] in subsequent charges or by lowering the pH of the system by adding mineral acids, CO_2, etc., or their ammonium salts.[2]

Colorimetric studies in sealed glass tubes indicate that ammonia combines with water, above the critical temperature of NH_3, to form ammonium hydroxide.[3] The curves of Fig. 8-1 show that the pH of 28 per cent aqueous ammonia decreases, however, with rising temperature, from 11.8 at room temperature to only 8.2 at 175°C, under approximately 500 psi pressure. The pH drops off more rapidly when hydrogen chloride or its ammonium salt is introduced, corresponding to conditions prevailing during ammonolysis. At 175°C, the pH of neutrality is 5.7.

Properties of Aqueous Ammonia. *Vapor Pressures.* Wilson has investigated the partial pressures of aqueous ammonia over a wide range of

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[1] Williams, U.S. 1,775,360 (1930); Hale, U.S. 1,932,518 (1933); Swallen, U.S. 1,926,691 (1933); Herold and Smeykal, U.S. 2,068,132 (1937); Arnold, U.S. 1,799,722; Reissue 19,632 (1935).

[2] Oxley, Thomas, and Nichols, Brit. 611,593 (1948).

[3] GROGGINS and STIRTON, *Ind. Eng. Chem.*, **25**, 42 (1933).

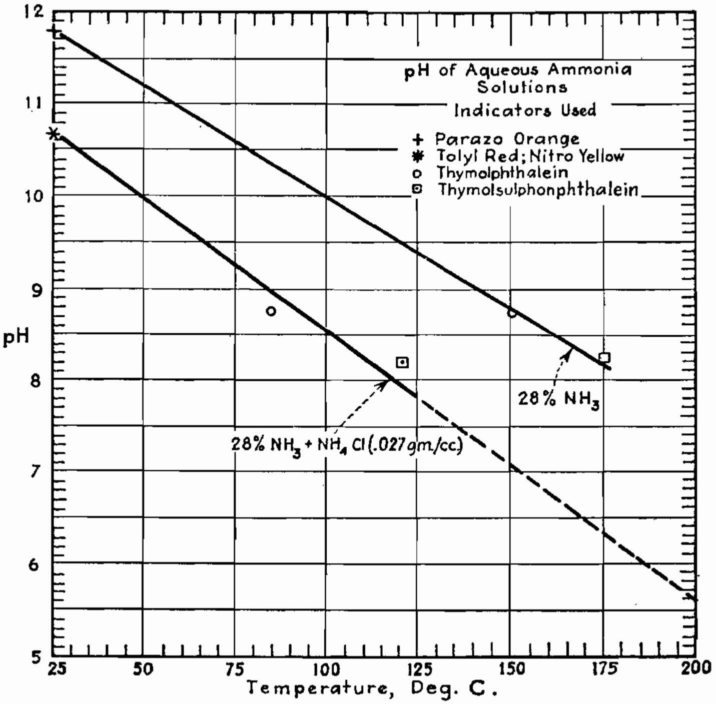

FIG. 8-1. pH of aqueous ammonia.

both concentration and temperature.[1] Some of his data are presented in Figs. 8-2 and 8-5. The curves (Fig. 8-2) show that the partial pressures of the water vapor in the vapor phase are not strictly proportional to the water content of the solution phase. There is a slight, consistent negative deviation from the ideal value entirely in harmony with the idea that, below the critical temperature of NH_3, solutions of ammonia are not completely physical mixtures of two components.

Perman also observed a similar deviation with respect to Henry's law; but on account of the slightness of the deviation, he concluded that an aqueous solution of ammonia behaves as a mixture of two liquids the boiling points of which are far removed from each other.[2] The lowering of the vapor pressure of water by the ammonia follows Raoult's law closely, showing that the molecular weight of NH_3 in solution is normal and no large quantity of hydrate is formed.

Surface Tension. King, Hall, and Ware, in studying the properties of the ammonia-water system, concluded that "It is evident from the surface

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[1] WILSON, *Univ. Illinois Eng. Expt. Sta. Bull.* 146, 1925.

[2] PERMAN, *J. Chem. Soc.*, **79**, 718 (1901); **83**, 1168 (1903).

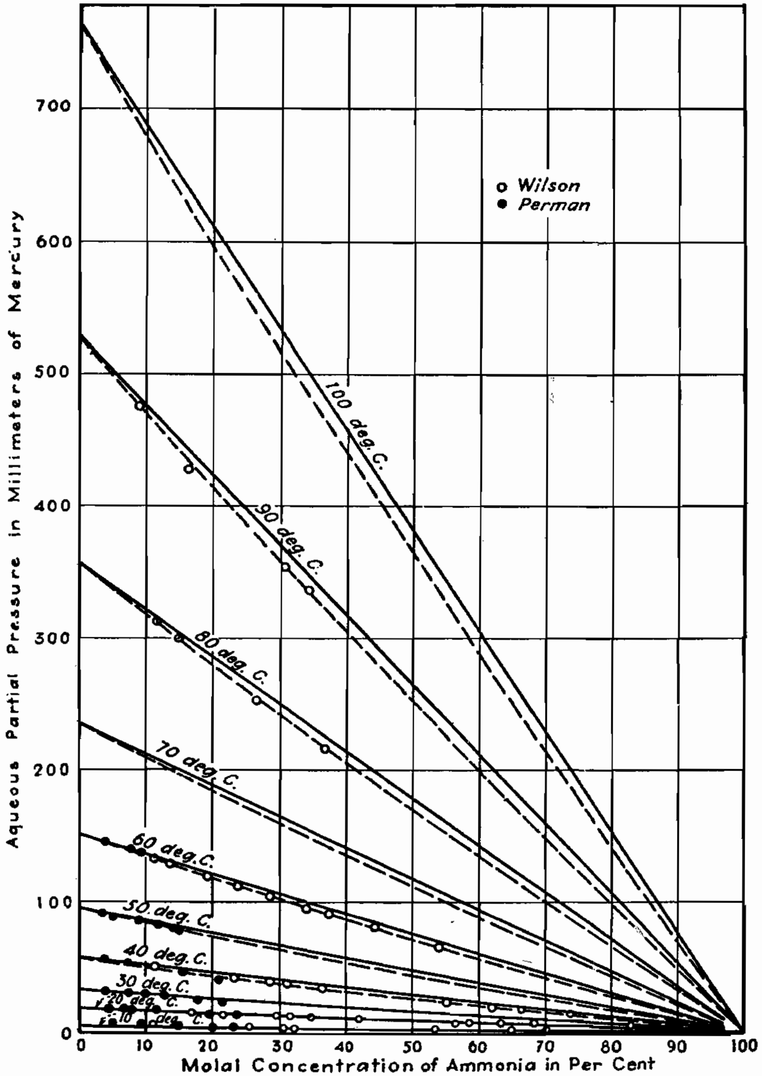

FIG. 8-2. Raoult's law and partial pressure of H_2O.

tension and thermodynamic standpoint that the system does not deviate radically from what is to be expected of a *perfect mixture*."[1]

It appears, therefore, that ammonolysis with aqueous ammonia is similar to ammonolysis with ammonia gas dissolved in any comparatively inert solvent. Indeed, the pH studies and the review of the properties and

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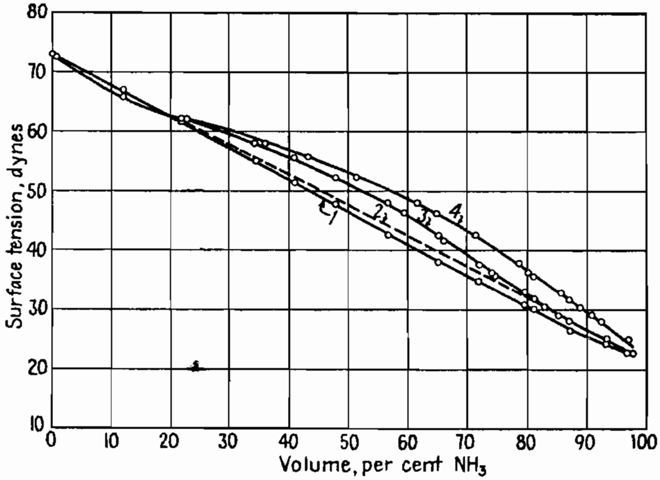
[1] KING, HALL, and WARE, *J. Am. Chem. Soc.*, **52**, 5128 (1930).

reactions of aqueous ammonia practically compel the adoption of this viewpoint. The presence of water or other solvent must, however, play an important role in ammonolytic reactions above the critical temperature (131°C) of ammonia. In sealed-tube experiments with 2-chloroanthraquinone, it was observed that suspended particles subjected to attack by essentially NH_3 vapors remained virtually unaltered, while the material in contact with the aqueous ammonia was converted.

In their studies on the properties of ammonia-water systems, King et al. found that theoretical and observed surface tensions were in good agreement (Fig. 8-3) except in the middle region.[1] In this connection it is to be noted that the vapor pressure of the system (see Fig. 8-2) shows a marked depression from normal in this region, conforming to Worley's rule[2] of perfectly miscible liquids: abnormalities of surface tension tend to move contrariwise to abnormalities in vapor pressure. Deviation of the ammonia-water system from the rule of admixtures may be due to absorption of one or the other component on the surface, and at temperatures over 131°C the absorption would have to be on the surface of water or other solvent. It is noteworthy that NH_3 is negatively absorbed in dilute solutions (i.e., up to 50 per cent) and positively absorbed in the range 50–70 per cent NH_3 concentration (Table 8-3), corresponding to the region



1 Surface tension calculated by Whatmough's rule
2 Theoretical values for a perfect mixture
3 Observed value for volume per cent, $V_0/V_a + V_w)$
4 Observed values for volume per cent, V_a/Vsol

FIG. 8-3. Theory of admixtures applied to surface tensions of ammonia-water mixtures.

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[1] KING, HALL and WARE, *J. Am. Chem. Soc.*, **52**, 5128 (1930).

[2] WORLEY, *J. Chem. Soc.*, **105**, 273 (1914).

TABLE 8-3. EXPERIMENTAL DATA FOR SURFACE TENSION OF WATER-AMMONIA MIXTURES
Temperature, 20°C ± 0.01°

Wt %, NH_3	Surface tension, dynes/cm	Moles/liter, NH_3	Ammonia adsorption, moles/sq cm × 10^{11}
100.00	22.03	35.836	0.000
90.81	24.57	34.826	
80.95	28.11	33.198	0.000
70.47	32.99	30.799	+29.271
61.16	37.90	28.192	+18.879
53.48	42.65	25.591	+11.491
44.56	48.08	22.132	−3.283
29.70	55.58	15.504	−5.746
24.14	58.02	12.891	−5.746
0.45	72.55	0.264	+9.850

exhibiting maximum deviation from calculated surface-tension data. In light of experimental evidence in the noncatalytic ammonolysis of *p*-chloronitrobenzene (Fig. 8-4) and the catalytic aminolysis of chlorobenzene with methylamine (Fig. 8-14, p. 432), that best conversions are obtained

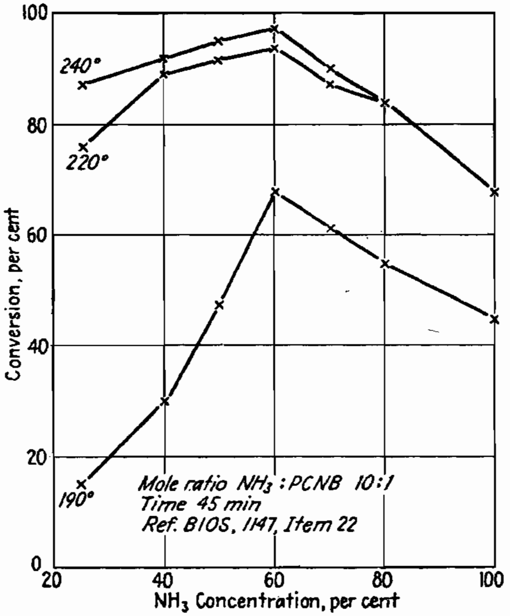

FIG. 8-4. Effect of NH_3 concentration: conversion of *p*-chloronitrobenzene to *p*-nitroaniline.

with reagents of 60–70 per cent concentration, there is need for further study to determine if these relationships have any bearing on the mechanism of reaction. The possibility exists that in this region—50–70 per cent concentration—a complex between dimeric ammonia and water is formed, which with the increasing influence of mass action creates a condition favorable for the formation of ionic complexes with the compound undergoing amination.

Comparative NH_3 and H_2O Vapor Pressures. The effects of operating with aqueous NH_3 solutions of various concentrations can be appreciated by a study of the curves of Fig. 8-5, which relate to the proportionality P_{NH_3}/P_{H_2O}.

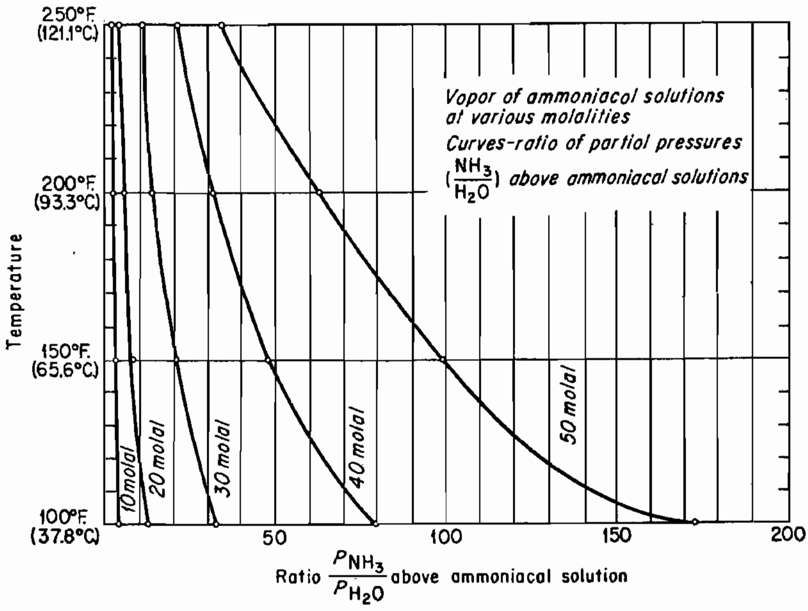

FIG. 8-5. Ratio $P_{NH_3}:P_{H_2O}$

From these data,[1] it can be observed that with increasing NH_3 concentration, there is a comparative acceleration in the quotient P_{NH_3}/P_{H_2O}. For a definite concentration, however, the partial pressure of ammonia does not increase so rapidly as the water-vapor pressure when the temperature of the solution is increased. From this, it may be predicted that there is a proportionally increased activity of water vapor at increasing temperatures. Thus, in order to obtain the highest conversion to primary amines during ammonolysis, it is advisable to employ the lowest possible temperature that produces the necessary energy-intensity factor. This

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[1] WILSON, *op. cit.*

condition is, in a measure, realized by increasing the molal concentration of NH_3 in the ammonia employed.

Ammonia Dissolved in an Inert Solvent. Organic compounds are soluble in liquid ammonia to some extent and, conversely, gaseous NH_3 is soluble in some organic liquids.

The use of an inert organic solvent to dissolve gaseous ammonia and also the compound to be aminated would seem to be a very attractive procedure since the reactants are in intimate contact and a side reaction such as hydrolysis would not be possible. Actually, however, there are some difficulties with the use of NH_3 in an organic solvent. The solvent (e.g., an alcohol) may not be entirely inert. A low ratio of the solvent must adequately dissolve both the ammonia and the compound to be aminated, and the solvent must be easily recovered.

The solubility of NH_3 in organic solvents is less than it is in water. Compared with the data of Table 8-2, the solubility of NH_3 in CH_3OH at 0, 10, 20, and 30°C is as follows, respectively: 29.3, 24.2, 19.2, and 14 per cent. The solubility of NH_3 in hydrocarbons and halogeno compounds is usually less than 1 per cent at room temperature.

Liquid ammonia is a better solvent for organic compounds than organic compounds are for gaseous ammonia. The lower aliphatic alcohols, benzyl alcohol, ethylene glycol, and glycerol, are miscible with liquid ammonia, and phenol and the polyhydroxybenzenes dissolve readily. Benzene dissolves readily at 20°C; the lower chloroalkanes are readily soluble; and chlorobenzene is slightly soluble. Data are lacking on the solubility of NH_3 in organic solvents under the various temperature and pressure conditions that might be used in ammonolysis.

III. SURVEY OF AMINATION REACTIONS

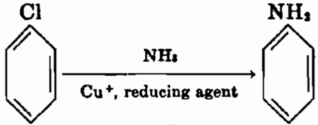
Class 1. Conversion of Halogeno Compounds

The halogen of alkyl halides is generally readily susceptible to replacement by the $—NH_2$ group, but aromatically bound halogen usually requires more drastic treatment. Because of economic considerations, the chlorine derivatives are ordinarily employed, but bromine-substituted compounds are sometimes used because they usually lead to the formation of primary amines of higher purity under milder operating conditions.

When a catalyst is essential, copper, its oxides, and salts are preferred, and these are almost always used in the ammonolysis of compounds wherein the halogen is attached to an aromatic nucleus not containing negative substituents (e.g., chlorobenzene, chlorobiphenyl (chloroxenene), and chloronaphthalene). In the treatment of alkylene, nitrophenyl, and anthraquinone halides, copper catalysts are not essential but may be used to accelerate the reaction. In the typical reactions of Class 1, presented below, it will be noted that copper in a reduced form is required for the production of aniline, because it is readily susceptible to oxidation; cupric salts and oxidants, such as chlorates and nitrobenzene, are required, however, for the preparation of aminoanthraquinone from either chloroanthraquinone or anthraquinonesulfonic acid to obviate reduction of ketonic groups.

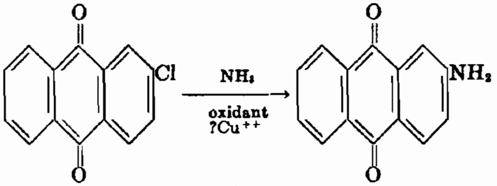
Replacement of Halogen.

1. Aniline from chlorobenzene:



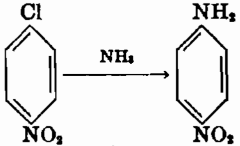
Liquid Phase
Vapor Phase

2. 2-Aminoanthraquinone from 2-chloroanthraquinone:



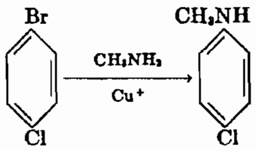
Liquid Phase

3. *p*-Nitroaniline from *p*-nitrochlorobenzene:

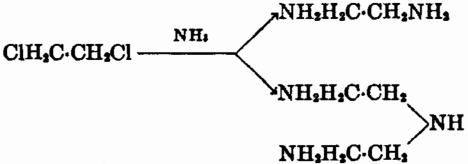


Liquid Phase

4. 4-Chloro-(N-methyl-)aniline from 4-chlorobromobenzene:



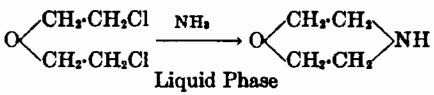
5. Ethylenediamine and diethylenetriamine from ethylene dichloride:



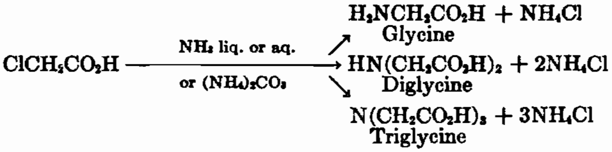
$$ClH_2C\cdot CH_2Cl \xrightarrow{NH_3} \begin{cases} NH_2H_2C\cdot CH_2NH_2 \\ \begin{matrix} NH_2H_2C\cdot CH_2 \\ NH_2H_2C\cdot CH_2 \end{matrix} \Big\rangle NH \end{cases}$$

Liquid Phase and Vapor Phase

6. Morpholine from *sym*-dichloroethyl ether.



7. Glycines from chloroacetic acid:



$$ClCH_2CO_2H \xrightarrow[\text{or } (NH_4)_2CO_3]{NH_3 \text{ liq. or aq.}} \begin{cases} H_2NCH_2CO_2H + NH_4Cl \ \text{(Glycine)} \\ HN(CH_2CO_2H)_2 + 2NH_4Cl \ \text{(Diglycine)} \\ N(CH_2CO_2H)_3 + 3NH_4Cl \ \text{(Triglycine)} \end{cases}$$

Although only 2 moles of NH_3 is required theoretically to convert a monohalogen compound to a primary amine, better yields of primary amine are obtained when a large excess of ammonia is used alone or partly as an ammonium salt of a strong acid. It is reported that when *n*-butyl chloride is aminated with a mixture of 2.16 moles of NH_3 and 10.6 moles of NH_4Cl an 81 per cent yield of *n*-butylamine is obtained.[1] In plant practice, the ratio used is governed by such factors as (1) desired purity of product, (2) yield, (3) reaction time, (4) formation of secondary and tertiary amines, and (5) expense of ammonia recovery. A German process for sarcosine (N-methylglycine) requires 15–16 moles of methylamine per mole of chloroacetic acid to produce a sodium sarcosinate solution containing about 5 parts of N-methyldiglycine per 100 parts of sarcosine.[2] Purer glycines, however, can be made from cyanohydrins plus amines (see Class 3, Conversion of Alcohols to Amines). In the manufacture of *p*-nitroaniline, about 16 moles of NH_3 per mole of *p*-nitrochlorobenzene is used in the reactor. In the production of aniline, only 5–6 moles of NH_3 is used per mole of chlorobenzene treated. Here it is necessary to use the minimum amount of ammonia since aniline manufactured by this route must compete with aniline manufactured by reducing nitrobenzene. In the two routes,

$$\text{Benzene} \xrightarrow{Cl_2} C_6H_5Cl \xrightarrow{NH_3} \text{aniline}$$

and

$$\text{Benzene} \xrightarrow{HNO_3} C_6H_5NO_2 \xrightarrow{H_2} \text{aniline}$$

the cost of introducing the nitrogen-containing group is a most important item of expense. Since nitric acid is produced economically by NH_3 oxidation, the advantage of one route over the other is dependent on which raw materials the manufacturer produces. An ammonia, nitric acid, hydrogen, and nitrobenzene producer can compete with an ammonia, chlorine, and chlorobenzene producer.

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[1] Oxley, Thomas, and Nichols, Brit. 611,593 (1948).

[2] *O.P.B. Rept.* 57925 (Office of Publications Board, U.S. Department of Commerce).

The comparative ease in replacing the bromine atom in chlorobromo compounds can be used advantageously in the preparation of chloroamines (see example 4, p. 398).

The direct replacement of both chlorine atoms from *p*- or *o*-dichlorobenzene is very difficult, and a satisfactory process has not as yet been developed. A high ammonia ratio and 40–50 per cent ammonia are desirable. The presence of cuprous copper in quantities sufficient to form an organo copper complex is helpful. The difficulty in effecting the ammonolysis of dichlorobenzenes is attributed to the establishment of an equilibrium after the formation of a monoamine and to the change in the pH of the aminating solution due to the concentration of HCl or NH_4Cl.

In the amination of aliphatic halides, it is comparatively easy to replace the halogen by the amino group. The alkyl chlorides are readily converted to the corresponding amines by treatment with aqueous ammonia under pressure. The primary, secondary, and tertiary amines thus formed can be separated by taking advantage of slight differences in their physical constants or chemical reactivity.

In contrast with dichlorobenzene, ethylenediamine can readily be obtained by reacting ethylene dichloride (1,2-dichloroethane) with either aqueous or anhydrous ammonia under pressure. Even with a large excess of ammonia, a considerable amount of secondary amine formation takes place, owing to the fact that ethylenediamine, having two unhindered primary amino groups and being much more basic than ammonia, is much more reactive than ammonia toward dichloroethane. Higher conversions to ethylenediamine are obtained with anhydrous ammonia, but under practical operating conditions ethylenediamine yields are less than 70 per cent, since a considerable portion of the dichloroethane is converted to diethylenetriamine, triethylenetetramine, and higher polyamines, including piperazine derivatives. For example, a continuous process operated in a German I.G. Farbenindustrie plant specifies an hourly feed rate of about 2,000 liters (1,325 kg at 0°C) of anhydrous NH_3 and 300 kg of dichloroethane to a series of packed columns kept at 100°C under 90 atm pressure, to produce 150 kg of distillable amines per hour.[1] In this case, where about 26 moles of NH_3 per mole of dichloroethane is employed, 80 per cent of the amines produced is ethylenediamine and the remainder is diethylenetriamine and triethylenetetramine. Based on dichloroethane the yield of ethylenediamine is 65.9 per cent. Assuming that the diethylenetriamine and triethylenetetramine are obtained in a 3:2 ratio, the combined yield of these amines is 8.8 per cent, and the over-all yield of distillable amines is 74.7 per cent. When the ethylene chloride feed is increased to 400 kg per hr, thereby lowering the ammonia: dichloroethane

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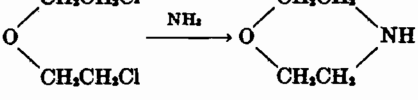
[1] *B.I.O.S. Final Rept.* 1154, Item 22 (P.B. 80,401) (British Intelligence Objectives Sub-committee).

molar ratio to 19.4:1, the distillable amines contain only about 70 per cent ethylenediamine. In this case, if the same weight yield of distillable amines is obtained, the yield of ethylenediamine falls to 57.7 per cent and the combined yield of the tri- and tetraamine, calculated on a 3:2 ratio, increases to 13.2 per cent, making the over-all yield of distillable amines about 70.9 per cent.

Fortunately, many uses have been discovered for the polyamine by-products in the manufacture of emulsifiers, ion-exchange resins, asphalt additives, corrosion inhibitors, etc., so that ethylenediamine has been manufactured for many years from dichloroethane either in an aqueous or anhydrous system. However, if the demand for ethylenediamine should greatly exceed the demand for by-product polyamines, the procedure of hydrogenating aminoacetonitrile in the presence of excess ammonia appears to have promising economic possibilities, since yields of better than 90 per cent can be obtained. (See Glycine from Cyanohydrin, p. 407, for aminoacetonitrile from CH_2O, HCN, and NH_3.) In a procedure whereby heat-unstable aminoacetonitrile is purified by subjecting its aqueous solution to a vacuum-flash distillation technique, a 92.5 per cent yield of ethylenediamine is obtained by continuously hydrogenating the freshly distilled, concentrated aqueous solution which was passed together with a large excess of ammonia over a cobalt catalyst.[1] This process has the advantage that the amine base is produced directly. The amine hydrochlorides produced from dichloroethane must be neutralized with strong alkali to obtain the free amines.

In either the hydrogenation or amination procedure, a large excess of ammonia is used to obtain optimum conversions to ethylenediamine. When only a 10:1 molar ratio of 17.5 per cent aqueous ammonia is reacted with 200 g of dichloroethane for about 1 hr at 140–150°C, the resulting amine mixture consists approximately of the products shown in Table 8-4.

When the two chlorine atoms of *sym*-dichlorodiethyl ether are replaced by the imino group through the action of anhydrous ammonia, morpholine is obtained (example 6, p. 399). The synthesis is carried out by treating *sym*-dichlorodiethyl ether dissolved in benzene with anhydrous ammonia at 50°C.[2]



When β-halogen acids are reacted with aqueous ammonia, unsaturated acids are formed, and very little amination occurs. The similar treatment

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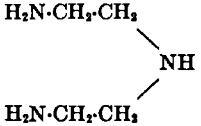
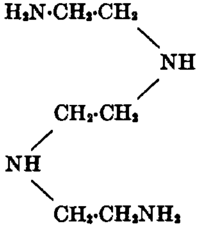
[1] Weber and Bell, U.S. 2,519,803 (1950).

[2] Campbell, U.S. 2,034,427 (1937).

TABLE 8-4. AMMONOLYSIS OF ETHYLENE DICHLORIDE WITH A 10:1 MOLAR RATIO OF 17.5 per cent NH_3 (Aqueous)

Substance	Bp, °C	Formula	%
Ethylenediamine	118	$H_2N{\cdot}CH_2{\cdot}CH_2NH_2$	40
Diethylenetriamine	208		30
Triethylenetetramine	266		20
Higher polyamines	...	...	10

of α-halogen acids leads not only to the corresponding primary amino acids but also to secondary and tertiary derivatives in spite of the use of a large excess of ammonia. To reduce secondary and tertiary amine formation below 30 per cent in the preparation of glycine an NH_3:$ClCH_2{\cdot}CO_2H$ molar ratio of 60 is necessary.

Cheronis has found that 4 moles of ammonium carbonate gives as good results as 60 moles of aqueous NH_3 in the preparation of glycine.[1] The efficacy of these two agents is compared in Fig. 8-6. The difference between conversion and ammonolysis to primary amine indicates the extent of formation of di- and triglycine and glycolic acid, $CH_2OHCOOH$. The results obtained when the secondary and tertiary amines are reintroduced in subsequent batches have not been reported. A similar void in the literature exists regarding the conditions favorable for the maximum production of the polycarboxylic acid triglycine.

The conclusions that may be drawn from reaction-rate studies in the ammonolysis of halogen fatty acids are:

1. The reaction of most bromo acids with aqueous NH_3 proceeds rapidly. Branched chains show a decrease in reactivity.

2. Ammonolysis of chloro acids, with the exception of chloroacetic, is not practical even with a 60 molar NH_3 ratio.

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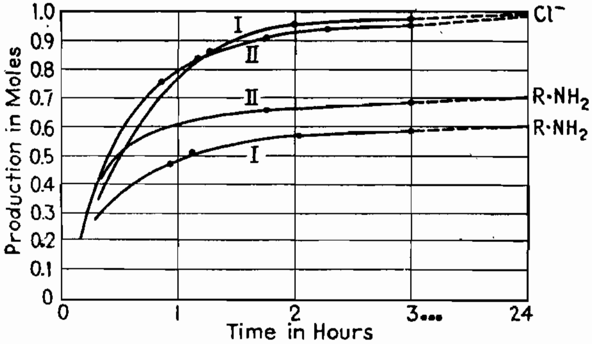
[1] CHERONIS and SPITZMUELLER, *J. Org. Chem.*, **6**, 349–375 (1941).



I Sixty moles of ammonia (aqueous) at 25°C
II Four moles of ammonium carbonate at 60°C

FIG. 8-6. Ammonolysis of 1 mole of chloroacetic acid (according to Cheronis).

3. The rate of ammonolysis is increased by raising the temperature; and as is to be expected, this results in an increase in the amounts of secondary and tertiary amino derivatives as well as hydroxy compounds.

Class 2. Replacement of —SO_3H and —OSO_3H Groups

Ammonolysis of Anthraquinonesulfonic Acids. The replacement of the —SO_3H group by —NH_2 is limited to the anthraquinone series. The amination can be carried out readily at 165°C with concentrated aqueous ammonia. Compared with the similar ammonolysis of halogenoanthraquinones, the reaction takes place at lower temperatures and purer amines can be obtained.

The need of oxidants in the ammonolysis of anthraquinonesulfonic acids has long been recognized. If it is not oxidized, the sulfurous acid that is split off gives rise to the formation of soluble reduction products. The yield of 2-aminoanthraquinone, according to the following reaction, is consequently only about 60 per cent of the theoretical:

$$C_{14}H_7O_2 \cdot SO_3H + NH_3 \rightarrow C_{14}H_7O_2 \cdot NH_2 + H_2SO_3$$

Lauer has found that inorganic oxidants have a specific value, depending on the particular anthraquinonesulfonic acid undergoing treatment as well as on the operating conditions employed.[1] Certain oxidants give rise to impurities that are not entirely removed by simple technical purification. When present even in traces, the impurities may interfere with the use of the amine in dyestuffs, this, in the final analysis, being the best criterion of purity.

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[1] LAUER, *J. prakt. Chem.*, **135**, 7 (1932).

The results obtained by Lauer in the ammonolysis of sodium anthraquinone-2-sulfonate are indicated by the curves in Fig. 8-7. When a mixture of sodium chlorate and ammonium nitrate was used as oxidants, yields of 90–94 per cent of a product of 99 per cent purity were obtained without the use of a copper catalyst.[1]

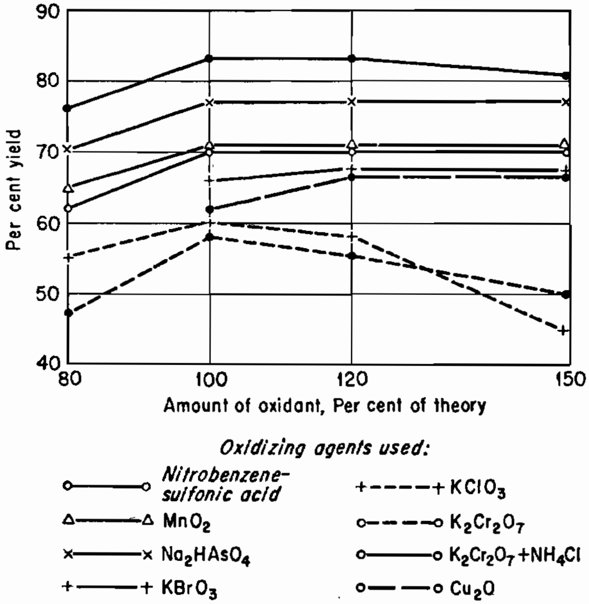

FIG. 8-7. Effect of oxidants: ammonolysis of anthraquinone-2-sulfonic acid.

Ammonolysis of Aminoalkyl Hydrogen Sulfates. Later, in discussing the replacement of —OH groups, it will be shown that, when hydroxyethanesulfonic (isethionic) acid is treated with ammonia, taurine is obtained by the preferential replacement of the hydroxyl group.

$$HOCH_2CH_2SO_3Na \xrightarrow[Na_2SO_3]{NH_3} H_2NCH_2CH_2SO_3Na$$

By contrast, the —OSO₃H groups of aminoalkyl hydrogen sulfates can readily be replaced by reaction with ammonia or amines.[2] The reaction of ethanolamine with aminoethyl hydrogen sulfate thus yields hydroxyethyl-ethylenediamine.

$$H_2NC_2H_4OSO_3H + HOC_2H_4NH_2 \xrightarrow{NaOH} H_2NC_2H_4NHC_2H_4OH$$

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[1] GROGGINS and STIRTON, unpublished research, 1935.

[2] Wilson, U.S. 2,364,178 (1944).

The simplest example of replacement of the $—OSO_3H$ group by an amino group is the preparation of ethylenediamine by the action of ammonia on aminoethyl hydrogen sulfate.

$$H_2NC_2H_4OSO_3H + NH_3 + 2NaOH \rightarrow H_2NC_2H_4NH_2 + Na_2SO_4 + 2H_2O$$

The products of reaction are not exclusively the di-primary amine but consist of the following related materials:

Products	*Yield, %*
Ethylenediamine	61.5
Diethylenetriamine	16
Tetra- and pentaethylene polyamines	9
Monoethanolamine	7
Hydroxyethyl-ethylenediamine	2
Total yield of amino compounds	95.5

It is clear that some hydrolysis occurs and an excess of mineral alkali is to be avoided. The recovered amino alcohols can, however, be converted readily to the corresponding aminoalkyl hydrogen sulfates for reuse.

When ethylenediamine replaces ammonia as the aminating agent, diethylenetriamine is the principal product.

$$H_2NC_2H_4OSO_3H + H_2NC_2H_4NH_2 \xrightarrow{NaOH} H_2NC_2H_4NHC_2H_4NH_2$$

Class 3. Conversion of Alcohols to Amines

In general, three commercially feasible methods are available for the preparation of alkylamines: (1) ammonolysis of alcohols over alumina catalysts, (2) hydroammonolysis of alcohols over hydrogenation catalysts, and (3) hydroammonolysis of aldehydes, ketones, and carboxylic acids (Class 4). The choice of reactants depends on the particular amine and plant economics. Thus, methyl and *n*-propylamines are generally derived from the corresponding alcohols, ethylamines from either ethanol or acetaldehyde,[1] while isopropylamines and butylamines are obtained by the hydroammonolysis of acetone and butyraldehyde, respectively. In each instance, a mixture of mono-, di-, and triamines is obtained. The control of production of specific amines in conformity with commercial requirements is made by a proper choice of ratio of reactants and operating conditions, the use of specific catalysts, and the recycling of undesired products. Continuous vapor-phase reactions are used for the preparation of lower alkylamines, while both liquid- and vapor-phase techniques are employed for the higher-molecular-weight amines.

Conversion of Alcohols. Practically the whole range of primary alcohols from methanol and butanol to cetyl and octadecyl alcohols has been in-

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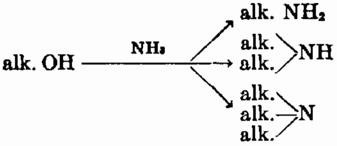
[1] *F.I.A.T. Rept.* 1081, I.G. Farbenindustrie, Ludwigshafen, practice (Field Information Agency Technical).

vestigated. The synthesis of low-molecular-weight alkylamines from alcohols is almost always carried out in the vapor phase, according to the method of Sabatier and Mailhe in which the reacting alcohol and ammonia are passed over a dehydrating catalyst at 350–500°C and under pressures of 10–150 atm.[1] Compounds of aluminum or phosphorus (e.g., alumina,[2] aluminum silicate,[3] aluminum phosphate,[4] and diammonium phosphate) are most frequently employed for this purpose. As in the amination of alkyl halides, the product of reaction may comprise primary, secondary, and tertiary amines, depending on the specific alcohol, the NH_3 ratio, and other conditions employed. The net reaction may be expressed thus:



The presence of secondary and tertiary amines is due to the concurrent reactions of the amines, as formed, with the alcohol. In commercial operations, steps are taken to obtain maximum yields of desired amines. Thus, in ammonolysis of methanol, the proportions of trimethylamine produced can be reduced by a proper choice of space velocities and temperature, or by adding water to the feed, and can be completely eliminated by recycling the trimethylamine.[5] At high operating temperatures, cracking as well as amination occurs in such vapor-phase reactions. There appears to be an optimum space velocity for any given temperature and pressure at which maximum conversions are obtained. Equilibriums are essentially independent of pressure, but pressure operation permits increased throughput capacity from a given reactor.

The amines of the high-molecular-weight fatty alcohols are best prepared in a pressure system. Cetylamine is thus obtained by conducting cetyl alcohol and ammonia through a catalytic-reaction chamber containing aluminum oxide which is kept at 380–400°C and under a pressure of 125 atm.[6] The vented vapors are condensed and yield an oily liquid containing some water. Upon distillation of the oil, cetylamine is obtained. Oleyl and stearyl alcohols react in a similar fashion. When alkylamines are employed instead of ammonia, the corresponding alkylamino compounds

[1] Sabatier and Mailhe, *Compt. rend.*, **148**, 898 (1909).

[2] Arnold, U.S. 1,799,722 (1931); Reissue 19,632 (1935); Smolenski, *Roczniki Chem.*, **1**, 232 (1921).

[3] Arnold, U.S. 1,799,722 (1931); Reissue 19,632 (1935); Martin and Swallen, U.S. 1,875,747 (1932); *F.I.A.T. Rept.* 1313, 336 (1948).

[4] Andrews, U.S. 2,073,671 (1937).

[5] Elgy and Smith, *Chem. Eng. Progr.*, **44** (5), (1948).

[6] Smeykal, U.S. 2,043,965 (1936).

are formed. Thus, monoisobutyldodecylamine is prepared from 1 part *n*-dodecyl alcohol and 10 parts monoisobutylamine.[1] It is also possible to carry out the ammonolysis of the higher fatty alcohols in the vapor phase.[2] A mixture of primary, secondary, and tertiary amines is usually obtained.

When the lower aliphatic alcohols are treated with ammonia in the vapor phase in the presence of a *hydrogenation* catalyst, nitriles are obtained as the principal product. Upon hydrogenation, these yield the corresponding amines, thus:

$$\text{alk. } CH_2OH + NH_3 \xrightarrow[\text{catalyst}]{\text{Ni}} \text{alk. } CN \xrightarrow[\text{Ni catalyst}]{H_2} \text{alk. } CH_2NH_2$$

Alkylamines, such as butylamines, can be obtained by direct catalytic amination if the amination reaction is carried out in the presence of a fairly large excess of hydrogen. With specific nickel- , copper- , and cobalt-based catalysts which promote hydrogenation and dehydrogenation reactions, yields and conversions per pass of better than 95 per cent are obtained. See Sec. V for more detailed information on this procedure.

Glycine from Cyanohydrin. As previously stated, it is not possible to aminate chloroacetic acid without obtaining a mixture of primary and secondary amines. However, amination of cyanohydrin with about 5 moles of anhydrous ammonia, followed by alkaline hydrolysis of the nitrile group, gives a practically quantitative yield of glycine.[3]

$$HO{\cdot}CH_2{\cdot}CN + NH_3 \rightarrow H_2N{\cdot}CH_2{\cdot}CN + H_2O \qquad (1)$$

$$H_2N{\cdot}CH_2{\cdot}CN + Ba(OH)_2 + 2H_2O \rightarrow (H_2N{\cdot}CH_2{\cdot}CO_2)_2Ba + 2NH_3 \qquad (2)$$

$$(H_2N{\cdot}CH_2{\cdot}CO)_2Ba + CO_2 + H_2O \rightarrow 2H_2NCH_2{\cdot}CO_2H + BaCO_3 \qquad (3)$$

Note that the above scheme gives the free acid of glycine uncontaminated with inorganic chlorides. The I.G. Farbenindustrie process for producing pharmaceutical-grade glycine on a small scale calls for the gradual addition, over a period of about 4 hr, of 20 kg of 85 per cent cyanohydrin to 40 liters of anhydrous ammonia charged into a water-cooled iron autoclave. The pressure slowly rises to 10 to 12 kg per sq cm (about 140–170 psi) while cooling continually with water. The cyanohydrin was made by the slow addition of HCN to aqueous formaldehyde at 20–30°C followed by continuously stripping-out water under reduced pressure to obtain cyanohydrin concentrated to 85 per cent. The reaction mass from the autoclave was slowly added to hot $Ba(OH)_2$ suspension in a stainless-steel vessel [Eq. (2)], CO_2 was added to the barium salt solution [Eq. (3)], and the $BaCO_3$ was filtered from the glycine solution. After concentration of the solution, the product was crystallized out, filtered off, and purified by crystallizing from a carbon-treated clarified solution. The filtrates were recycled.

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[1] Smeykal, U.S. 2,043,965 (1936).

[2] Arnold, U.S. 2,078,922 (1937).

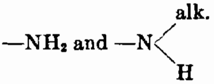
[3] *O.P.B. Rept.* 35,193.

Based on cyanohydrin, a yield of about 99 per cent of the theoretical quantity of dry pharmaceutical-grade glycine is claimed.

Taurine from Hydroxyethanesulfonic Acid (Isethionic Acid).

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3Na \xrightarrow[Na_2SO_3]{NH_3} H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3Na$$

Taurine and some ditaurine can be obtained by reacting 256 parts by weight of sodium hydroxyethanesulfonate with 800 parts of 25 per cent ammonia liquor at 210°C for 3 hr. The addition of 10 parts of sodium sulfite aids materially in increasing the conversion, which falls off as the quantity of sodium sulfite is reduced. The synthesis is of particular interest, because it shows that, in aliphatic compounds containing both sulfonic and hydroxyl groups, the —OH group can be replaced preferentially by



$$—NH_2 \text{ and } —N\begin{matrix}\diagup \text{alk.}\\ \diagdown H\end{matrix}$$

Class 4. Conversion of Carbonyl Compounds: Hydroammonolysis

The conversion of aldehydes, ketones, and carboxylic acids to amines by the action of ammonia or amines is carried out in the presence of hydrogen and a hydrogenation catalyst. The reactions involving the lower aliphatic aldehydes usually take place in the vapor phase, whereas the treatment of the high-boiling aldehydes, aldose sugars, or ketones is generally effected in the liquid phase. In liquid-phase reactions, better results are generally obtained if hydroammonolysis is carried out under pressure in the presence of an alcohol as a diluent or solvent. Anhydrous ammonia, either as a liquid or gas, is the preferred aminating agent, although concentrated aqueous ammonia can be satisfactorily employed in some of the liquid-phase reactions.

It will be recalled that, in the ammonolysis of alcohols, the substitution of a nickel catalyst for alumina results in the appreciable formation of nitriles. Similarly, by an appropriate choice of catalysts, nitriles can be obtained by the ammonolysis of aldehydes:

$$CH_3CH_2{\cdot}CHO + NH_3 \xrightarrow[300\text{–}350°C]{Cu\text{–}Zn} CH_3CH_2CN + H_2O + H_2$$

Gresham[1] has found that cobalt or copper and zinc are specific catalysts for the preparation of nitriles by reacting aldehydes and ammonia. The yields are about 75 per cent, the chief by-product being 2-ethyl-3,-5-dimethylpyridine.

Conversion of Aldehydes. The lower alkylamines are obtained by the vapor-phase hydroammonolysis of aldehydes and ketones under a pressure

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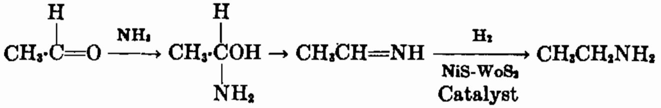
[1] Gresham, U.S. 2,443,420; 2,452,187 (1948).

of 200 atm, at approximately 320°C, on a nickel sulfide–tungsten sulfide catalyst and of fatty acids under the same conditions, using a catalyst comprising the sulfides of nickel, tungsten, and molybdenum. A typical reaction—ethylamine from acetaldehyde—is shown below.



$$CH_3{\cdot}\overset{H}{C}{=}O \xrightarrow{NH_3} CH_3{\cdot}\underset{NH_2}{\overset{H}{C}}OH \rightarrow CH_3CH{=}NH \xrightarrow[\substack{\text{NiS-WoS}_2\\ \text{Catalyst}}]{H_2} CH_3CH_2NH_2$$

Large excesses of both ammonia and hydrogen are required for such reactions, and the excess of these reactants is recovered separately and recycled. The two recycle lines are, however, combined before entering the preheater and reaction chamber where the mixture reacts with preheated carbonyl compound which is injected separately by means of a pressure pump (Fig. 8-25, p. 477).

When unsaturated aliphatic aldehydes such as acrolein are treated, saturation as well as hydroamination occurs, and a normal primary amine is obtained. The general procedure is similar to that for saturated aldehydes,[1] but lower temperatures, 125–150°C, have been found satisfactory. The hydroammonolysis of acrolein and crotonaldehyde may be represented as follows:

$$\underset{\text{Acrolein}}{CH_2{:}CH{\cdot}CHO} \xrightarrow[\text{hydrogenation catalyst}]{NH_3 + H_2} \underset{n\text{-Propylamine}}{CH_3{\cdot}CH_2{\cdot}CH_2NH_2}$$

$$\underset{\text{Crotonaldehyde}}{CH_3{\cdot}CH{:}CH{\cdot}CHO} \xrightarrow[\text{hydrogenation catalyst}]{NH_3 + H_2} \underset{n\text{-Butylamine}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2NH_2}$$

In the liquid phase, propionaldehyde is converted to propylamine in 81 per cent yields by adding, at subzero temperatures prior to hydrogenation, 1.9 moles of NH_3 to a methyl alcoholic solution of the aldehyde. At the low temperature employed, undesired aldol formation is minimized. Hydrogenation in the presence of a nickel catalyst from the low temperature up to a final temperature of 130°C and under about 97 atm pressure completes the reaction.[2]

Under similar conditions, propionaldehyde and propylamine in a molar ratio of 1.17:1 gives a 90 per cent yield of dipropylamine from propylamine.

$$CH_3CH_2CH_2NH_2 + CH_3CH_2CHO \xrightarrow{H_2} (CH_3CH_2CH_2)_2NH + H_2O$$

Conversion of Ketones. The hydroammonolysis of ketones to amines can be carried out in either the vapor or the liquid phase. The technique employed depends on the physical and chemical properties of the reactants and final products.

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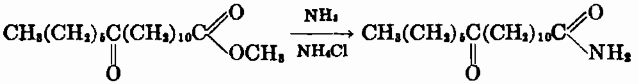
[1] Kautter, U.S. 2,051,486 (1936).

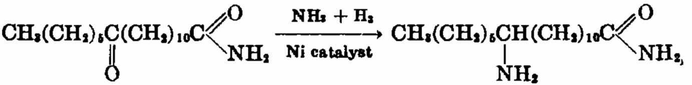
[2] Noeske and Kolling, Ger. 936,211 (1955).

Acetone is readily converted to isopropylamines in the vapor phase under conditions that apply for the lower (C_2–C_6) aldehydes. The preparation of 2-aminobutane from methylethyl ketone (butanone-2) is satisfactorily carried out in the liquid phase, preferably in the presence of butanol-2 since the latter can also be converted to amine by ammonolysis.[1] The intranuclear ketone cyclohexanone can be converted to cyclohexylamine by hydroammonolysis in the vapor phase.[2] The preparation of 12-aminostearamide from the corresponding keto acid is, however, best carried out in the liquid phase. The pertinent reactions are:



$$CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}C\begin{smallmatrix}\nearrow O\\ \searrow OCH_3\end{smallmatrix}\xrightarrow[NH_4Cl]{NH_3}CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}C\begin{smallmatrix}\nearrow O\\ \searrow NH_2\end{smallmatrix}$$

12-Ketostearamide



$$CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}C\begin{smallmatrix}\nearrow O\\ \searrow NH_2\end{smallmatrix}\xrightarrow[\text{Ni catalyst}]{NH_3\,+\,H_2}CH_3(CH_2)_5\underset{\overset{|}{NH_2}}{CH}(CH_2)_{10}C\begin{smallmatrix}\nearrow O\\ \searrow NH_2,\end{smallmatrix}$$

12-Aminostearamide

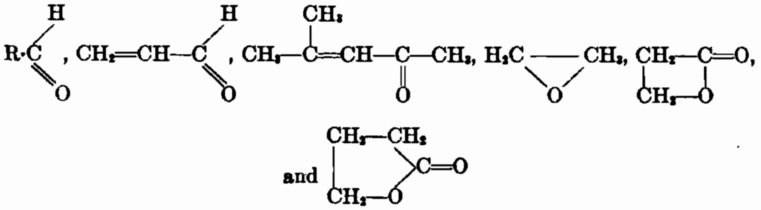
The ketostearins are converted to ketostearamides when treated with anhydrous ammonia and small amounts of ammonium chloride. When the amination takes place in the presence of hydrogen and a nickel catalyst, the keto acids and keto amides are converted to the corresponding amino compounds. In the treatment of the keto acids, it is desirable to add sufficient alkali and water to form the alkali soap.

Saturated fatty acids on hydroammonolysis in the presence of a catalyst comprising sulfides of nickel, tungsten, and molybdenum are converted directly to the corresponding amines.

Class 5. Addition Reactions

As would be expected, the formation of amines by addition reactions is confined to highly reactive compounds, such as

$R{\cdot}N{=}C{=}O$, $R{\cdot}N{=}C{=}S$, $R{\cdot}N{=}C{=}N{\cdot}R$, $CH{=}CH{\cdot}C{\equiv}N$, $H_2N{\cdot}C{\equiv}N$, $CH{\equiv}CH$,



Frequently, the primary addition compound is so unstable or reactive that secondary reactions occur before a stable amine is obtained. In some in-

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[1] Olin, U.S. 2,278,372; 2,278,373; 2,365,721 (1944).

[2] Kautter, U.S. 2,051,486 (1936).

stances, as in the amination of cyanamide to form guanidine, it is necessary to add an ammonium salt to inhibit further reaction.

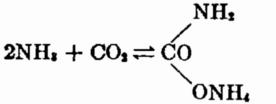
Unsaturated diamines are formed when alkylamines are reacted with acrolein. For example, when excess isopropylamine is reacted with acrolein at 5–10°C in the presence of K_2CO_3, a new compound, N,N′-diisopropyl-1,3-propenediamine is produced as shown below.[1]

$$2(CH_3)_2CH{\cdot}NH_2 + CH_2{=}CH{\cdot}CHO \rightarrow (CH_3)_2CHNH{\cdot}CH_2CH{=}CH{\cdot}NHCH(CH_3)_2 + H_2O$$

This compound can be hydrogenated to the saturated compound N,N′-diisopropyl-1,3-propylenediamine.[2]

Synthesis of Urea from CO_2. Although urea was the first of the organic compounds to be formed synthetically, its commercial production had to await the development of the synthetic ammonia process. Here the principal product, NH_3, and a by-product, CO_2, which constitute the raw materials for urea production, are prepared cheaply.

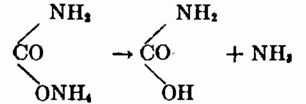
The reactions involved in the formation of urea from carbon dioxide and ammonia are as follows:



$$2NH_3 + CO_2 \rightleftharpoons CO\begin{matrix}\diagup NH_2\\ \diagdown ONH_4\end{matrix}$$

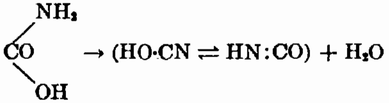
Ammonium
Carbamate

At elevated temperatures, urea is formed from ammonium carbamate by a series of reactions:



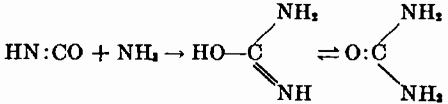
$$CO\begin{matrix}\diagup NH_2\\ \diagdown ONH_4\end{matrix} \rightarrow CO\begin{matrix}\diagup NH_2\\ \diagdown OH\end{matrix} + NH_3 \qquad (1)$$

Ammonium Carbamate — Carbamic Acid



$$CO\begin{matrix}\diagup NH_2\\ \diagdown OH\end{matrix} \rightarrow (HO{\cdot}CN \rightleftharpoons HN{:}CO) + H_2O \qquad (2)$$

Cyanic Acid
(Enol form) (Keto form)



$$HN{:}CO + NH_3 \rightarrow HO{-}C\begin{matrix}\diagup NH_2\\ \diagdown\!\!\diagdown NH\end{matrix} \rightleftharpoons O{:}C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$$

Cyanic Acid — Urea (Solution) — Urea (Crystalline)[3]

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[1] Finch and Peterson, U.S. 2,565,488 (1951).

[2] Finch and Ballard, U.S. 2,540,938 (1951).

[3] HENDRICKS, *J. Am. Chem. Soc.*, **52**, 3088 (1930).

Although the transformation of ammonium carbamate to urea is not a direct dehydration, the presence of water is, however, a limiting factor with respect to the extent that the reaction occurs. It has been found that at any temperature a definite equilibrium is established that can be approached from either direction.[1] Krase and Gaddy have shown that a real shift in the carbamate-urea-water equilibrium is obtained by employing an excess of anhydrous ammonia, which functions as a strong dehydration agent.[2] The employment of ammonia, up to 280 per cent of that combined as carbamate, gives conversions to urea between 81 and 85 per cent of the carbamate ammonia. These results are shown in the curve of Fig. 8-8.

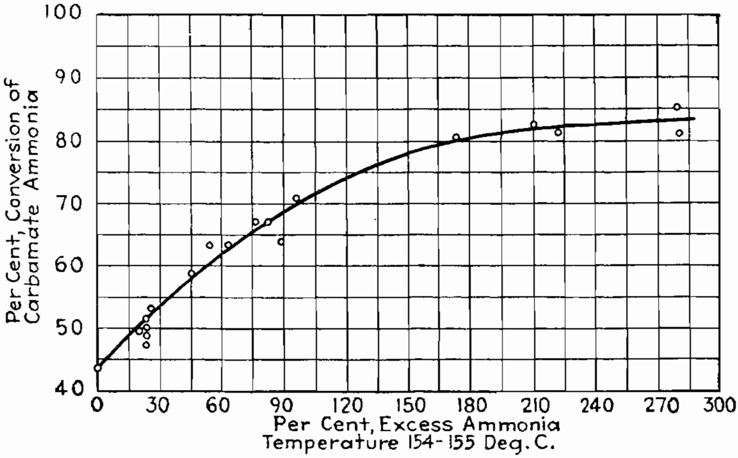

FIG. 8-8. Effect of NH_3 ratio on urea formation.

Synthesis of Dithiocarbamates from CS_2. The addition of ammonia or alkylamines to CS_2 to form the amine salts of dithiocarbamic acids is analogous to their addition to CO_2 to form the corresponding carbamate salts.

$$2NH_3 + CS_2 \rightarrow \underset{\text{Ammonium Dithiocarbamate}}{H_2N\cdot CS\cdot SNH_4}$$

However, free dithiocarbamic acid, $NH_2\cdot CS\cdot SH$, can be made and isolated by acidifying the ammonium salt in the cold, whereas free carbamic acid, $NH_2\cdot CO\cdot OH$, does not exist. Although thiocarbamic acid is not very stable, its ammonium salt is somewhat more stable and can be synthesized in high yields at atmospheric pressure. When ammonia is passed into a cold solution of CS_2 in a solvent in which the ammonium dithiocarbamate

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[1] CLARK, GADDY, and RIST, *Ind. Eng. Chem.*, **25**, 1092 (1933).

[2] KRASE and GADDY, *J. Am. Chem. Soc.*, **52**, 3088 (1930).

is practically insoluble, the product can be obtained in high yields. For example, when methylisobutyl ketone is used as the solvent, a 96.5 per cent yield of ammonium dithiocarbamate is obtained.[1] The stability of the dithiocarbamates versus the carbamates is shown by the fact that sodium salts of N-dialkyldithiocarbamates can be made in aqueous solution, whereas under similar conditions, carbonates are formed from CO_2 and dialkylamines.

$$(CH_3)_2NH + CS_2 + NaOH \rightarrow NaS{\cdot}CS{\cdot}N(CH_3)_2 + H_2O$$
$$(CH_3)_2NH + CO_2 + NaOH \rightarrow NaO{\cdot}CO{\cdot}ONH_2(CH_3)_2$$

The alkyl and dialkyldithiocarbamates are important commercially. Some of their heavy metal salts, produced by metathesis from the sodium or ammonium salt solution, are used as accelerators for the vulcanization of rubber (e.g., the zinc salt).

$$2(C_2H_5)_2N{\cdot}CS{\cdot}SNa + ZnCl_2 \rightarrow [(C_2H_5)_2N{\cdot}CS{\cdot}S\text{—}]_2Zn + 2NaCl$$

Amine salts, such as those produced from butylamine or piperidine, are also used. A much-used accelerator is bis(dimethylthiocarbamoyl)disulfide (tetramethylthiuramdisulfide), made by the oxidation of the corresponding dithiocarbamate with chlorine or hydrogen peroxide.[2]

$$2(CH_3)_2N{\cdot}CS{\cdot}SNa + H_2O_2 + 2HAc \rightarrow [(CH_3)_2N{\cdot}CS{\cdot}S\text{—}]_2 + 2NaAc + 2H_2O$$

Some sodium, iron, zinc, and manganese dithiocarbamate salts are powerful fungicides used to control potato and tomato blights, bean rust, etc. The most potent of these fungicides are the salts of ethylenebis (dithiocarbamic acid), produced from ethylenediamine and CS_2. The sodium salt is water-soluble and less stable than the insoluble heavy metal salts. The salts are readily synthesized in an aqueous medium. For example, the manganous salt (Manzate) is obtained by gradually adding 2.07 moles of CS_2 to a well-stirred aqueous solution containing 1.00 mole of ethylenediamine and 2.1 moles of NaOH, kept at 25–35°C. The alkaline disodium salt solution is made neutral to phenolphthalein indicator with acetic acid, and an aqueous solution of 0.95 mole of $MnCl_2$ is added to precipitate the insoluble manganous salt, $Mn(\text{—}S{\cdot}SC{\cdot}NH{\cdot}CH_2CH_2{\cdot}NH{\cdot}CS{\cdot}S\text{—})$.[3]

Conversion of Alkylene Oxides to Alkanolamines. The alkylene oxides, (e.g., ethylene,[4] isopropylene,[5] and isobutylene[5] oxides) can readily be converted to alkanolamines.

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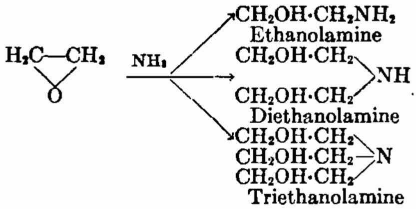
[1] Mathes, U.S. 2,123,370 (1938).

[2] For rubber-accelerator manufacturing processes, see *F.I.A.T. Final Rept.* 1018, P.B. 78,997.

[3] Flenner, U.S. 2,504,404 (1950).

[4] Kautter, U.S. 2,051,486 (1936).

[5] Wickert, U.S. 1,988,225 (1935).



These reactions are exothermic, and an operating temperature of 50–60°C usually suffices. When ordinary 28 per cent aqueous ammonia is employed, primary, secondary, and tertiary amines are obtained, the proportions being dependent on the NH_3 ratio (Fig. 8-9).

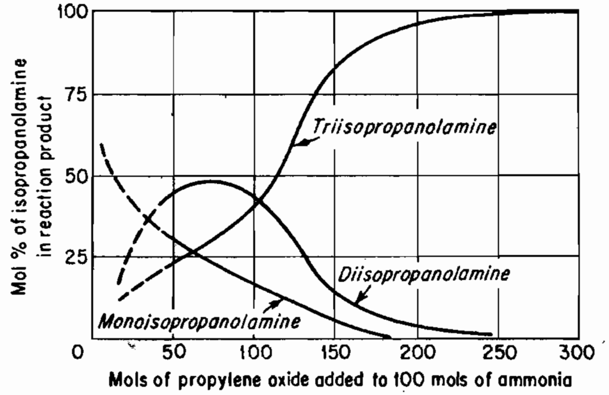


FIG. 8-9. Preparation of isopropanolamines: influence of NH_3 ratio.

Ferrero et al.[1] have found that the rate of reaction of ethylene oxide with primary and secondary amines is greater than with ammonia; consequently a large excess of ammonia is required if primary and secondary ethanolamines are desired. The reaction of ethylene oxide and ammonia follows a second-order reaction. With the addition of known amounts of primary and secondary ethanolamines to the reactants, the equilibrium is shifted to exclude further formation of the added amine. This effect, as well as the effect of ammonia:ethylene oxide molar ratio, is shown in Table 8-5.

In industrial practice, emphasis is usually placed on the production of triethanolamine because of its more numerous commercial applications. It is not feasible, however, to react 1 mole of ammonia with 3 moles of ethylene oxide, because the latter reacts with the —OH group of triethanolamine as formed, resulting in amino ethers of no commercial value. It is consequently necessary to increase the NH_3 ratio to give about 5 per cent primary and 10 per cent secondary amine. By the addition of CO_2

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[1] FERRERO, BERBE, and FLAMME, *Bull. soc. chim. Belges*, **56**, 349 (1947).

TABLE 8-5. ADDITION OF PRIMARY AND SECONDARY ETHANOLAMINES TO AN AMMONIA-ETHYLENE OXIDE SYSTEM

NH_3:ethylene oxide molar ratio	Mole of secondary ethanolamine added/mole of ethylene oxide	Product	
		% primary	% tertiary
3:1	0.18	30	70
5:1	0.23	40	60
10:1	0.33	55	45
15:1	0.43	65	35

	Moles of primary ethanolamine added/mole of ethylene oxide	Product	
		% secondary	% tertiary
3:1	0.39	40	60
5:1	0.65	60	40
10:1	1.31	75	25

(1:12 moles ethylene oxide) the formation of triamine ether is suppressed. The effect of CO_2 on the reaction of 1 mole ammonia with 1.8 moles ethylene oxide is shown in the accompanying table.

	With CO_2, %	Without CO_2, %
Monoethanolamine	0	0
Diethanolamine	5.5	5.1
Triethanolamine	92.5	73.5
Triethanolamine ether	0.3	19.6
Residue	1.7	1.8

The reaction product from CO_2 treatment on single distillation gives triethanolamine of 89.8 per cent purity. Without CO_2, the purity is only 39 per cent.[1]

The proportions of the various isopropanolamines formed as functions of NH_3:propylene oxide ratio are shown graphically in Fig. 8-9.

β-Alanine from Acrylonitrile. The amino group cannot be added directly to alkenes or doubly bound carbon atoms of fatty acids, such as oleic acid, by the action of ammonia. Such compounds must first be converted to halides or other derivatives susceptible to ammonolysis. When, however,

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[1] *F.I.A.T. Final Rept.* 845.

the double bond is conjugated with a C≡N group, addition of ammonia as well as primary and secondary amines occurs readily.[1]

Acrylonitrile can thus be converted to aminopropionitrile, which on hydrolysis with aqueous ammonia at 200°C yields β-alanine, an important intermediate in the preparation of pantothenic acid.[2]

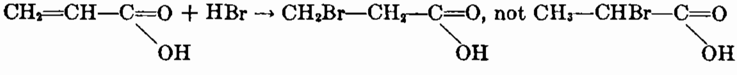
$$CH_2{=}CHC{\equiv}CN + NH_3\ \text{aq.} \rightarrow H_2NCH_2CH_2CN \xrightarrow{NH_3\ \text{aq.}} H_2NCH_2CH_2COOH$$

It should be noted that complicating side reactions can occur. Thus, the initial reaction product, β-aminopropionitrile, can add to another molecule of acrylonitrile to yield the corresponding secondary amine which can react again to produce a tertiary amine.

$$NH_3 + CH_2{=}CHC{\equiv}N \begin{array}{l} \nearrow H_2NCH_2CH_2CN \\ \rightarrow HN(CH_2CH_2CN)_2 \\ \searrow N(CH_2CH_2CN)_3 \end{array}$$

Reaction conditions must be adjusted critically to obtain optimum yields of the mono-addition product. In this connection, the reaction of secondary amines with acrylonitrile is less sensitive, inasmuch as only one addition product is possible. There is as yet no direct evidence of the mechanism of addition of bases to such conjugated unsaturated systems. It is known that unsaturated ketones $\left(\overset{4}{C}{=}\overset{3}{C}{-}\overset{2}{C}{=}\overset{1}{O}\right)$ in general undergo 1-2, 3-4, and 1-4 additions. The product of addition, however, is not always determined by the relative rates of two competing reactions.[3] In fact, it seems probable—particularly in the reaction under consideration—that the relative stability of the products resulting from competing reactions is of major importance. The highly polar C=O or C≡N group would be expected to confer electrophylic (i.e., electron-accepting) character on the olefin carbon atom 4 by electromeric relay, as follows:[4] $\overset{4}{C}H_2{=}\overset{3}{C}H\cdot\overset{2}{C}{\equiv}\overset{1}{N}$.

The effect of conjugation of a C=C with a C=O or C≡N bond would be to permit the formation of addition products that would not be expected from Markownikoff's rule, as is evidenced by the following reactions:[5]



$$CH_2{=}CH{-}C(OH){=}O + HBr \rightarrow CH_2Br{-}CH_2{-}C(OH){=}O,\ \text{not}\ CH_3{-}CHBr{-}C(OH){=}O$$

$$CH_2{=}CH{-}C{\equiv}N + H{\cdot}NH_2 \rightarrow H_2NCH_2{-}CH_2{-}C{\equiv}N,\ \text{not}\ CH_3{-}CHNH_2{-}C{=}N$$

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[1] "Organic Reactions," vol. 5, pp. 82–87, John Wiley & Sons, Inc., New York, 1949.

[2] Carlson and Hotchkiss, U.S. 2,377,401 (1945).

[3] Cromwell, *Chem. Revs.*, **38**, 83–137 (1946).

[4] Remick, "Electronic Interpretation of Organic Chemistry," p. 123, John Wiley & Sons, Inc., New York, 1943.

[5] Branch and Calvin, "The Theory of Organic Chemistry," p. 469, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1941.

According to Cromwell, it appears logical that the driving force for the addition of $H \cdot NH_2$ to acrylonitrile is the attraction of the electrophylic carbon atom 4 for the unshared electrons of the ammonia nitrogen.[1] It is consequently reasonable to presume that the formation of aminopropionitrile as an intermediate compound in the synthesis of β-alanine is due to the direct attack of the unshared electrons of $:NH_3$ at the electron-deficient carbon atom 4.[2]

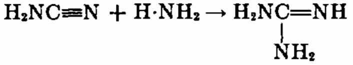
A similar addition reaction occurs when an acrylic acid ester, such as methyl acrylate, is treated under pressure with aqueous ammonia.[3] Ammonolysis and hydrolysis occur, and β-alanine is formed.

$$CH_2{=}CHCOOCH_3 \xrightarrow{NH_3\text{ aq.}} H_2NCH_2CH_2COOH$$

Whether the intermediate product is acrylic acid or acrylamide has not been reported.

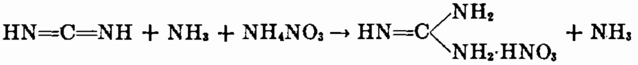
From the available information, it appears that the yields of β-alanine from methyl acrylate are considerably greater than those resulting from the ammonolysis of either cyanohydrin or acrylonitrile.

Guanidine from Cyanamide. Ammonia adds to cyanamide to form guanidine. It is presumed that addition occurs at the $—C{\equiv}N$ group with the formation of the amidine.



$$H_2NC{\equiv}N + H \cdot NH_2 \rightarrow H_2N\underset{\displaystyle NH_2}{\underset{|}{C}}{=}NH$$

In practice, the ammonolysis is carried out in the presence of ammonium salts—preferably ammonium nitrate—and the comparatively stable guanidine nitrate is formed. Such a technique is employed to prevent the relatively active guanidine from combining with unreacted cyanamide to form melamine. The reaction is carried out by heating calcium cyanamide,[4] cyanamide, or dicyandiamide with ammonia and ammonium nitrate for 2 hr at 160°C under autogenic pressure. During the course of the reaction, dicyandiamide is formed from cyanamide in the presence of ammonia and, in all probability, is the primary product. The monomeric reaction is



$$HN{=}C{=}NH + NH_3 + NH_4NO_3 \rightarrow HN{=}C\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \cdot HNO_3 \end{matrix} + NH_3$$

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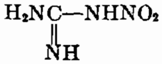
[1] CROMWELL, University of Nebraska, private communication.

[2] The mechanism of the formation of β-alanine from other types of nitriles may be explained in fundamentally the same manner. $R—O—CH_2—CH_2—C{\equiv}N \rightarrow R—O—H + H_2N—CH_2—CH_2—C{\equiv}N$, where R represents H, alkyl, or $—CH_2—CH_2—CN$.

[3] Babcock and Baker, U.S. 2,376,334 (1945).

[4] *B.I.O.S. Final Rept.* 1720, Item 22. Here CO_2 must be introduced to precipitate calcium carbonate, which is subsequently removed from the water-soluble guanidine nitrate.

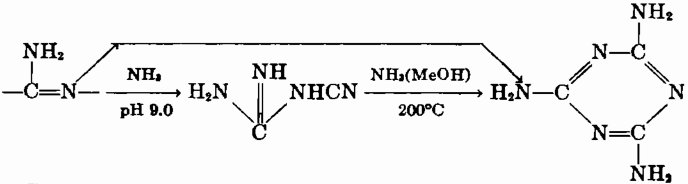
Upon removal of the elements of water with concentrated sulfuric acid, the important military and industrial explosive nitroguanidine



$$H_2N\underset{\underset{NH}{\|}}{C}{-}NHNO_2$$

is obtained.

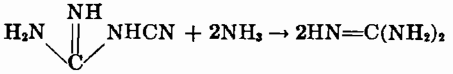
Dicyandiamide and Melamine from Cyanamide. Cyanamide solutions are stable when slightly acid and are polymerized when slightly alkaline. Thus, when cyanamide or dicyandiamide is heated in the presence of liquid ammonia, the triazine melamine is formed.



Cyanamide Dicyandiamide Melamine

It is believed that part of the cyanamide or dicyanamide first reacts with ammonia to form guanidine according to the following equations:[1]

$$H_2N\overset{+}{C}{\equiv}\overset{-}{N} + \overset{+}{H}{\cdot}\overset{-}{N}H_2 \rightarrow HN{=}C(NH_2)_2 \qquad (1)$$



$$H_2N\overset{NH}{\overset{\|}{C}}NHCN + 2NH_3 \rightarrow 2HN{=}C(NH_2)_2 \qquad (2)$$

The relatively reactive guanidine combines with unreacted starting material to form melamine with the regeneration of ammonia.

$$HN{=}C(NH_2)_2 + 2H_2NC{\equiv}N \rightarrow (H_2NCN)_3 + NH_3 \qquad (3)$$

$$HN{=}C(NH_2)_2 + (H_2NC{\equiv}N)_2 \rightarrow (H_2NCN)_3 + NH_3 \qquad (4)$$

To obviate such polymerizing reactions, it is necessary to introduce the nitrate or other acidic radicals as a coreactant. The initially formed guanidine is consequently bound as a stable salt which is no longer free to combine with further amounts of cyanamide.

The efficient conversion of cyanamide to the dimer depends on the control of the pH and the use of relatively concentrated solutions. The effect of hydrogen-ion concentration on the formation of dicyandiamide has been studied by numerous investigators, and it is generally agreed that the pH should be between 8.6 and 9.9.[2] The maximum reaction rate appears to be at pH 9.2 at 82°C and slightly higher at lower temperatures.

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[1] Hill, Swain, and Paden, U.S. 2,252,400 (1941).

[2] COCHET, *Congr. des engrais azotes de synthese*, May, 1927; BUCHANAN and BARSKY, *J. Am. Chem. Soc.*, **52**, 195 (1930); BARSKY, *News Ed. Am. Chem. Soc.*, **18**, 759 (1940); PINCK and HETHERINGTON, *Ind. Eng. Chem.*, **27**, 834 (1935); BAUGHEN, *Can. Chem. Process Ind.*, **28**, 805 (1944).

Numerous side reactions are possible and do occur, even under closely controlled conditions. Some of the impurities that are present after polymerization are urea, guanidine, melamine, ammeline, and ammelide. The total combined amount of these substances after a single polymerization is not great; but in continuous operations where mother liquors from the crystallization of dicyandiamide are recirculated for further extraction of cyanamide, there is a steady increase in the concentration of such by-products. It is necessary, therefore, to discard some of the mother liquor regularly in order to avoid contamination of the dicyandiamide and to obviate operating difficulties.

Pinck and Hetherington showed that the maximum conversion of cyanamide to dicyandiamide is obtained when the starting solution contains at least 20 per cent cyanamide and 2 per cent ammonia (Table 8-6).[1] Cyanamide is quantitatively polymerized to the dimer in liquid ammonia solution upon spontaneous evaporation of the solvent. The use of ammonia is, however, not essential inasmuch as cyanamide polymerizes readily in alkaline solution; and in commercial practice, the batch is "set" at the optimum pH (viz., about 9.2 at 180°C).

TABLE 8-6. POLYMERIZATION OF CYANAMIDE SOLUTIONS WITH VARYING CONCENTRATIONS OF CYANAMIDE AND AMMONIA

Conc. of initial solution			Analysis of product			
Expt.	Cyanamide, %	NH_3, %	Total N, g	Ammonia N, g	Dicyandiamide N, g	Conversion, %
1	38.0	0.6	1.446	0.001	0.766	53.0
2	38.0	2.4	1.924	0.004	1.228	95.2
3	38.0	4.5	1.252	0.009	1.195	96.2
4	21.7	0.6	0.734	0.001	0.381	51.9
5	21.7	2.4	0.708	0.003	0.680	96.6
6	21.7	4.5	0.700	0.004	0.671	96.5
7	10.0	0.6	0.351	0.003	0.039	10.8
8	10.0	2.4	0.365	0.004	0.110	30.6
9	10.0	4.5	0.395	0.006	0.204	52.3*

* Cyanamide nitrogen, 0.182 g, or 46.8 per cent.

Crystalline cyanamide (mp, 42°C), when heated to 150°C, polymerizes with explosive violence to melamine or 2,4,6-triamino-1,3,5-triazine. In practice, the trimer is obtained from the dimer, dicyandiamide, by heating with ammonia. Scholl and Davis obtained melamine as the principal product by heating dicyandiamide with 2 parts of liquid ammonia at

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[1] PINCK and HETHERINGTON, *loc. cit.*

155°C for 2 hr.[1] Subsequent research showed that economies in the use of ammonia could be realized by carrying out the reaction at higher temperatures[2] (380°C) or in the presence of a solvent such as methanol[3] or butanols.[4] When ammonium chloride is used instead of ammonia, the product contains guanidine hydrochloride in addition to melamine, the quantity of guanidine salt being approximately proportional to the molar ratio of ammonium chloride to cyanamide. The ammonia liberated during the guanidine synthesis serves to catalyze the polymerization reaction.

Class 6. Reaction of Ammonia with Hydrocarbons

Ammonia reacts catalytically with alkyl or alkanyl side chains on aromatic hydrocarbons to form aromatic nitriles, or with olefins, and to some extent alkanes, to form aliphatic nitriles.[5] It also reacts catalytically with methane (natural gas) in the presence of a regulated amount of oxygen to form hydrogen cyanide.[6] The following equations illustrate the reactions involved with substituted aromatic compounds:

$$C_6H_5CH_3 + NH_3 \xrightarrow[\text{catalyst}]{524\text{–}552°C} C_6H_5{\cdot}CN + 3H_2$$

$$C_6H_5{\cdot}CH{=\!=}CH_2 + NH_3 \xrightarrow[\text{catalyst}]{480\text{–}600°C} C_6H_5{\cdot}CN + CH_4 + H_2$$

$$C_6H_5{\cdot}C_2H_5 + NH_3 \xrightarrow[\text{catalyst}]{480\text{–}600°C} C_6H_5{\cdot}CN + CH_4 + 2H_2$$

Denton et al. describe a procedure for aminating alkyl aromatic hydrocarbons, particularly toluene, which is converted to benzonitrile. Toluene and ammonia, at various reactant ratios and liquid space velocities, are passed at atmospheric pressure over a supported molybdenum trioxide catalyst at about 525–550°C. The conversion per pass is 5–10 per cent, and the yields are 60–85 per cent based on the toluene consumed. The process, as operated commercially, involves the continuous feed of toluene and NH_3 to one of two reactors followed by continuous removal of ammonia and toluene, for recycle, from the benzonitrile. Catalyst in one reactor is regenerated over a 3–6 hr period by oxidizing carbon deposits with air diluted with an inert gas, while the other reactor is on stream.

For the preparation of aliphatic nitriles, mainly acetonitrile, 2-4 carbon olefins have been reacted over a supported vanadium oxide catalyst in a

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[1] Scholl and Davis, *Ind. Eng. Chem.*, **29**, 202 (1937).

[2] U.S. 2,164,706 (1939); 2,191,361 (1940); 2,287,597 (1942).

[3] U.S. 2,301,629 (1942); 2,373,869 (1945); Hoover, *Chem. Eng.*, **57**, 150 (1950).

[4] *B.I.O.S. Final Rept.* 1754, Item 22; *F.I.A.T. Final Rept.* 886.

[5] Denton, Bishop, Caldwell, and Chapman, *Ind. Eng. Chem.*, **42**, 796 (1950); Denton and Bishop, U.S. 2,450,636 (1948).

[6] Updegraff, *Petroleum Refiner*, **32**(9), 197 (1953).

similar fashion.[1] For example, a 5.9 per cent conversion of ethylene to acetonitrile was obtained per pass by feeding a 2:1 molar ratio of NH_3 and $CH_2{=}CH_2$ over a 10 per cent V_2O_5 on Al_2O_3 catalyst at about 555°C and 1.2 sec contact time.

Hydrocyanic acid, the nitrile of formic acid, is a very important product which can be produced catalytically from methane (natural gas), ammonia, and air, using noble metal or noble-metal alloy catalysts.[2] The over-all reaction $CH_4 + NH_3 + 1.5O_2 \rightarrow HCN + 3H_2O$[3] is exothermic, generating about 113,300 cal per g mole of HCN formed, whereas $CH_4 + NH_3 \rightarrow HCN + 3H_2O$ is a difficult endothermic reaction requiring about 60,000 cal. Thus far, HCN from CH_4 and NH_3 alone appears to be too costly, since the high temperature required for HCN formation causes too much dissociation of ammonia to hydrogen and nitrogen. However, if oxygen is added to generate heat at the catalyst surface, conditions can be chosen under which HCN formation is much greater than ammonia dissociation.

Natural gas has become an important starting material for the manufacture of hydrogen, acetylene, and synthesis gas for producing methanol, Fischer-Tropsch hydrocarbons, ammonia, etc. The early processes for producing HCN from CH_4, NH_3, and air have been greatly improved, so that HCN can be added to the growing list of products derived from natural gas. An example of an important end product is Orlon, the du Pont polyacrylonitrile synthetic fiber. The addition of HCN to acetylene yields the required acrylonitrile.

An improved process for producing HCN from CH_4, NH_3, and air over a platinum-alloy screen catalyst has been developed by the Freeport Sulphur Company.[4] It involves a novel method of separating the HCN and NH_3 from the gas mixture coming from the reactor. About 67 per cent of the ammonia is converted to HCN in a single pass through the converter, and only about 18 per cent is dissociated. Most of the remaining ammonia is recovered and recycled. Based on the use of recycled ammonia, the over-all yield is about 74 per cent. A flow diagram and a description of the operation for the production of liquid HCN will be found in Sec. X.

Class 7. Miscellaneous Ammonolytic Reactions

It is possible to include in this book only the more important ammonolytic reactions and to emphasize the simpler commercial processes that permit elucidation of fundamental principles. There are, however, a

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[1] Denton and Bishop, U.S. 2,450,642 (1948).

[2] I. G. Farben, Brit. 361,004 (1931); Andrussow, U.S. 1,934,838 (1933).

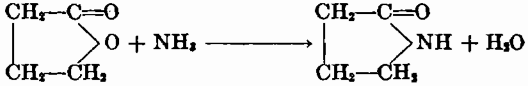
[3] Lacy, U.S. 2,076,953 (1937), covers a two-step catalytic process involving the following reactions: (1) $NH_3 + O_2 \rightarrow NO + H_2O$; and (2) $NO + CH_4 \rightarrow HCN + H_2O + 0.5H_2$

[4] UPDEGRAFF, *Petroleum Refiner*, **32** (9), 197 (1953).

number of reactions not previously classified that deserve brief consideration, because of either their unique character or their technical importance. These include the conversion of phenols and naphthols, the replacement of nitro groups, and the formation of heterocyclic nitrogen compounds such as hexamethylenetetramine and pyrollidone.

Conversion of Phenols to Amines. Aniline and some diphenylamine are formed when phenol and NH_3 solution are heated under pressure in the presence of $FeCl_3$, $Al(OH)_3$, or $Fe(OH)_2$. When NH_3 and phenol or ortho- or para-cresols are reacted in the vapor phase over an Al_2O_3 catalyst, yields of up to 88 per cent of the corresponding amines are obtained.[1] However, these amines are customarily obtained by reducing the parent nitro compound, except in cases where it is difficult to obtain the required nitro isomer. For example, it is considered that the amination of *sym*-xylenol is the best method of preparing *sym*-xylidine (1-amino-3,5-dimethylbenzene). When *sym*-xylenol is heated under pressure to 320°C with ammonium chloride, about equal amounts of *sym*-xylidine and *sym*-dixylylamine (5-imino-bis-1,3-dimethylbenzene) are formed. The ortho- and para-nitrophenols and nitrocresols can be aminated more readily. 2-Nitro-*p*-cresol [OH(1), NO_2(2), CH_3(4)] and *o*-nitrophenol have been aminated in aqueous ammonia containing ammonium salts of weak acids to inhibit decomposition. Phosphoric, boric, carbonic, and formic acids were used. In one case it is claimed that 55–65 per cent yields of 2-nitro-*p*-toluidine (MNPT of commerce) were obtained when 2-nitro-*p*-cresol, 28 per cent aqueous NH_3, and monoammonium phosphate, 1:11.5:0.2 molar ratio, were heated under pressure for 10 hr at 140–150°C and then 5 hr at about 160°C.[2] Earlier workers, employing somewhat similar conditions, claimed excellent yields of MNPT when 1 mole of ammonium formate was used per mole of 2-nitro-*p*-cresol.[3]

Conversion of γ-Butyrolactone to α-Pyrrolidone.



α-Pyrrolidone is a technically important compound, used in the manufacture of N-vinylpyrrolidone, the monomer for polyvinylpyrrolidone. γ-Butyrolactone is converted to α-pyrrolidone by heating with anhydrous ammonia, for 8 hr at 230°C, in an agitated steel autoclave. The pressure falls from an initial 40 atm to 20–25 atm.[4]

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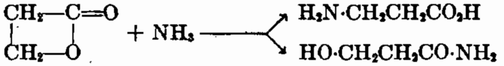
[1] Kozlov and Akhmetshina, *J. Gen. Chem.* (*U.S.S.R.*), **25** (3), 453 (1955) (Eng. trans.).

[2] Weaver and Farkas, Brit. 664,025 (1952).

[3] Frye and Vagenious, U.S. 2,128,700 (1938).

[4] Kern, Murray, and Sudhoff, *O.P.B. Rept.* 485 (Office of Publications Board, U.S. Department of Commerce); *C.I.O.S. Rept.* XXVIII-85 (Combined Intelligence Objectives Sub-committee).

Conversion of β-Propiolactone to Either β-Alanine or β-Hydroxy Propionamide.



$$\begin{matrix}CH_2—C{=}O \\ | \quad\;\; | \\ CH_2—O\end{matrix} + NH_3 \longrightarrow \begin{cases} H_2N{\cdot}CH_2CH_2CO_2H & (1) \\ HO{\cdot}CH_2CH_2CO{\cdot}NH_2 & (2)\end{cases}$$

The addition of ammonia to β-propiolactone is of interest in that the reaction can be made to go in two ways, i.e., to form β-alanine [Eq. (1)] or β-hydroxy propionamide (hydracrylamide) [Eq. (2)].

If anhydrous ammonia is reacted, at about room temperature or below, with β-propiolactone in certain unreactive solvents, good yields of β-alanine are obtained.[1] Solvents such as alcohols, esters, ketones, and aliphatic nitriles can be used. For example, a yield of about 97 per cent is obtained by adding gaseous ammonia gradually to a solution of β-propiolactone in acetonitrile, cooled to 3–7°C. The β-alanine formed precipitates from the acetonitrile solution. A practically pure product is obtained by filtering from the solvent, washing with ether, and drying. When the reaction is run in *tert*-butanol at 30°C, the yield is about 82 per cent.

When β-propiolactone is heated under pressure with anhydrous ammonia, β-hydroxypropionamide is obtained.[2] A mole of β-propiolactone (72 g) is heated under pressure with 5.87 moles (100 g) of ammonia for 16 hr at 100°C to obtain a 50 per cent yield of crude β-hydroxypropionamide, which can be purified by vacuum distillation. By a dehydration reaction, the amination of the lactone of a γ-hydroxycarboxylic acid yields a stable cyclic amide or lactam, as is the case when γ-butyrolactone is converted to α-pyrrolidone. However, owing to the instability of the four-membered ring, a lactam cannot be formed from ammonia and the lactone of a β-hydroxycarboxylic acid, such as β-propiolactone. When β-hydroxypropionamide is dehydrated, no lactam is formed. Only unsaturated acid derivatives can be obtained, as shown in the equation below.

$$HOCH_2CH_2CO{\cdot}NH_2 \xrightarrow{-H_2O} CH_2{=}CH{\cdot}CONH_2 \xrightarrow{-H_2O} CH_2{=}CH{\cdot}CN$$

For example, β-hydroxypropionamide is completely dehydrated to acrylonitrile by passing its vapors over alumina at 400°C.

Conversion of Naphthols to Naphthylamines. *Sulfurous Acid Salts as Catalysts (Bucherer Reaction).* The most general method for the replacement of —OH by —NH_2 groups in naphthols is the use of ammoniacal solutions containing salts of sulfurous acid. The alkali metal bisulfites are ordinarily employed in the preparation of primary amines; but other compounds, such as the sulfite of methylamine $(CH_3{\cdot}NH_3)_2SO_3$, can be used in making substituted amines. As can be seen from the reaction

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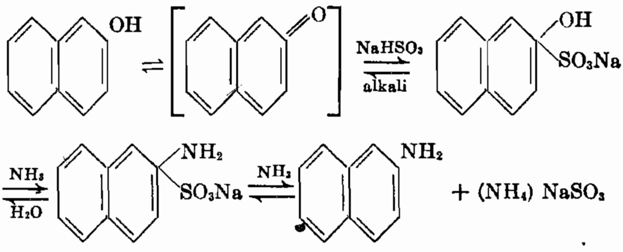
[1] Gresham and Shaver, U.S. 2,525,794 (1950).

[2] Kung, U.S. 2,375,005 (1945).

mechanism below, the reaction is reversible and also permits the conversion of naphthylamines to naphthols.



According to Fuchs and Stix, the formation of a naphthylamine from a naphthol, sodium bisulfite, and ammonia involves the addition of the bisulfite to the keto form of the naphthol.[1] The bisulfite (or sulfite) addition products of naphthols and naphthylamines are comparatively stable and, by adjusting the subsequent conditions of reaction, can be converted to either naphthols or naphthylamines. Compared with the corresponding naphthols, these addition compounds are more readily soluble in water. Those of monohydroxy compounds do not combine with diazo or tetrazo solutions, but those derived from some dihydroxy- and aminohydroxynaphthalenes still possess the power of combination, although in a lesser degree than do the dihydroxynaphthalenes and aminonaphthols themselves. Some of the aminonaphthol addition compounds can be diazotized and the diazo compounds used in the manufacture of azo colors. The addition compounds are, in general, fairly stable against the action of dilute hydrochloric acid and sulfuric acid but are readily decomposed by alkali. They are hydrolyzed, however, on heating with concentrated sulfuric acid, yielding the corresponding hydroxy compounds. When heated with ammonia, they are converted into the amino derivatives.

It is, of course, unnecessary to prepare the intermediate addition compound first in order to prepare amino derivatives from the corresponding hydroxy compounds. By adding the reacting proportions of ammonium sulfite and providing sufficient ammonia, it is indeed entirely practical to go directly from hydroxy compound to amino derivatives or vice versa.

Sodium bisulfite may be substituted for the ammonium salt without decreasing the yields of β-naphthylamine obtained by the Bucherer reaction. In the course of the reaction, this is converted to the sodium ammonium salt in the presence of an excess of ammonia. About 0.6 mole of sodium ammonium sulfite per mole of β-naphthol is necessary.

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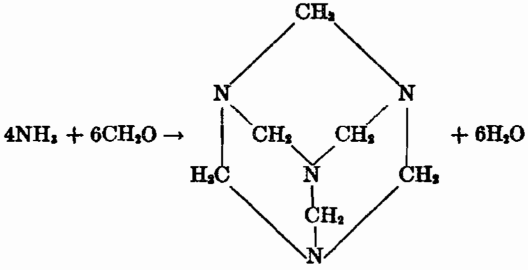
[1] Fuchs and Stix, *Ber. deut. chem. Ges.* **55**, 658 (1922). For a comprehensive review of the Bucherer reaction, the reader is referred to the contribution by Drake in "Organic Reactions," vol. 1, John Wiley & Sons, Inc., New York, 1949.

Liquid sulfur dioxide[1] (200 kg, approximately 3.1 moles) is introduced into an autoclave containing 2,800 kg β-naphthol (19.5 moles) and 2,750 kg 28 per cent ammonia (about 45 moles). The charge is heated at 180°C, under 15 atm pressure, for 18–20 hr. A yield of 91–92 per cent of theory of distilled β-naphthylamine is obtained.

The ammonolysis of β-naphthol in the vapor phase has been reported from Germany.[2] Best results are obtained with a clay catalyst at 340–370°C. The naphthylamine is of good quality, contains no unreacted naphthol and only 3–4 per cent of β,β-dinaphthylamine.

Polymerization of Ammonia and Formaldehyde to Hexamethylene Tetramine.



Ammonia like urea, melamine, and casein reacts readily with formaldehyde to form polymer molecules. With aqueous reactants under controlled temperature conditions, hexamethylenetetramine of high purity is obtained. The process comprises mixing 30 per cent formaldehyde with 27 per cent ammonia, cooling the mixture, evaporating, centrifuging, drying, and milling.[3]

Aqueous ammonia from steel tanks and formaldehyde from aluminum tanks are passed through rotameters in the ratio of 3:1 to a mixing chamber. The reaction is exothermic, and the temperature of the mixture rises to 100–102°C. The product goes through a tubular cooler, and then to a four-stage continuous evaporator, operating at atmospheric pressure, from which it flows as a 38–40 per cent hexamine solution to a receiving tank. Concentration to 75 per cent is effected in batch vacuum (150 mm) evaporators, after which the slurry is centrifuged. The filter cake containing 5 per cent moisture is delivered to continuous rotary driers to give a hexamethylenetetramine of 99.0–99.5 per cent purity. The mother liquor from the centrifugal is diluted with water, clarified with activated charcoal, filtered, and returned to the vacuum evaporators for reprocessing.

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[1] According to *F.I.A.T. Final Rept.* 1313, vol. 1, describing I.G. Farbenindustrie operations at Leverkusen.

[2] Kaupp, *O.P.B. Rept.* 622, 1941.

[3] *B.I.O.S. Final Repts.* 330 and 1331, Item 22; *C.I.O.S. Rept.* XXIII-25.

IV. PHYSICAL AND CHEMICAL FACTORS AFFECTING AMMONOLYSIS

A number of factors accelerate or retard the replacement of atoms or radicals by the amino group. These will be discussed in the following order: (1) solubility, (2) agitation, (3) halogen derivative treated, (4) presence of nitro groups, and (5) temperature of amination and NH_3 concentration.

Solubility. The soluble anthraquinonesulfonic acids are more readily converted to amines than the insoluble halogeno compounds. A similar comparison cannot be drawn, however, between 4′-chloro-2-benzoylbenzoic acid and the 2-chloroanthraquinone derived from it upon ring closure. In the soluble keto acid, the halogen is attached to the benzene nucleus, and it is consequently more difficult to replace than the chlorine atom linked to the anthraquinone nucleus. It is thus absolutely necessary to employ a metal catalyst in the ammonolysis of the halogeno keto acid, whereas its use in the conversion of the anthraquinone derivative is not essential, although the use of a copper compound accelerates the reaction.

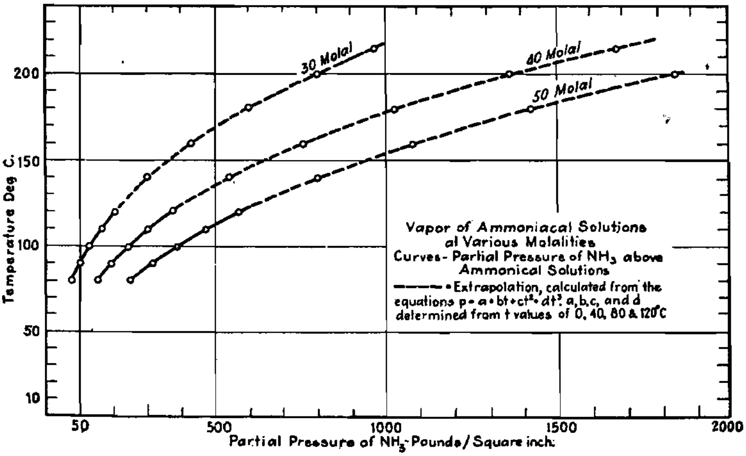

FIG. 8-10. Extrapolation NH_3 vapor pressure.

When a compound such as 2-chloroanthraquinone is being aminated, solution is facilitated by increasing either the NH_3 concentration or the temperature. Both of these factors incidentally increase the partial pressure or activity of the dissolved ammonia.

From Fig. 8-10, showing the vapor pressure (extrapolated) of ammoniacal solutions at various molalities, it can be seen that an ammonia partial pressure of 800 psi can be obtained at 200°C with a 30 molal solution, at 165°C with a 40 molal solution, and at 140°C with a 50 molal solution.

Experience in the ammonolysis of halogenoanthraquinones has shown that lower temperatures suffice when the NH_3 concentrations are increased. The permissible diminution in operating temperature is not, however, so great as one would expect from the vapor-pressure curves.

When more dilute NH_3 solutions are employed, the results obviously suffer from the increased activity of the solvent—water. Experience in the preparation of aniline, *p*-nitroaniline, aminoanthraquinones, and ethylenediamine from the corresponding halogeno compounds demonstrates that the yields and purity of primary amine are invariably favored by the utilization of the highest practical concentrations of ammonia.

Effect of Agitation. In liquid-phase ammonolysis, the rate of amination depends upon the homogeneity of the reaction mass. Without agitation, some insoluble compounds would, on account of their greater density, settle to the bottom of the autoclave while the ammonia liquor remained as a distinct layer above it. Reaction would then take place only at the interface, and a complete conversion of the compound to the amino derivative would not be feasible.

Such a problem exists in the ammonolysis of 2-chloroanthraquinone. In this instance, the solid aromatic compound does not wet out and has a tendency to remain on the surface of the ammoniacal solution. Since this amination apparently takes place in the liquid phase, it is impossible to obtain satisfactory results in this operation unless the type of agitation provides a practically homogeneous reaction mass.

In commercial manufacture, most batch operations require agitation to obtain optimum results. In many continuous operations, nonhomogeneous reaction masses are passed through tubular reactors under turbulent flow conditions in order to obtain good mixing and efficient heat transfer. In some cases, however, turbulent flow is not required to obtain a satisfactory amination. The continuous amination of chlorobenzene to produce aniline, described in Sec. X, is a case in point. The influence of the speed of stirring on the reaction velocity of a number of unit processes has been worked out by Huber and Reid,[1] who found that three classes existed:

> . . . (1) those in which the rate of reaction is a linear function of the speed of stirring; (2) those in which this relation becomes linear only after a certain speed is attained, it being very slow without stirring, the rate increasing at first far more rapidly than the speed of stirring; and (3) those in which the rate is independent of the speed of stirring.

Ammonolysis of sparsely soluble substances in aqueous ammonia is largely included in the second class—without agitation practically no reaction taking place. A slight stirring brings about a substantial increase

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[1] HUBER and REID, *Ind. Eng. Chem.*, **18**, 535 (1926).

in the reaction velocity, but a proportionate increase in the rate of reaction is not produced by a more vigorous agitation.

When soluble substances such as chloroacetic acid and 4′-chloro-2-benzoylbenzoic acid are aminated, the problem of agitation ceases to be of major importance.

There is a dearth of information regarding the efficacy of emulsifying and wetting agents in the amination process. Such agents appear to have important potential utility in the ammonolysis of aryl halides such as chlorobenzene and chloroanthraquinone, which have only limited solubility and which, on ammonolysis, yield weak bases that do not form stable hydrochlorides under operating conditions.

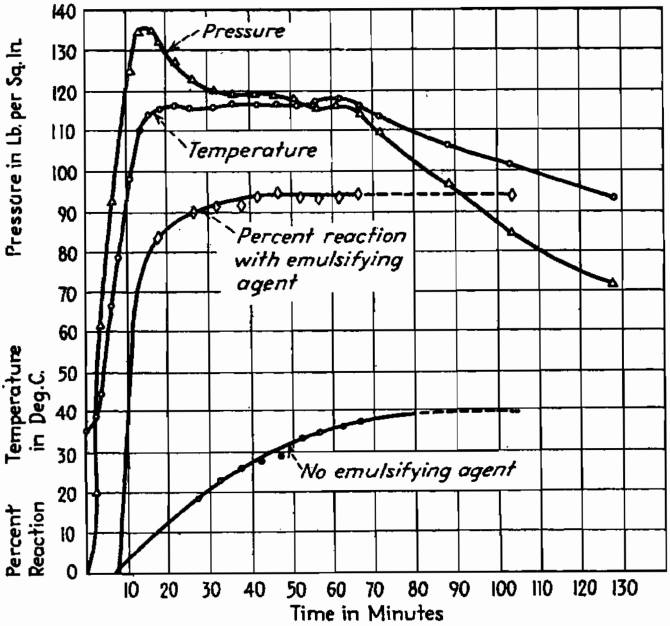

FIG. 8-11. Amination of ethylene dichloride: effect of emulsifying agent.

The accelerating influence of soap on the speed of reaction in aminating ethylene dichloride is evidenced by the curves in Fig. 8-11.[1]

Effect of Halogen Derivative. From the known activity of the halogens and the heats of formation of the halides, it would be expected that replacement of bromine atoms could be accomplished more readily than that of chlorine atoms. This has been found to be true in the treatment of the respective halogenoanthraquinones. Thus, without the employment of

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[1] Barbieri, U.S. 2,078,555 (1937); Barbieri and Heard, U.S. 2,113,640 (1938).

catalysts, bromoanthraquinone is approximately twice as reactive as the chloro derivative. When a copper catalyst is used, 2-aminoanthraquinone of 97–98 per cent purity can be obtained with a 28.5 per cent NH_3 solution, whereas the maximum purity of product from the chloro derivative under the same conditions is only 93 per cent.

The comparative ease in replacing —Br by $—NH_2$ is brought out in the conversion of 4-bromochlorobenzene to 4-chloroaniline. By heating with aqueous ammonia at 120°C for 10 hr, only the bromine atom is replaced by the amino group.

Effect of Nitro Substituents. The conversion of chlorobenzene to aniline requires a comparatively high temperature—200°C or above—and the presence of a catalyst. When certain negative groups such as the $—NO_2$ or —COOH are introduced in the ortho or para position of the phenyl nucleus, the replacement of the halogen atom takes place more readily. Thus, it is a comparatively easy procedure to produce the nitroanilines from the corresponding halogenonitrobenzenes and chloronitroanilines from dichloronitrobenzenes. No catalyst is required in these operations, and a temperature of 170°C suffices. The introduction of more than one nitro group greatly increases the activity of the halogen atom.

The ease in replacing halogen in halogenonitrobenzenes is, in all probability, due to the activity of the nitro group in forming addition complexes. Garner and Gillbe have shown that dinitrobenzene forms addition complexes with ammonia that show measurable conductivities.[1]

Energy Factors in Ammonolysis. *Effect of Temperature.* The generally accepted explanation for the temperature coefficient of reactions is essentially the Arrhenius hypothesis of activated molecules. An increase in the temperature of amination increases not only the solubility and internal energy of the compound that is being treated but also the partial pressure of the ammonia. Since the activity of the aqueous ammonia is a function of the total and NH_3 partial pressures, the probabilities of reacting are increased in proportion to the temperature. The partial pressure of H_2O in aqueous NH_3 increases at a greater rate with increasing temperature, causing hydrolysis to occur to a greater extent (see Fig. 8-5).

Effect of NH_3 *Concentration.* It is necessary to distinguish between the terms *ammonia ratio* and *ammonia concentration.* The first concerns the capacity factor of the system; the second, the intensity factor. Aside from economic considerations, there are no disadvantages in using a large ratio of aqueous ammonia (25–50 per cent NH_3 solution) with respect to the compound being treated. Within reasonable limits, an increase in this ratio promotes both the yield and purity of primary amine by ammonolysis or

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[1] GARNER and GILLBE, *J. Chem. Soc.*, **1928**, 2889.

secondary amine by aminolysis (Fig. 8-12).[1] The larger volume of concentrated aqueous ammonia (or amino compound) promotes solubility and, therefore, causes the reaction to take place more readily.

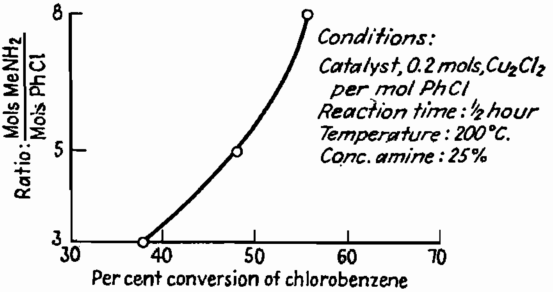

FIG. 8-12. Effect of CH_3NH_2 ratio in aminolysis of chlorobenzene.

Extensive investigations in the ammonolysis of halogeno compounds have shown that the practical advantages to be obtained by utilizing a more concentrated NH_3 solution for noncatalytic aminations may be summed up as follows: (1) amination is more rapid, (2) conversion of reacting compound to primary amine is more complete, (3) formation of

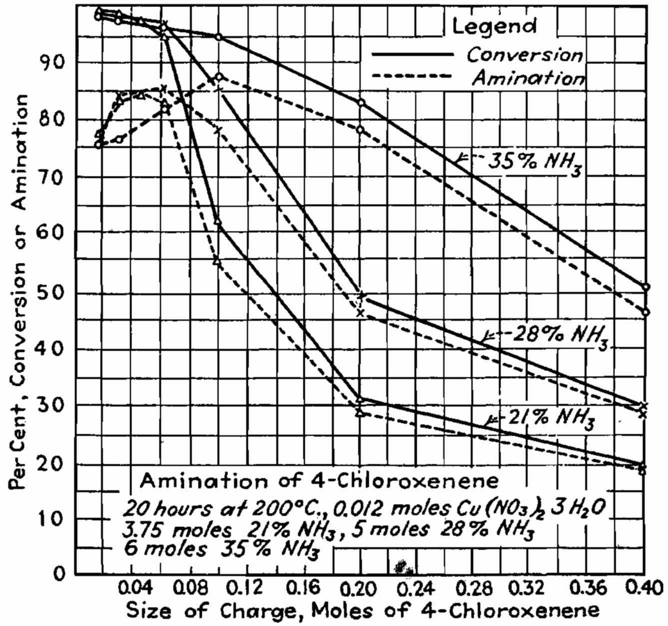

FIG. 8-13. Amination of 4-chloroxenene.

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[1] HUGHES, VEATCH, and ELERSICH, *Ind. Eng. Chem.*, **42**, 787 (1950).

secondary and tertiary amines and hydroxy compounds is inhibited, (4) lower reaction temperatures can be used, and (5) since larger batches can be treated with the same quantity of liquor, economies in the number of pieces of equipment can be effected. To a large extent, these observations are confirmed by the curves of Fig. 8-13 relating to aminobiphenyl.

The effect of NH_3 concentration in catalytic ammonolysis has been investigated by Vorozhtzov and Kobelev[1] and by Groggins and Stirton.[2] The practical benefits of employing higher ammonia concentrations are brought out clearly by the data in Table 8-7. In these experiments, as in plant practice, a constant ratio of ammonia and copper to 4-chloroxenene was provided. From the tabulated data, it can be concluded: (1) for any particular NH_3 concentration, within limits, the rate of conversion is a function of the copper-ammonia concentration; (2) most of the generalizations relating to the noncatalytic ammonolysis of halogeno compounds are equally valid; (3) the difference between conversion, i.e., decomposition of halogeno compound as determined by chloride ion and amination, for 18 per cent copper, is approximately twice as great as that for 12 per cent

TABLE 8-7. INFLUENCE OF AMMONIA CONCENTRATION IN PREPARATION OF XENYLAMINE*
16 Hr at 200°C

Expt.	NH_3 conc., %	Aqueous NH_3, g	4-Chloroxenene, mole	$Cu(NO_3)_2 \cdot 3H_2O$, mole	Catalyst conc., g atom copper per liter	Conversion, A, %	Amination, B, %	100 × mole ratio, Cu: R·Cl	Mole ratio NH_3: R·Cl	Difference, A−B
1	14	304	$1/6$	0.03	0.0932	55.31	45.14	18	15	10.17
2	21	304	$1/4$	0.045	0.1360	66.20	57.68	18	15	8.52
3	28	304	$1/3$	0.06	0.1770	86.35	80.15	18	15	6.20
4	35	292	$2/5$	0.072	0.2169	93.26	88.77	18	15	4.49
5	21	304	$1/4$	0.072	0.2175	85.56	73.82	28.8	15	11.74
6	14	304	$1/6$	0.02	0.0621	41.20	35.73	12	15	5.47
7	21	304	$1/4$	0.03	0.0906	58.38	53.44	12	15	4.94
8	28	304	$1/3$	0.04	0.1180	74.10	71.35	12	15	2.75
9	35	292	$2/5$	0.048	0.1446	87.02	84.41	12	15	2.61
10	35	292	$1/4$	0.048	0.1446	98.92	88.99	19.2	24	9.93
11	21	304	$1/4$	0.048	0.1450	73.38	64.06	19.2	15	9.32

*GROGGINS and STIRTON, *Ind. Eng. Chem.*, **28** (1936).

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[1] VOROZHTZOV and KOBELEV, *J. Chem. Soc.* (*U.S.S.R.*), **4**, 310 (1934).

[2] GROGGINS and STIRTON, *Ind. Eng. Chem.*, **28**, 1051 (1936).

copper; and (4) as the ammonia concentration is increased, this "difference" becomes less despite the fact that the reaction has proceeded farther.

Reaction-rate studies with aryl chlorides showed that the effect of NH_3 concentration on the rate of conversion in catalytic ammonolysis depends upon (1) the ammonia ratio, (2) the reaction temperature, and (3) the halogeno compound.[1]

In the preparation of N-methylaniline by aminolysis of chlorobenzene, Hughes et al.[2] found that the maximum rate of conversion was obtained with a methylamine concentration of 50–70 per cent (Fig. 8-14). It will be recalled that similar concentrations of aqueous NH_3 gave the highest conversions of *p*-chloronitrobenzene to *p*-nitroaniline (Fig. 8-4).

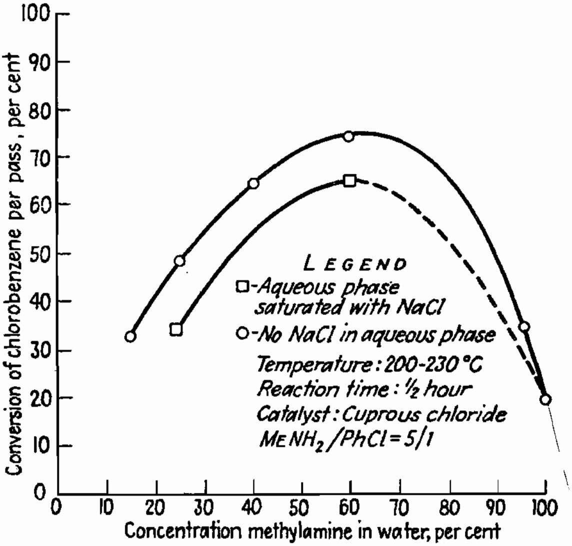

FIG. 8-14. Effect of methylamine concentration: aminolysis of chlorobenzene.

V. CATALYSTS USED IN AMINATION REACTIONS

Metal Catalysts in Ammonolysis of Halogen Compounds. In the amination of many aromatic halogen compounds, particularly those which are not activated with negative groups, such as $-NO_2$, some metals or compounds of metals following hydrogen in the electromotive series are advantageously used as catalysts (e.g., copper, arsenic, and silver). Copper, copper oxides, and copper salts are most widely used. Cuprous salts

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[1] *Ibid.*

[2] HUGHES, VEATCH, and ELERSICH, *loc. cit.*

are preferred in those cases where a cupric salt oxidizes the amine to undesirable by-products. In the manufacture of aniline from chlorobenzene, cuprous salts give better results and air is kept from the system to prevent the formation of cupric ions. However, Groggins and Stirton[1] point out that in some instances cupric salts are effective catalysts, since cupric nitrate effectively catalyzes the amination of chlorobiphenyl (chloroxenene), chloronaphthalene, and chloroanthraquinone. The anion accompanying the copper affects the reaction, since the introduction of hydroxyl or nitrate ions noticeably changes the results. In connection with the use of cuprous and cupric salts, Groggins and Stirton state that under certain conditions (1) cuprous and cupric compounds are about equally active in the preparation of amines that are not readily oxidized, (2) in the preparation of easily oxidizable amines, low catalyst concentration results in a smaller difference in reaction rates when cuprous and cupric compounds are compared, and (3) the treatment of aniline with cupric nitrate leads to oxidation of the amine. If the chloro compound contains groups which can be reduced to by-products during the amination, cupric compounds are used. In the case of anthraquinone, for example, the —CO— group is readily reduced and an oxidizing agent is used together with cupric compounds to prevent the formation of undesired reduction products.

In aminations requiring copper, it appears that copper ammonia cations complex with the chloro compound and that this complex addition compound acts as a cyclic catalyst by reacting with ammonia, —OH ion, and the amine.[2]

Dehydration Catalysts. In the production of amines from alcohols and ammonia or from alcohols and various amines, catalysts prepared by dehydrating alumina or silica gel are generally used. For specific reactions, these catalysts are promoted with various metals, their oxides or salts. For example, a dehydration catalyst has been made by incorporating aluminum phosphate in alumina gel prior to dehydrating the gel. An amination catalyst made by treating absorptive alumina with calcium and copper nitrates, followed by calcination and then reduction with hydrogen in a vapor-phase reactor, was used to produce an excellent yield of monomethylaniline from aniline and methanol.[3]

Catalysts which are effective in hydrogenation and dehydrogenation procedures are often used to obtain amines from alcohols and ammonia or amines. The above copper-containing catalyst may be considered in this category. In the vapor-phase production of aliphatic amines from alcohols

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[1] Groggins and Stirton, *loc. cit.*

[2] Vorozhtzov and Kobelev, *Compt. rend. acad. sci.* (*U.S.S.R.*), **3**, 108, 111–114 (1934) (Eng. trans.).

[3] Deahl, Stross, and Taylor, U.S. 2,580,284 (1951).

and NH_3 mixed with H_2, nickel- , copper- , and cobalt-based catalysts have been used. In the absence of hydrogen, a high amount of the amine formed is converted to nitrile by dehydrogenation, $RCH_2NH_2 \rightarrow R{\cdot}CN + 2H_2$. For example, without hydrogen in the amination of *n*-butanol over a pelleted nickel catalyst, 45 per cent of the alcohol was converted to butyronitrile and only 33.5 per cent to mono- and dibutylamines. With hydrogen, only 2.4 per cent was converted to butyronitrile, while 85.9 per cent was converted to mono- , di- , and triamine mixtures.[1] Although the precise reaction mechanism is not known, it is not considered a simple dehydration reaction between the alcohol and the amine. The reactions involved might be:

$$R{\cdot}CH_2OH \xrightarrow{\text{catalyst}} H_2 + R{\cdot}CHO \xrightarrow{NH_3} R{\cdot}CH(OH)NH_2 \xrightarrow{-H_2O} R{\cdot}CH{=}NH \xrightarrow{H_2} RCH_2NH_2$$

In this scheme the alcohol is dehydrogenated to aldehyde, and the aldehyde-ammonia-addition compound loses water to form an aldimine which is then hydrogenated to the amine. The hydrogen generated balances the hydrogen consumed, so that there is no consumption of hydrogen added, even if the aldehyde-amine-addition compound is hydrogenated directly without losing water as shown.

Very good results have been obtained with "foraminate" catalysts (i.e., Ni, Co, and Cu catalysts) described below. When butanol was aminated over a copper "foraminate" catalyst, the per-pass conversion was 96 per cent and a 97 per cent yield of a mixture of mono- , di- , and tributylamine was obtained. The operating conditions were:[2] mole ratio, butanol:NH_3:H_2, 1:1.25:3.0; temperature, 250°C; pressure, 17 atm; liquid space velocity, 0.22 hr^{-1}.

Foraminate Metal Hydrogenation Catalysts[3]

BY A. W. TAYLOR[4]

The surface extraction of one constituent of an alloy has received increasing attention during recent years as a means whereby an active metal catalyst, such as nickel or copper, can be produced in a robust granular form. As these catalysts are wholly metallic, they are very good heat conductors, a property which sometimes can make them exceptionally suitable for use in strongly exothermic reactions.

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[1] Olin and McKenna, U.S. 2,365,721 (1944).

[2] Davies, Reynolds, Coats, and Taylor, U.S. 2,609,394 (1952).

[3] Brit. 611,987 (1948); 621,749; 624,035; 628,405; 630,161; 633,531 (1949); 642,861; U.S. 2,604,455 (1950); Brit. 650,251; 658,863; U.S. 2,673,189 (1951); Brit. 664,851; U.S. 2,650,204 (1952).

[4] Imperial Chemical Industries.

It is possible, if one component of a binary alloy is soluble in either an acid or an alkaline medium while the other component is unattacked, to extract the soluble metal to a controlled depth from granules of the fine-grain alloy. After extraction, there remains in each granule a central core of virtually unattacked alloy surrounded by a firmly attached layer of the insoluble metal which, by virtue of its spongy or "foraminous" character, possesses very active catalytic properties toward hydrogenation, dehyrogenation, and reductive amination reactions.

Aluminum is usually employed as the extractable component, which can be dissolved out of the alloy by the action of alkaline media such as caustic soda solution. Acid-soluble metals such as magnesium or zinc have also been employed.

The principal alloys which have been used in the preparation of foraminate catalysts are as follows:

Copper	55:45*	Cu-Ni-Al	40:10:50
Nickel	42:58	Cu-Ni-Al	25:25:50
Cobalt	30:70	Cu-Ni-Al	15:35:50
Iron	51:49	Cu-Ni-Al	5:45:50

*Parts by weight.

The alloys are prepared by suitable melting of the metals together followed by chill-casting to produce a fine-grain structure of uniform composition. The preferred copper-aluminum alloy, Coppal 55:45, corresponds to the crystalline phase $CuAl_2$; alloys containing a higher percentage of copper are less readily extracted by caustic soda. The preferred nickel-aluminum alloy, Nikal 42:58, corresponds to the crystalline phase $NiAl_3$; the Ni_2Al_3 phase is readily activated but suffers from the liability to disintegrate to powder on storage. The choice of initial alloy composition depends on factors such as ease of activation, life and mechanical strength, and catalytic activity.

Activation of the alloy is usually carried out by removal of 20 per cent by weight of the total aluminum content. Although a 5–10 per cent extraction will frequently yield an equally active catalyst, such catalysts are likely to possess shorter working lives. An extraction of 40–50 per cent, on the other hand, produced a foraminate layer that is deeper but much softer (i.e., approaching a Raney type of catalyst) and thus is much more susceptible to damage by mechanical abrasion. The quantity of hydrogen liberated during the activation process is a measure of the degree of activation:

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$

Precautions must be taken to avoid the deposition of alumina on the active granules because of the hydrolytic reaction:

$$2NaAlO_2 + H_2O \rightleftharpoons Al_2O_3 + 2NaOH$$

Not only does the presence of alumina decrease the hydrogenation activity by reducing the active metal surface area, but also it possesses strong hydration-dehydration tendencies which may promote undesirable side reactions. The deposition of alumina can be limited by strict control during the activation of the alloy. The deleterious activity of the residue of alumina which invariably remains can be reduced by treatment of the catalyst with baryta solution.

Preparation of Catalyst. Alloy of requisite metal composition, screened and graded to ⅛–¼ in. granules, is charged into mild steel activation vessels. Here the granules are treated with a sodium hydroxide solution of ½–2 per cent strength at about 80°C. The dissolution of the aluminum and hence the progress of activation is followed by the measurement of the evolved hydrogen. When the desired degree of activation has been reached, the flow of sodium hydroxide to the activation kettle is stopped. Water at 40°C is then circulated through the charge to wash the catalyst free of alkali. The activated catalyst is discharged into a steel hopper and stored under water prior to treatment with barium hydroxide solution if necessary and transferred to the amination reactor.

The Reductive Amination of Alcohols with Foraminate Catalysts.[1] The remarkably good results which can be obtained with the foraminate-catalyst system in this type of reaction can be easily demonstrated by the following experimental results obtained in the reductive amination of three butanols over a baryta-treated nickel-aluminum foraminate catalyst operating at 190°C, 250 psi, and a liquid-alcohol space velocity of 0.2 hr^{-1}. In this series of experiments an alcohol ammonia hydrogen mole ratio of 1:1.25:2.5 was used. From these results certain general features of the reaction can be illustrated:

Alcohol	% Yield amine			Total yield	% Alcohol converted
	Mono-	Di-	Tri-		
Butanol-1	16	61	21	98	98
Butanol-2	74.5	20	1.5	96	82
Isobutanol	28.5	67	1.5	97	87

1. Only when aminating primary alcohols is it possible to obtain good yields of trialkylamines.

2. With primary alcohols a molar ratio of ammonia:alcohol of between 1 and 2 gives the dialkylamines as the main product, and a further increase in ammonia:alcohol ratio leads to increased monoalkylamine formation.

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[1] Brit. 79,014; 79,712; 679,713; (1952); U.S. 2,636,902 (1953).

3. Under comparable conditions, secondary alcohols give more monoamine than primary alcohols.
4. As indicated from the very high yields obtained, there is substantially no dehydration of the alcohol to olefin and no appreciable nitrile formation.

Other general points are that tertiary alcohols are extremely resistant to amination by this method, resulting in very small conversions per pass. Highly branched alcohols in general require rather more vigorous conditions, which result in higher proportions of monoalkylamines being formed, and since an equilibrium is not generally set up under the conditions of reaction, the proportions of mono:di:trialkylamines can be influenced by the space velocity of the reactants.

Foraminate catalysts appear to have a number of desirable characteristics which make for economic and efficient operations in converting alcohols to amines. The advantages gained by using them are: (1) high conversions and yields are obtainable, (2) relatively high space velocities can be employed, (3) the ratio of product amines can be varied over a wide range, and (4) the cost of the catalyst is comparatively low.

Catalysts for Hydroammonolysis. The hydrogenation type of catalysts referred to above (i.e., nickel- , cobalt- , and copper-based catalysts) and also noble-metal catalysts are used in the hydroammonolysis of aldehydes and ketones. A foraminate nickel catalyst, made from a 42:58 nickel: aluminum alloy was used to convert acetone to isopropylamine by a vapor-phase reaction employing an excess of ammonia and hydrogen.[1]

Other catalysts, used in types of reactions not listed above, vary with the specific reaction involved. A few examples are cited. For the reaction involving the removal of hydrogen from NH_3 and CH_4 to produce HCN, noble-metal catalysts are used. For the synthesis of benzonitrile from toluene and NH_3 by splitting out hydrogen, molybdenum trioxide is used. 2-Methyl-5-ethylpyridine is produced by reacting methylvinyl ether and NH_3 at elevated temperatures and pressures over a titanium phosphate or manganese phosphate catalyst supported on calcined silica.[2]

VI. CORROSION AND THE pH OF THE AUTOCLAVE CHARGE

Groggins and Stirton showed that the pH of aqueous ammonia decreases with rising temperature and more rapidly under such conditions when ammonium salts are introduced.[3] During the course of the reaction in the liquid-phase treatment of halogeno compounds, the concentration of NH_3 in the charge diminishes while that of the hydrohalide increases. It is important to remember that, during ammonolysis of halogeno com-

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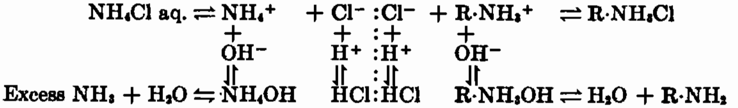
[1] Reynolds and Bremner, Brit. 632,219 (1949).

[2] ANZILOTTI, *F.I.A.T. Final Rept.* 1314, P.B. 85,173.

[3] GROGGINS and STIRTON, *Ind. Eng. Chem.*, **25**, 42 (1933).

pounds, the molar concentration of the hydracid must be *at least* equivalent to the molar concentration of the amino compound, because of the concomitant formation of hydroxy compounds and secondary and polyamines. The hydrohalide may be distributed as free acid, as ammonium halide in solution, and as the salt of the newly formed amino compound. These are all acidic compounds (proton donors); and unless their activity is neutralized, they will corrode steel vessels. The pH of the molar solutions of such compounds at 25°C is closely as follows: NH_4Cl, 4.7 $CH_3NH_2 \cdot HCl$, 5.5; $C_2H_5NH_2 \cdot HCl$, 6.0; $C_6H_5NH_2 \cdot HCl$, 2.3.

In closed systems containing an excess of aqueous ammonia in addition to corresponding molar concentrations of hydrochloric acid and primary amine, the equilibriums involved may be represented as follows:



$$\begin{array}{rllll}
NH_4Cl\ aq. \rightleftharpoons & NH_4^+ & + Cl^- : Cl^- & + R\cdot NH_3^+ & \rightleftharpoons R\cdot NH_3Cl \\
 & + & \;\;+ \;\;: + & + & \\
 & OH^- & \;H^+ : H^+ & OH^- & \\
 & \downharpoonleft\upharpoonright & \;\downharpoonleft\upharpoonright : \downharpoonleft\upharpoonright & \downharpoonleft\upharpoonright & \\
\text{Excess } NH_3 + H_2O \leftrightarrows & NH_4OH & \;HCl : HCl & R\cdot NH_3OH & \rightleftharpoons H_2O + R\cdot NH_2
\end{array}$$

The available information regarding these reactions at high temperatures is inadequate, and our knowledge concerns only certain segments of the whole. There is little doubt, however, that the principal factors affecting the equilibriums are (1) the temperature of the system, (2) the relative basicity of the amine, and (3) the solubility of the amine.

Because of its volatility, NH_3 can be displaced from $[H(NH_3)]Cl$ by basic substances of higher boiling point. The rate at which such displacement occurs, however, obviously depends on the strength of the base [e.g., $Ca(OH)_2$, alkyl-NH_2, etc.], the reaction temperature, and the counter influence of free NH_3. It is known, however, that with increasing temperature NH_3 has a diminishing capacity to form the ionogen NH_4OH; and at 290°C, the union of NH_3 to HCl in aqueous $[H(NH_3)]$ Cl is so weak that the two components react as if they were alone, and ammonium chloride in aqueous solution can be employed to convert methanol to dimethylamine[1] and *sym*-xylenol to dixylylamine. The fact that the charge and free space in the autoclave contain a large excess of gaseous ammonia does not, therefore, signify that the hot aqueous ammonia has the capacity to displace the amine from all amino hydrohalides, for there is ample evidence to the contrary. When the amino hydrohalide is insoluble, then the concentration of the $\overset{+}{R\cdot NH_3}$ ions in solution is diminished. In general, it can be concluded that the slightly basic arylamines do not form stable hydrohalides at the high temperatures necessary for conversion, but the highly basic alkyl and alkanolamines do form stable salts of limited solubility.

From the extensive literature on inhibitors, it would be expected that the amino compound being synthesized should serve as its own inhibitor,

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[1] **Bottoms, U.S. 2,085,785 (1937).**

and indeed it would form a protective film if sufficient free base were available. It is well known that the addition of aniline to aniline hydrochloride will reduce the dissociation and, consequently, the corrosive action of the latter. This probably explains why it has been found efficacious to add acid inhibitors (e.g., alkylamines, secondary amines, and pyridine) to the autoclave charge in the preparation of nitroamines, for this procedure ensures the presence of free base during ammonolysis.

There are two other useful methods of controlling the pH of the autoclave charge: the introduction of copper-ammonio hydroxides and the use of buffer salts, such as soap or chlorates, which are attacked and decomposed when the concentration of the hydracid is sufficiently great. The oxidants cannot be used to advantage, however, when the amino compound (e.g., aniline) is readily susceptible to oxidation.

VII. KINETICS OF AMMONOLYSIS

BY A. C. STEVENSON,[1] R. W. GRIMBLE,[1] AND E. K. GLADDING[1]

In reacting ammonia with organic compounds it is usually the practice to use a substantial excess of ammonia. Under this condition there is no appreciable change in concentration of ammonia compared to the other reactant, and the rate expression for the process becomes pseudo first order. Actually, the reaction is bimolecular in nature and involves the reaction of one molecule of ammonia with one molecule of the other reactant so that the second-order rate expression is more indicative of the actual mechanism.

$$\frac{dC}{dt} = kCC'$$

The terms C and C' refer to the concentration of the two reactants, and k is the reaction-rate constant.

Reactions of ammonia and organic compounds are effected in both vapor and liquid phases. The liquid-phase systems include anhydrous liquid ammonia, anhydrous ammonia in an organic diluent, and aqueous ammonia, occasionally in the presence of an organic solvent.

Studies of the kinetics of the reaction have been concerned principally with the liquid-phase ammonolysis of esters and aromatic chloro compounds, presumably because the reactions are more cleancut and there is less tendency to form by-products. For example, in the ammonolysis of esters, the amide is essentially the only product, whereas with the reaction of aliphatic alcohols and ammonia an equilibrium mixture of mono-, di-, and trialkylamines is obtained.

The reaction of esters and ammonia proceeds directly to the amide according to the following equation:

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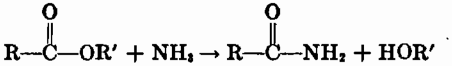
[1] E. I. du Pont de Nemours & Company.



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OR' + NH_3 \rightarrow R{-}\overset{O}{\overset{\|}{C}}{-}NH_2 + HOR'}$$

In the presence of water, the reaction is complicated to some extent by hydrolysis.

With the objective of determining the effect of the nature of the alkyl group on the reaction rate, Gordon et al.[1] undertook a study of the ammonolysis of a series of esters including acetates, benzoates, and lactates in an aqueous dioxane system. They concluded that the greater the molecular weight and the more complex the alkyl or aryl group, the lower the rate of ammonolysis. The benzoate and lactate esters follow essentially the same order. French and Wrightsman[2] had previously observed a similar effect of structure of alkyl and aryl radicals on the rate of ammonolysis in an aqueous ammonia system.

While the second-order rate expression was applied to these reactions, there was much better agreement in the values of the rate constant through a range of concentrations of the reactants in some cases than in others. However, in all cases studied, an appreciable drift in the value of the rate constant over the interval of the reaction was observed. This investigation has been extended considerably.[3] Water and various hydroxylated com-

TABLE 8-8. RELATIVE REACTION RATES OF AMMONOLYSIS OF ACETIC ACID ESTERS AT 25°C*
Methyl Acetate Used as Reference

Ester	100 hr	300 hr
Phenyl acetate	1,365.0	1,443.0
Vinyl acetate	909.0	957.0
Methyl acetate	1.000	1.000
Benzyl acetate	0.649	0.678
Ethyl acetate	0.358	0.300
n-Propyl acetate	0.341	0.264
n-Butyl acetate	0.185	0.149
n-Amyl acetate	0.174	0.148
Isopropyl acetate	0.156	0.128
Isobutyl acetate	0.136	0.109
sec-Butyl acetate	0.0986	0.0721
tert-Butyl acetate	0.0750	0.0643
β-Naphthyl acetate	0.0554	0.0429
α-Naphthyl acetate	0.0473	0.0429

* GORDON, MILLER, and DAY, *J. Am. Chem. Soc.*, **70**, 1946 (1948).

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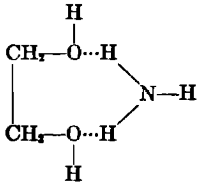
[1] GORDON, MILLER, and DAY, *J. Am. Chem. Soc.*, **70**, 1946 (1948).

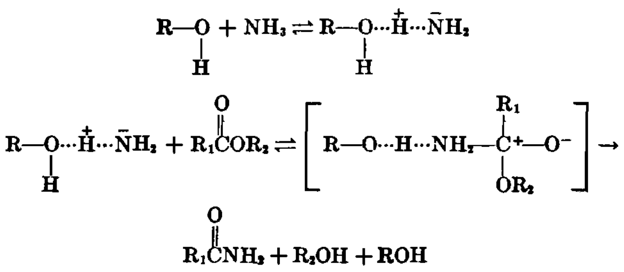
[2] FRENCH and WRIGHTSMAN, *J. Am. Chem. Soc.*, **60**, 50 (1938).

[3] JUNG, MILLER, and DAY, *J. Am. Chem. Soc.*, **75**, 4664 (1953); WETZEL, MILLER, and DAY, *ibid.*, **75**, 1150 (1953); KOCH, MILLER, and DAY, *ibid.*, **75**, 953 (1953); ARNETT, MILLER, and DAY, *ibid.*, **73**, 5393 (1951); ARNETT, MILLER, and DAY, *ibid.*, **71**, 1245 (1949).

pounds were found to exert an appreciable catalytic effect. Ethylene glycol was found to be a better catalyst than water, which, in turn, was better than methanol, when their respective catalytic activities were compared at equivalent hydroxyl concentrations. A cyclic hydrogen-bonded structure was proposed to account for the unusual activity of ethylene glycol.



Results of kinetic studies were in accord with the following mechanism:



$$R{-}\underset{\underset{H}{|}}{O} + NH_3 \rightleftharpoons R{-}\underset{\underset{H}{|}}{O}\cdots\overset{+}{H}\cdots\overset{-}{N}H_2$$

$$R{-}\underset{\underset{H}{|}}{O}\cdots\overset{+}{H}\cdots\overset{-}{N}H_2 + R_1\overset{\overset{O}{\|}}{C}OR_2 \rightleftharpoons \left[R{-}O\cdots H\cdots NH_2{-}\underset{\underset{OR_2}{|}}{\overset{\overset{R_1}{|}}{C^+}}{-}O^- \right] \rightarrow$$

$$R_1\overset{\overset{O}{\|}}{C}NH_2 + R_2OH + ROH$$

ROH represents the hydroxylated catalyst. R_1 and R_2 represent the aliphatic or aromatic hydrocarbon residues of the ester. Treatment of rate data, in accordance with the above mechanism, gave the energies and entropies of activation shown in Table 8-9.

TABLE 8-9. ENERGIES OF ACTIVATION AND ENTROPIES OF ACTIVATION AT 20 PER CENT AMMONOLYSIS OF VARIOUS ACETATES

Ester, acetate	E_a, cal/mole	Error	ΔS cal/mole/deg	Error
Methyl†	6735	±85	−67.7	±0.20
Methyl‡	7710	120	−64.7	0.28
Methyl§	7090	380	−70.8	0.84
Ethyl†	5925	350	−71.5	0.80
n-Propyl†	6685	340	−69.3	0.78
Isopropyl†	8085	220	−67.1	0.52

† Catalyzed by ethylene glycol, concentration of 5 moles/liter.

‡ Catalyzed by water, concentration of 10 moles/liter.

§ Catalyzed by methanol, concentration of 10 moles/liter.

The marked catalytic effect of water is illustrated further by the data in Table 8-10.

The amination of ethyl thioacetate with butyl amine is also catalyzed by water.[1] It seems probable that there is no essential difference in kinetic behavior between the thioesters and their oxygenated counterparts.

The ammonolysis of aromatic halides follows a pattern similar to the esters. For example, substituted chloronitrobenzenes containing a labilized chlorine atom react in aqueous ammonia at a rate proportional to the concentration of both reactants—indicating that the mechanism is second order.[2]

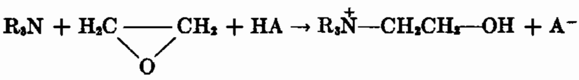
TABLE 8-10. CATALYTIC EFFECT OF WATER ON AMINOLYSIS OF ETHYL PHENYL ACETATE*

H_2O, moles/liter	Conc. amine, moles/liter	Conc. ester, moles/liter	$k \times 10^3$	$t\frac{1}{2}$ calc.	$t\frac{1}{2}$ obs.
....	5.49	2.81	0.95	156	141
0.2	5.40	2.81	1.33	113	114
0.5	5.44	2.79	1.51	99	94
1.0	5.43	2.76	2.06	72	72
2.0	5.17	2.81	3.22	49	54
2.8	5.07	2.67	4.22	39	41
5.6	5.00	2.53	7.1	23	23
8.4	4.57	2.38	8.25	22	18
11.2	4.36	2.24	10.4	18	16

* GLASOE, SCOTT, and AUDRIETH, *J. Am. Chem. Soc.*, **63**, 2965 (1941).

Ammonolysis of aromatic halides, however, may lead to unexpected products. For example, Gilman and Martin[3] report that aryl ethers, thio ethers, and sulfones with ortho-halogen substituents rearrange to meta-substituted anilines when treated with sodamide in liquid NH_3.

A kinetic investigation of the addition of ammonia and amines to ethylene oxide was undertaken by Eastham et al.[4] The reaction was represented as follows:



$$R_3N + H_2C\underset{O}{\text{---}}CH_2 + HA \rightarrow R_3\overset{+}{N}\text{—}CH_2CH_2\text{—}OH + A^-$$

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[1] HAWKINS and TARBELL, *J. Am. Chem. Soc.*, **75**, 2982 (1953).

[2] VOROZHTZOV and KOBELEV, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 1043–1046 (1930).

[3] GILMAN and MARTIN, *J. Am. Chem. Soc.*, **74**, 5317 (1952).

[4] EASTHAM, DARWENT, and BEAUBIEN, *Can. J. Chem.*, **29**, 575 (1951); EASTHAM and DARWENT, *ibid.*, **29**, 585 (1951).

where the R's may be hydrogen or hydrocarbon residues and where HA represents an acid. In aqueous media, second-order kinetics were obeyed and the rate of disappearance of oxide was proportional to the product of oxide and amine concentrations. In the amine as solvent, however, the reaction rate was proportional to the acid concentration. Amines investigated included diethylamine, triethylamine, aniline, and ammonia. No relationship was found between reaction rate and structure or base strength of the amine.

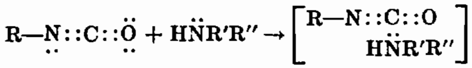
The rate of reaction of propylene oxide with amines has been studied also.[1]

The vapor-phase ammonolysis of alcohol is much more complicated, because of side reactions. Although much information is available concerning operating conditions, effect of flow rates, and the effects of catalysts, there is little to be found in the literature on actual mechanism.

Egly and Smith[2] have studied the effect of operating variables on methylamine production from methanol and ammonia over activated alumina. Nine reactions are postulated as probable under commercial operating conditions. These include reaction of methanol with di- and trimethylamines as well as decomposition of the amines. Optimum space velocities were found for a given temperature and pressure at which maximum conversion was obtained (e.g., a 97 per cent conversion of alcohol to a product consisting of 54 per cent mono-, 26 per cent di-, and 20 per cent trimethylamine was attained at 50°C with a space velocity of 720 per hr). The existence of optimum space-velocity conditions was interpreted qualitatively on the basis of the rate of the various possible reactions. Trimethylamine in the product can be reduced by adding water to the feed or eliminated by recycling.

Rates of addition of various primary amines to phenylisocyanate have been measured.[3] Alkyl amines are 8–10 times as reactive as NH_3, whereas a simple aromatic amine (aniline) is about one-half as reactive. Greater reactivity is apparently associated with increased base strength of the amine.

It seems very likely that the primary step in the amination of an isocyanate consists of an attack by the unshared electron pair of the amine nitrogen at the relatively positive carbon atom of the isocyanate function; thus:



$$R{-}\underset{\cdot\cdot}{N}::C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} + H\overset{\cdot\cdot}{N}R'R'' \rightarrow \left[\begin{matrix} R{-}N::C::O \\ \quad\quad H\overset{\cdot\cdot}{N}R'R'' \end{matrix}\right] \qquad (C)$$

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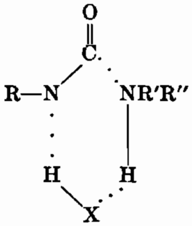
[1] HANSSON, *Svensk. Kem. Tidskr.*, **60**, 183 (1948).

[2] EGLY and SMITH, *Chem. Eng. Prog.*, **44**, 387 (1948).

[3] DAVIS and EBERSOLE, *J. Am. Chem. Soc.*, **56**, 885 (1934).

The complex, C, is converted subsequently to the urea by transfer of an amine hydrogen to the O or N of the isocyanate. Similar complexes have been postulated to account for amine catalysis of urethane formation.[1]

Hydrogen transfer appears to be a mechanistically difficult step, as judged by the complex kinetics of the isocyanate-amine reaction. The reaction of phenylisocyanate with aniline, for example, is self-catalyzed by the amine and autocatalyzed by the product urea.[2] This complicated kinetic behavior may result from formation of a six-membered cyclic complex which facilitates hydrogen transfer.



In the above formula, X represents the nitrogen atom of the amine or urea.

VIII. THERMODYNAMICS OF AMMONOLYSIS

BY A. C. STEVENSON and R. W. GRIMBLE[3]

In order to simplify this discussion, only gas-phase reactions are considered in this treatment of the thermodynamics of ammonolysis. Heats of reaction and standard free-energy changes for the principal types of ammonolytic reactions are summarized in Table 8-11.

Examination of these data indicates:

Ammonolysis and aminolysis in the gas phase are generally exothermic in nature except in the case of hydrocarbons.

The ammonolysis of unsaturated carbonyl compounds in the presence of hydrogen is the most exothermic type. Reaction of phenols, alcohols, and halides with ammonia is only slightly exothermic. Aminolysis of alcohols is much more exothermic than the ammonolysis. Reactions of hydrocarbons with ammonia to form nitriles seem to be special cases in that they are extremely endothermic in nature.

The free-energy change for most ammonolysis reactions is favorable at moderate temperatures (e.g., 300°C) except for aromatic hydrocarbons.

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[1] BAKER and GAUNT, *J. Chem. Soc.*, 1949, 9, 19, 27.

[2] CRAVEN, Symposium on Isocyanate Polymers, ACS Meeting, September, 1956.

[3] E. I. du Pont de Nemours & Company.

TABLE 8-11. ΔH, ΔS, AND ΔF FOR VARIOUS AMMONOLYTIC REACTIONS
Basis: Gaseous State at 1 Atm and 25°C

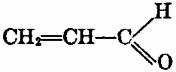
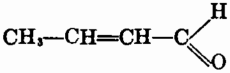
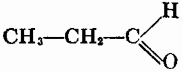
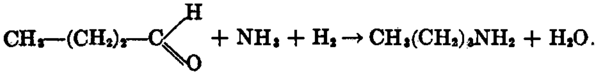
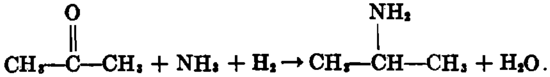
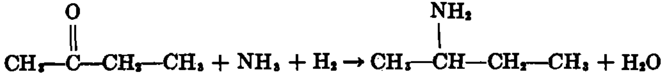
Reaction	$\Delta H^\circ_{298^\circ}$, cal/g mole	$\Delta F^\circ_{298^\circ}$, cal/g mole	ΔF_T, cal/g mole
Ammonolysis of phenols and alcohols:			
$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O$	−5,600	−5,330	$-5{,}600 + 0.9T$
$C_2H_5OH + NH_3 \rightarrow C_2H_5NH_2 + H_2O$	−3,000		
$CH_3(CH_2)_3OH + NH_3 \rightarrow CH_3(CH_2)_3NH_2 + H_2O$	−1,400		
$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$	−3,300	−1,300	$-3{,}300 + 6.7T$
$CH_3{\cdot}C_6H_4{\cdot}OH(p) + NH_3 \rightarrow CH_3{\cdot}C_6H_4NH_2(p) + H_2O$	−1,800	+680	$-1{,}800 + 8.3T$
$C_{10}H_7OH(\beta) + NH_3 \rightarrow C_{10}H_7NH_2(\beta) + H_2O$	−1,800	+680	$-1{,}800 + 8.3T$
Aminolysis of alcohols:			
$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O$	−10,200	−8,700	$-10{,}200 + 5.1T$
$CH_3OH + (CH_3)_2NH \rightarrow (CH_3)_3N + H_2O$	−12,600	−10,900	$-12{,}600 + 5.8T$
$CH_3(CH_2)_3OH + CH_3(CH_2)_3NH_2 \rightarrow [CH_3(CH_2)_3]_2NH + H_2O$	−7,200		
$CH_3(CH_2)_3OH + [CH_3(CH_2)_3]_2NH \rightarrow [CH_3(CH_2)_3]_3N + H_2O$	−2,400		
$C_6H_5NH_2 + C_2H_5OH \rightarrow C_6H_5{\cdot}NH{\cdot}C_2H_5 + H_2O$	−7,400		
Ammonolysis of halides:			
$C_6H_5{\cdot}Cl + NH_3 \rightarrow C_6H_5{\cdot}NH_2 + HCl$	−600	+1,220	$-600 + 6.1T$
$ClCH_2CH_2Cl + 2NH_3 \rightarrow NH_2CH_2CH_2NH_2 + 2HCl$	+2,400	+6,060	$-2{,}400 + 12.2T$
Ammonolysis of carbonyl compounds:			
 $CH_2{=}CH{-}CHO + NH_3 + 2H_2 \rightarrow CH_3CH_2CH_2NH_2 + H_2O$	−44,800	−25,800	$-44{,}800 + 63.6T$
 $CH_3{-}CH{=}CH{-}CHO + NH_3 + 2H_2 \rightarrow CH_3(CH_2)_3NH_2 + H_2O$	−42,800	−24,400	$-42{,}800 + 61.9T$
 $CH_3{-}CH_2{-}CHO + NH_3 + H_2 \rightarrow CH_3CH_2CH_2NH_2 + H_2O$	−15,500	−6,200	$-15{,}500 + 31.2T$

Table 8-11. ΔH, ΔS, and ΔF for Various Ammonolytic Reactions (*Continued*)

Reaction	$\Delta H^\circ_{298^\circ}$, cal/g mole	$\Delta F^\circ_{298^\circ}$, cal/g mole	ΔF_T, cal/g mole
 $CH_3—(CH_2)_2—CHO + NH_3 + H_2 \rightarrow CH_3(CH_2)_3NH_2 + H_2O$	−14,800	−5,400	−14,800 + 31.6T
 $CH_3—\overset{\overset{\displaystyle O}{\parallel}}{C}—CH_3 + NH_3 + H_2 \rightarrow CH_3—\overset{\overset{\displaystyle NH_2}{\mid}}{CH}—CH_3 + H_2O$	−13,300	−2,200	−13,300 + 37.2T
 $CH_3—\overset{\overset{\displaystyle O}{\parallel}}{C}—CH_2—CH_3 + NH_3 + H_2 \rightarrow CH_3—\overset{\overset{\displaystyle NH_2}{\mid}}{CH}—CH_2—CH_3 + H_2O$	−13,500	−1,800	−13,500 + 39.3T
Ammonolysis of aromatic hydrocarbons:			
$C_6H_5·CH_3 + NH_3 \rightarrow C_6H_5CN + 3H_2$	+50,000	+31,900	+50,000 − 60.7T
$CH_3·C_6H_4·CH_3(o) + NH_3 \rightarrow CH_3·C_6H_5·CN(o) + 3H_2$	+50,000	+31,900	+50,000 − 60.7T
Ammonolysis of olefins:			
$CH_2{=}CH_2 + NH_3 \rightarrow CH_3CN + 2H_2$	+18,200	+8,700	+18,200 − 31.7T
$CH_2{=}CH—CH_3 + NH_3 \rightarrow CH_3CN + CH_4 + H_2$	+8,000	−1,700	+8,000 − 32.6T
$CH_2{=}CH—CH{=}CH_2 + 2NH_3 \rightarrow 2CH_3CN + 3H_2$	+17,500	−5,600	+17,500 − 77.8T

Ammonolysis of aromatic hydrocarbons requires temperatures in excess of 400°C.

The column at the extreme right in Table 8-11 gives approximate expressions for the effect of temperature on the free-energy change. These expressions assume that the total heat capacity of the reaction products equals that of the reactants. In all cases, the values were computed for the gaseous state at 1 atm pressure and 25°C. Where literature data were not available, the method of calculation from group contributions of Anderson et al.[1] was used. Unfortunately, thermodynamic data computed from group contributions are not sufficiently accurate for anything other than estimation of order of magnitude of reaction equilibrium constants.

IX. DESIGN OF REACTORS AND AUXILIARIES

By Clyde Reeder[2]

Aminations by ammonolysis are usually carried out most economically at elevated temperatures and pressures. Autoclaves are commonly used for both batch and continuous processing at pressures up to 700–800 psi, whereas tubes or reaction vessels having small diameters are preferred for higher pressures. A few low-pressure reactions are carried out by batches in tubs and jacketed kettles or continuously in tubes and pipelines.

Autoclaves. Steel autoclaves, which commonly operate at pressures up to 700–800 psi, are employed for most commercial aminations. An autoclave is a vessel with an integral bottom and with a removable head which contains connections for (1) charging, (2) discharging, (3) a thermowell, and (4) a line to a frangible disc, a pressure indicator, and a vent line. Indirect heating is accomplished by using steam for temperatures up to 190°C and a circulating oil system for higher temperatures. Since the walls of autoclaves are thick, improved heat-transfer rates may be obtained with internal coils rather than a jacket.

Mechanical agitation, which is usually desirable, is necessary when the reactants are immiscible. For example, in the ammonolysis of *p*-nitrochlorobenzene using aqueous ammonia, the denser molten aromatic compound settles to the bottom if no agitation is provided. Agitation is frequently accomplished by means of high-speed propellers or vaned discs. Less intense agitation is provided by gate, anchor, and paddle types of agitators. In laboratory shaker tubes, the agitation is accomplished by shaking the entire vessel.

Two techniques have proved useful for the ammonolysis of compounds, such as 2-chloroanthraquinone, which are difficult to wet out. A vertical

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[1] Anderson, Beyer, and Watson, *Natl. Petroleum News, Tech. Sec.*, **36**, R476 (July 5, 1944).

[2] E. I. du Pont de Nemours & Company.

autoclave can be used if agitation is provided by a sleeve-and-turbine agitator (draft tube) which drags the organic compound down into the aqueous ammonia. Alternately, a horizontal autoclave can be employed. This design provides the necessary freeboard (vapor space to absorb pressure variations) with a much smaller distance between the charge level and the top of the vessel. A number of rotating splash arms wash suspended material from the top of the autoclave.

Tubular Reactors. Reactions taking place at pressures exceeding 700–800 psi are usually carried out in long tubes or in heavy walled vessels up to several feet in diameter and 50 ft in height. These reactors, for both gas-phase and liquid-phase reactions, are particularly useful where continuous processing is indicated.

In the design of high-pressure vessels, both the size and the pressure involved will dictate the type of construction used. In general the following four types[1] are used.

1. A solid-walled vessel, produced by forging or by boring a solid rod of metal, is most commonly used for vessels less than 12 in. in diameter or when the pressure exceeds 7,000 psi.
2. A bent sheet of metal with a single longitudinal weld is generally employed for wall thicknesses less than 6 in. and for pressures below 4,000 psi.
3. A vessel of any size built up of successive layers is generally more economical for working pressures in the range of 5,000–6,000 psi or when the vessel is larger than 100 tons total weight.
4. A vessel built up by wrapping a central cylinder, which by itself is not strong enough to withstand the desired working pressures, with successive layers of wire or of interlocking tape.

In choosing a vessel for the higher pressures, it is usual to obtain quotations on both the layer and forged types.

Small tubes are commonly employed where the reaction is rapid and/or the heat of reaction must be removed rapidly. The two conventional types of tubular reactors are (1) coils immersed in a constant-temperature bath and (2) a jacketed pipeline in which the inner tube is designed to withstand the reaction pressure. A modification of the conventional jacketed-pipe reactor can be used where it is desirable to minimize the thickness of the inner tube in order to reduce the area required for heat transfer. An example of this type of equipment is the liquid-phase heat exchanger of the Bureau of Mines,[2] in which the outside pipe has an outside diameter of $4\frac{1}{32}$ in. and a wall thickness of 1.005 in. The outside diameter of the inner tube is $1\frac{1}{2}$ in., but the wall thickness is only 0.16 in. The working

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[1] WILLIAMS, Pressure Technique, in "Encyclopedia of Chemical Technology," vol. 11, The Interscience Publishers, Inc., New York, 1953.

[2] *Ibid.*

pressure is 10,300 psi, but only a differential pressure is involved across the inner pipe since the heat-transfer fluid in the jacket is under pressure.

Some gas-phase reactions are carried out continuously in reactors which are essentially shell-and-tube heat exchangers. This design is useful because the high ratio of heat-transfer surface to volume simplifies temperature control and because there is only a small quantity of material in process. In a converter which is typical of this type of reactor, gaseous ammonia and a vaporized organic compound are heated in the first of two exchangers in series. The first (upper) section consists of an Inconel shell and sheet into which 170 Inconel tubes, 0.56 in. inside diameter by 22⅝ in. long, are welded. Each preheater tube is filled with crushed quartz. The lower converter section contains 55 Inconel tubes, 2.31 in. inside diameter by 44⅝ in. long, filled with the solid catalyst. Thermocouple wells are installed in five of the tubes to varying depths. The entire converter unit is surrounded by an Inconel jacket through which hot flue gases circulate.

Auxiliaries. Methods of sealing pressure in the reaction system are important in the design of equipment for amination reactions. Closures have been designed that (1) tighten up easily, (2) seal the pressure positively, and (3) open easily. Of the various closures which are now in use, only one of the simplest, the delta or triangular type of gasket, is discussed here. Other designs are discussed elsewhere.[1] The delta gasket (Fig. 8-15) is an "unsupported" type designed by E. I. du Pont de Nemours & Company. Its seal depends on the pressure inside the vessel, rather than on any external pressure applied by bolting. The chief advantages are economy and ease of vessel opening.

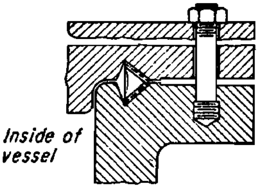

FIG. 8-15. Delta gasket.

Asbestos and lead gaskets are satisfactory for sealing flanged connections. The metal gasket is usually employed for joints that are rarely opened.

Valves for pressures below 5,000 psi are designed according to ASA standards and are generally available from stock. Valves for higher pressures may be purchased from companies which design and produce special valves.

Reactors should be protected against overpressuring by the use of a rupture disc or a relief valve. A rupture disc is a metal diaphragm supported between two steel flanges which are part of a pipeline leading directly from the autoclave to a vent. The discs, which may be stainless steel (Type 304), platinum, steel, tin, or nickel, are designed to burst at a predetermined pressure.

Since the ordinary type of spring-loaded check valve does not always reseat satisfactorily and as rupture discs have the disadvantage of allowing

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[1] *Ibid.*

the entire reactor contents to escape, the two devices are often used in parallel. In such an installation the safety valve has a lower setting and provides ordinary protection. The rupture disc for emergency protection may be designed to burst at a pressure slightly above the maximum working pressure of the vessel. Owing to the presence of the rupture disc, it is permissible to valve the line leading to the safety valve so that it may be removed for reseating if necessary.

Another method is also employed to prevent loss of the contents of the reactor. A safety valve, placed after the rupture disc, is set to open about 50 psi below the bursting point of the frangible disc. Thus, a rupture of the diaphragm is sure to be followed by the opening of the relief valve which has been protected from the corrosive vapors of the autoclave. It is usually feasible to complete the run and then replace the disc and overhaul the safety valve.

X. TECHNICAL MANUFACTURE OF AMINO COMPOUNDS

Synthetic Ammonia Manufacture

Since the technical manufacture of many important amines employs ammonia as a reactant, a resumé on its manufacture is presented.

Most of the world's ammonia supply is manufactured by the addition of hydrogen to nitrogen over an iron-based catalyst at elevated temperatures and pressures. A typical catalyst is prepared by fusing iron oxides with a small amount of potassium and aluminum oxides as promoters and reducing the granulated oxide mixture with synthesis gas to reduce the iron oxide to free iron.

The reaction of nitrogen with hydrogen to form ammonia is a highly exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

$\Delta H_{18^\circ C} = 22{,}000$ cal, and $\Delta H_{659^\circ C} = -26{,}600$ cal. It is a reversible reaction,

$$N_2 \text{ (1 vol.)} + 3H_2 \text{ (3 vol.)} \rightleftharpoons 2NH_3 \text{ (2 vol.)}$$

Since the reaction is exothermic and the volume of ammonia formed is less than the combined volume of the reactants, the amount of ammonia formed at equilibrium decreases as the temperature is increased and increases as the pressure is increased, in accordance with the Le Chatelier–Braun principle. Without catalysts, the rate of reaching equilibrium is much too slow. Even with the best-promoted iron catalysts, high temperatures around 500°C are required to give a satisfactory rate of conversion. The rate of reaching equilibrium is still too slow, however, to permit the reaction to reach equilibrium in a single pass of the reactants through a converter, and unless several converters are operated in series, it is necessary to recycle unreacted gases together with that part of the ammonia which cannot be removed economically. To compensate for the reverse effect of operating at high temperatures, pressures in the range of 200–1,000 atm are employed. Fortunately, pressure increases cause higher conversions than those calculated from the equilibrium-constant expression for ideal gases,

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}}$$

This is due to the nonideal change in the fugacities of the three gases as the pressure is increased.[1] The favorable pressure effect overbalances the adverse effect of temperature increases, which cause lower conversions than those calculated for an ideal-gas system. As the temperature approaches 700°C, the equilibrium concentration of NH_3 becomes impractically low. To obtain maximum conversion percentages at the selected operating pressures and temperatures, the law of mass action dictates that nitrogen and hydrogen be kept at the stoichiometric ratio of 1:3 and that gases which would cause lower partial pressures of the reactants should not be present. Therefore, inert gases such as methane and argon, present in the synthesis gas, must be purged at some point in the system, and the amount of ammonia recycled must be kept within practical limits.

Preparation of Synthesis Gas. Highly purified synthesis gas is a prime requirement for synthetic ammonia manufacture, and since its nitrogen content originates from air, hydrogen is the more costly component. Most of the hydrogen for ammonia production in the United States is made now by catalytically reforming either natural gas (mainly methane) or water gas with steam (see Chaps. 10 and 11). Gases containing propane and butane are also reformed. Natural gas is the major source of hydrogen. In reforming methane with steam, the reactions are as follows:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

and $$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \text{(Step 1)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (water-gas shift reaction)} \qquad \text{(Step 2)}$$

A mixture of carbon oxides and hydrogen, containing about 75 per cent hydrogen by volume, is obtained by reacting natural gas with steam over an iron or an iron-chromium catalyst.[2] The nitrogen required can be added to the natural gas before or after it goes through a reforming step. Air, combustion gases, producer gas, and blow-run gas from a water-gas unit are nitrogen sources.

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[1] PERRY, "Chemical Engineers' Handbook," 3d ed., p. 311, McGraw-Hill Book Company, Inc., New York, 1950, discusses the effect of pressure and temperature on the equilibrium constant and the position of equilibrium.

[2] SHEARON, *Ind. Eng. Chem.*, **42**, 1266 (1950); UPDEGRAFF, *Can. Chem. Processing*, **38**, 28 (1954).

After the water-gas shift reaction, the CO_2 is scrubbed from the gas with aqueous monoethanolamine solution followed by NaOH solution. The purified gas is compressed from about 0.6 to 1,000 atm (15,000 psi), and residual CO, about 1.5 per cent, is catalytically hydrogenated to methane and water.[1] Methane does not poison the ammonia synthesis catalyst, but as previously explained, it must be purged from the system with other inerts in order to maintain the optimum partial pressure of the reactants.

Commercial Manufacture: NH_3. Thompson et al.[2] give a detailed description of an operation of a modified Claude plant and pertinent data on the gas streams at various stages of the operation (Fig. 8-16). In this high-pressure plant with the converters operating at 480–620°C, about 65 per cent over-all conversion is obtained: 40 per cent in the first converter and 25 per cent in the second. Conventional plants operating at pressures between 200 and 350 atm and temperatures between 500 and 550°C obtain conversions in the range of 20–30 per cent. Although larger converters must be used in these plants for an equivalent daily output, other features, such as much longer catalyst life, less expensive high-pressure equipment, etc., counterbalance the features of the high-pressure processes.[3]

Hydrogen Cyanide from Ammonia and Natural Gas. In the general discussion of the reaction of ammonia with hydrocarbons, reference was made to the synthesis of HCN from ammonia, methane (natural gas), and air. The over-all reaction $CH_4 + NH_3 + 1.5O_2 \rightarrow HCN + 3H_2O$ can be carried out effectively at about 1000°C over platinum-alloy screen catalysts. In order to obtain optimum yields, it is necessary to use less oxygen (as air) than the amount shown in the above equation, to prevent excessive oxidation of ammonia to nitrogen oxides and methane to carbon oxides, and at the same time adjust the reactant ratios so that the reaction heat will maintain the catalyst at the proper temperature. The improved process developed by the Freeport Sulphur Company[4] is based on the somewhat incomplete information available on the operation of an I.G. Farbenindustrie pilot plant operated in Germany.[5] Pilot-plant studies by the American investigators showed that the prior procedure had the following shortcomings: (1) too much HCN decomposed after it was formed, since it was well above the decomposition temperature as it flowed from the reactor; (2) carbon was deposited on the catalyst screen, causing a loss in its activity; and (3) the catalyst screens were corroded too rapidly. The plant design and operating conditions were changed to minimize these defects.

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[1] SHEARON and THOMPSON, *Ind. Eng. Chem.*, **44**, 254 (1952).

[2] THOMPSON, GUILLAUMERON, and UPDEGRAFF, *Chem. Eng. Prog.*, **48**, 468 (1952).

[3] HEIN, *Chem. Eng. Prog.*, **48** (8), 412 (1952); MITCHELL, *Petroleum Refiner*, **25** (6), 245 (1946).

[4] UPDEGRAFF, *Petroleum Refiner*, **32** (9), 197 (1953).

[5] *O.P.B. Rept.* 73,566.

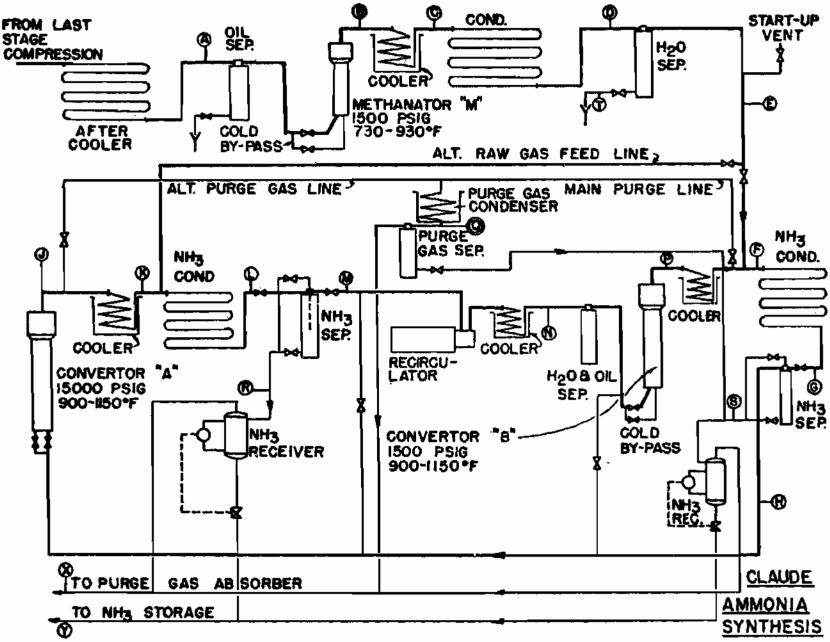

Fig. 8-16. Claude ammonia synthesis. Under 15,000 psi, a nitrogen and hydrogen mixture containing about 1.0 per cent CO, a catalyst poison, goes through a cooler and oil separator to remove moisture and oil and then through a high-pressure methanator (*A*,*B*). The methanator, loaded with iron catalyst similar to the synthesis catalyst, reduces the CO content to as low as 0.001 per cent, by hydrogenating it to methane and water. The gas entering the methanator is preheated in an interchanger by the outgoing methanator gas stream. The flow goes on through a cooler, condenser, and water separator (*B*,*C*,*D*,*E*) to join the recirculated gas from converter "*B*," (*PF*) and then passes through an NH_3 condenser. Liquid NH_3 from here goes to the NH_3 separator and then to an NH_3 receiver (*FGS*). The recycle gas (*P*) contains unrecovered ammonia and a regulated amount of inerts (CH_4 and argon), controlled by purging at the points indicated, i.e., after the reactor coolers and at the NH_3 receivers. From the ammonia separator, the gas (*H*) enters the first ("*A*") of two small converters in series, and then after conversion it flows through a precooler, ammonia condenser, and ammonia separator (*K*,*L*,*M*). It is then compressed by a recirculator and after passing through a cooler (*MN*) and a water and oil separator, enters the second converter ("*B*"). From this converter, after passing through a cooler, the flow joins the dewatered make-up gas flow (*E*) from the methanator system to complete the cycle.

A major feature of the improved process is the unique method of separating ammonia and HCN. An aqueous solution of a polyalcohol–boric acid complex is used in an absorption and desorption operation for this separation.[1]

A comparison of the data available on the two processes shows that each specifies that less than 1.5 moles of oxygen (as air) be fed to the converter

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[1] **Barsky**, U.S. 2,590,146 (1952).

per mole of NH_3. The methane:ammonia ratio is higher in the American process. The gas mixture fed to the German plant converter analyzed, in volume per cent, 11.0 NH_3, 11.5 CH_4, 14.8 O_2, and 62.7 N_2. It was fed to the converter at a rate of 183.4 cu m per hr. The outflow was 200 cu m (STP) per hr. Both converters were operated at about 1000°C. The mole per cent composition of the converted gas, per cent conversion, and the decomposition of ammonia are shown in Table 8-12.

TABLE 8-12. COMPARISON OF HYDROGEN CYANIDE PROCESSES
Mole Per Cent of Reactor Effluent (STP)

	I. G. Farbenindustrie	Freeport Sulphur Co.
Hydrogen cyanide	6.0	5.9
Ammonia	2.8	1.6
Carbon dioxide	0.35	0.2
Carbon monoxide	....	4.4
Methane	....	0.5
Hydrogen	7.75	7.5
Oxygen	4.0	0.1
Nitrogen	56.7	56.7
Water	22.8	23.1

Conversion and Decomposition

% Conversion NH_3 to HCN	60.0	67.0
% Decomposition of NH_3	12.0	18.0

In the Freeport operation, when recovered NH_3 from the 15 per cent unreacted is recycled, the over-all conversion to HCN is 74 per cent, including NH_3 and HCN lost in the recovery operation.

Figure 8-17 shows the flow through a heat-resistant alloy-metal converter joined to a waste-heat boiler, and the recovery system. The absorber is loaded with a water solution of polyalcohol–boric acid complex made from 8.3 parts pentaerythritol and 2.5 parts boric acid. In the cold, this solution dissolves HCN and ties up NH_3 as the ammonium salt of the complex, thereby preventing polymerization of HCN in the presence of free NH_3. The HCN is removed first in the stripper under moderately reduced pressure (10 in. Hg) at about 88°C, after which the NH_3 is stripped out by breaking up the ammonium salt at about 132°C under 25 psig.

For the operation of the process, the reactants are filtered from suspended scale, etc., mixed, and fed to the converter operating at about 1000°C. In order to prevent decomposition of the HCN, the gases flowing from the converter are cooled in a waste-heat boiler connected directly to the catalyst screen chamber. The steam generated is used in the recovery section. The

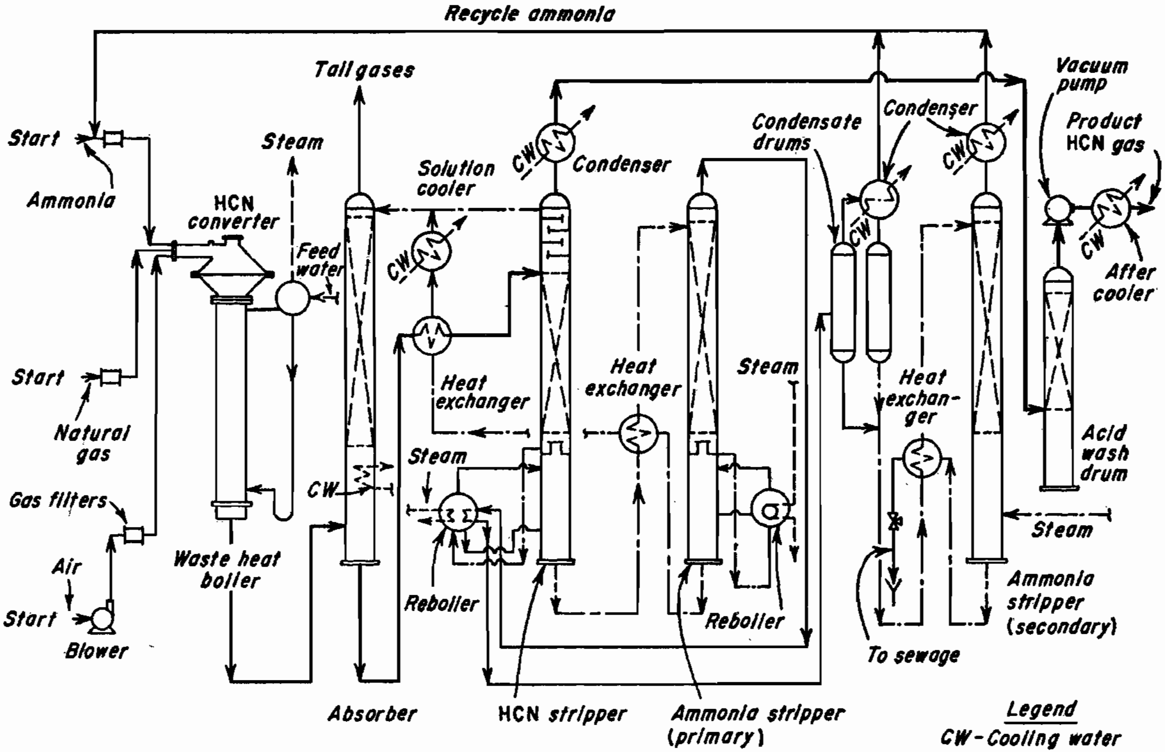
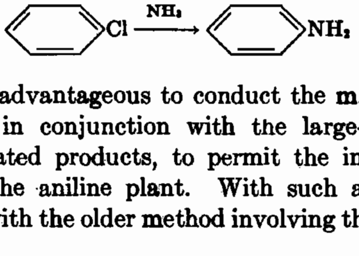


FIG. 8-17. Flow diagram: hydrogen cyanide process.

gas temperature is kept above the dew point to prevent hydrolysis of HCN. The gas enters the bottom section of the absorber, which contains a water-cooling coil, to remove the sensible and reaction heat of the gas. Tail gases are vented to the atmosphere. The solution from the absorber, containing the dissolved HCN and ammonium salt, goes through a heat exchanger into the HCN stripper, from which the HCN is stripped under reduced pressure. The upper section of the stripper is fed with fresh polyalcohol–boric acid solution to scrub out the last traces of NH_3. The washed HCN next passes through an acid washer prior to going through the vacuum pump and condenser system. Thus 99 per cent (or better) HCN is delivered at atmospheric pressure. A two-coil reboiler heats the HCN stripper. One coil uses 50 psig steam, and the other uses the steam containing overhead gases from the primary ammonia stripper. The HCN-stripped solution from the bottom of the stripper goes through a heat exchanger to the primary ammonia stripper where NH_3 is completely desorbed. A 50-psig steam reboiler heats this stripper. The overhead NH_3 and steam go to the two-coil reboiler, which heats the HCN stripper, and then to the ammonia dewatering system. From here NH_3 is recycled to the converter. Water build up in the stripping solution, arising from the H_2O formed in the converter, is eliminated from aqueous NH_3 collected in the condensate drums by employing a secondary NH_3 stripper.

A cost estimate for producing 100 per cent HCN in a 11,500-ton per year plant is presented in Table 8-13.[1]

Manufacture of Aniline from Chlorobenzene.



It is economically advantageous to conduct the manufacture of aniline from chlorobenzene in conjunction with the large-scale production of chlorine and chlorinated products, to permit the introduction of cheap chlorobenzene into the aniline plant. With such a setup, this process competes favorably with the older method involving the iron-acid reduction of nitrobenzene.

The toxic character of aniline vapors and the vicissitudes of industrial operations make it desirable to provide a fireproof housing with ample headroom and also adequate ventilation. It is, furthermore, customary to separate the high-pressure autoclave work from the subsequent separation and distillation operations. The autoclaves, which may be either vertical or horizontal, are ordinarily made of rolled steel. They are generally jacketed for use with high-pressure steam or a fluid heat-transfer agent. It

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[1] Through an agreement with Freeport Sulphur Company, the Girdler Company offers the complete process and license to use it.

TABLE 8-13. OPERATING COST ESTIMATE
11,500 Tons per Year HCN Capacity

Utilities and chemicals	Quantity/lb HCN	Unit cost	Operating cost, cents/lb HCN
Ammonia	0.85	$80/ton	3.40
Natural gas	28 std cu ft	15¢/M std cu ft	0.42
Steam (100 psig)	1.87 lb	30¢/M lb	0.06
Electric power	0.14 kwhr	0.7¢/kwhr	0.10
Cooling water	56 gal	3¢/M gal	0.17
Catalyst and chemical make-up	....	....	0.20
Total utilities and chemicals			4.35
Operating labor and overhead at $2.25/hr, 2 operators per shift			0.17
Supervision and control: 50% of operating labor			0.08
Plant maintenance: 4%/year on investment			0.24
Fixed costs: 11.5%/year on investment*			0.70
Royalty rate: 6.7%/year on paid-up fee			0.10
Total cost of HCN, ¢/lb			5.64

* Comprises 6.7 per cent depreciation, 1.3 per cent taxes and insurance, and 3.5 per cent interest on investment.

TABLE 8-14. PREPARATION OF ANILINE: EFFECT OF AMMONIA RATIO*
0.2 Mole CuO per Mole Chlorobenzene. Operating Pressure 70 Atm = 980 Psi.
Size of Charge Adjusted for 21 per cent Freeboard at Room Temperature

Mole ratio NH_3:chlorobenzene	Temp, °C	Decomposition, %	Yield of aniline, % of theory		Yield of phenol, % of theory	Ratio aniline: phenol	Yield of diphenylamine, % of theory
			% of C_6H_5Cl used	% of C_6H_5Cl which enters into the reaction			
3	187–244	89.1	78.3	87.8	5.2	15.1	1.7
4	188–239	98.5	89.0	90.5	5.3	16.8	1.8
3	193–242	84.2	72.2	85.7	5.5	13.1	1.5
4	193–237	95.5	83.5	87.5	5.5	14.8	1.9
5	192–230	99.1	88.2	88.9	5.6	15.8	1.5
6	196–229	99.6	89.8	90.2	5.5	16.6	1.0
8	194–222	99.5	90.0	90.4	5.2	17.3	1.0
12	192–215	98.2	90.6	92.3	5.0	17.9	0.0

* Vorozhtzov and Kobelev, *J. Gen. Chem.* (*U.S.S.R.*), **4**, 310 (1934).

is most important to provide thorough and turbulent mixing so that a uniform reaction mixture prevails.

Amination proceeds slowly below 160°C and very rapidly at 210°C. At still higher temperatures, there is a distinct tendency to decomposition, and the increased pressure on the system makes gastight operation more difficult. A temperature range of 200–210°C for the conversion of chlorobenzene to aniline gives very satisfactory rates. At this temperature, with a 6:1 ammonia ratio of 28 per cent NH_3, the pressure on the system will be about 850–950 psi. The influence of temperature on the course of amination is shown in Fig. 8-18.[1]

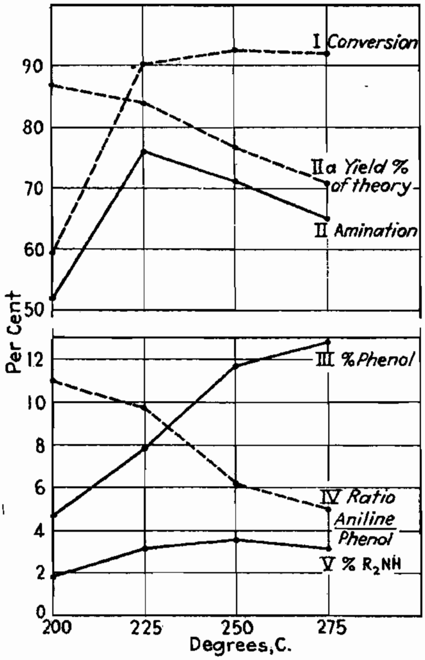

FIG. 8-18. Ammonolysis of chlorobenzene: effect of temperature (freeboard 21 per cent). Time 4 hr; 0.2 mole Cu_2O; NH_3 (33 per cent) ratio = 5.

The data in Table 8-14 show that an increase in the NH_3 ratio results in (1) a better yield of aniline, (2) an increase in the ratio of aniline to phenol, and (3) a slight diminution in the yield of diphenylamine. These characteristics are especially marked in proceeding from 3 to 5 to 6 moles of NH_3 per mole of chlorobenzene. A further increase in the ratio of aqueous NH_3 has only a relatively small effect on the conversion and yield of aniline, and its use would only diminish the productivity of the autoclaves. When very small ammonia ratios are employed, there is not only a pronounced diminution in the NH_3 concentration of the liquor toward the end of the reaction, but there is also a corresponding increase in the NH_4Cl concentration, which markedly retards the reaction.

The vapors leaving the reaction system are first expanded and then cooled below 100°C in a suitable pipe condenser or dephlegmating column. Most of the ammonia continues to an absorption system in which the gas is recovered.

Treatment of Autoclave Charge. The aqueous aniline, containing some ammonia, unconverted chlorobenzene, phenol, and diphenylamine, as well as copper and ammonium compounds, is led to a still. Here the charge may be treated with a calculated quantity of alkali to (1) decompose the am-

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[1] VOROZHTZOV and KOBELEV, *J. Gen. Chem.* (*U.S.R.R.*), **4**, 310 (1934).

monium chloride, (2) convert the phenol to alkali phenoxide, and (3) precipitate the copper as a sludge upon the removal of the free ammonia. By distillation with steam, the ammonia, chlorobenzene, aniline, and diphenylamine are removed. The remaining aqueous portion, which contains dissolved sodium phenoxide, is filtered from the copper sludge and transferred to another vessel. The phenol is recovered from the acidified solution by distillation.

An alternate and more economical procedure consists in cooling and settling the reaction mass from the autoclaves, whereby the charge separates into two layers—a dark-brown lower layer, comprising principally aniline, and an almost colorless upper aqueous layer, which rapidly becomes blue on exposure to air. The volume of the water layer will, of course, be considerably greater than that of the aniline layer and will vary with the ammonia liquor ratio. When 5 moles of 32 per cent ammonia and 0.1 mole of cuprous oxide were used per mole chlorobenzene, Vorozhtzov and Kobelev found that the products of reaction were distributed as follows:

Aniline-layer components, % by weight	Substance	Water-layer components, % by weight
81.55	Aniline	4.9
4.9	Phenol	0.33
0.85	Diphenylamine	None
Traces	Chloride ion (NH_4Cl)	8.84
Traces	Cu_2O	2.9
Traces	NH_3	13.8

To recover the aniline and other products, 50 per cent sodium hydroxide is added to the aniline-layer charge in an amount corresponding to 0.2 per cent of its volume. The batch is then subjected to fractional distillation, using jacket heat. The first fraction is aniline water, and this is followed by a technically pure aniline of 97–99 per cent purity, which contains neither phenol nor diphenylamine. The weight of aniline thus recovered corresponds to 90 per cent of the amine originally present. After the removal of the aniline, the charge still contains sodium phenoxide and diphenylamine. The latter is separated by distillation with steam, while the phenol is recovered by acidifying the residue and distilling.

Alkali is also added to the water fraction in an amount sufficient to react with all ammonium compounds and with phenol. Upon fractional distillation, ammonia is first expelled and then recovered in a suitable absorption system. An aniline-water fraction is next distilled, from which an aniline layer separates out on cooling. The supernatant aqueous portion containing a small quantity of amine can be used in the NH_3 absorption system. The residual solution of sodium phenoxide and sodium chloride is then filtered from the precipitated copper oxides. The recovered copper oxide catalyst is washed and again used alone or with fresh copper in subsequent operations.

Continuous Process for the Manufacture of Aniline from Chlorobenzene.[1] A continuous process has been patented which minimizes the corrosion difficulties encountered in the usual procedures for aminating chlorobenzene. At the high temperatures employed, even alloy steels are corroded by the ammonium chloride solution formed. This is particularly true in the batch process, where the reaction mass is stirred rapidly to obtain good mixing and where the chances of exposing the apparatus to air are greater. Excessive corrosion is also encountered in a tubular type of reactor when the tubes are externally heated as the reaction mass is passed through at a rapid rate to maintain a state of emulsification. However, if the reactant mixture is forced rapidly through a heat exchanger, which heats it to a temperature at which the reaction starts, the rate of flow can be adjusted so that scarcely any reaction takes place in the heater. The hot mixture can then be fed to an unheated reactor large enough to reduce the linear flow rate well below that required for emulsification, thereby eliminating conditions that promote corrosive attack (i.e., turbulent flow of the hot partially reacted mixture over heated metal surfaces). Since the reaction is exothermic, there is sufficient reaction heat to maintain a practical conversion rate in an insulated reactor which is not externally heated.

In the operation of the process in the above manner, the reactant mixture contains 5–6 moles of ammonia as a concentrated aqueous solution per mole of chlorobenzene and as catalyst, 0.1–0.2 atomic weights of copper in a compound such as cuprous oxide or diamino cuprous chloride. The mixture is quickly heated in the heat exchanger and slowly passed upward through the reactor while at reaction temperatures between 180 and 220°C and under autogenous pressure or higher. The preferred rate of flow through the heat exchanger is such that the residence time is less than 5 min. The residence time in the reactor is between 30 and 90 min, depending on the temperature. The preferred flow rate through the reactor corresponds to a Reynold's number less than 125,000. In the unheated insulated reactor, the exothermic ammonolysis reaction usually causes a temperature rise of 10–20°C. The reactor may be constructed with mild carbon steel. In order to provide the desired residence time and for the purpose of limiting the proportion of the reaction mixture in contact with its walls at any instant, its diameter is one-fifth or more of its height.

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[1] Williams, Holmes, and Freuhauf, U.S. 2,432,551 (1947); Williams, U.S. 2,432,552 (1947); and contribution from Dow Chemical Co.

The admixture flowing from the reactor is cooled, and the aqueous and organic layers are separated. The organic layer contains the aniline together with unreacted chlorobenzene and minor amounts of phenol, ammonia, water, diphenyl oxide, and diphenylamine. It is fractionally distilled to separate the components. Recovered chlorobenzene, water, and ammonia are recycled. The aqueous layer contains unreacted ammonia, ammonium chloride, the copper-containing catalyst, and small quantities of the organic components. A large part (e.g., one-half to two-thirds of the aqueous layer) is recycled in admixture with fresh ammonia make-up. The resulting mixture as such, or in further admixture with recycled and freshly added chlorobenzene, is fed through the heat exchanger into the reactor. It is fortunate that in this scheme of operation a considerable amount of ammonium chloride can be present in the feed mixture without causing undue corrosion and diminution of the reaction rate. If a regulated amount of the aqueous layer is recycled, the ammonium chloride concentration in the reactor system can be kept within practical limits.

The remainder of the aqueous layer is processed to recover its several valuable ingredients. This involves vaporizing unreacted ammonia and part of the water, cooling to crystallize part of the ammonium chloride, removing the crystalline material, and treating the remaining aqueous solution with an alkali, such as caustic soda or lime, to precipitate the copper compounds as cuprous oxide or hydroxide. The precipitate is separated and returned to the ammonolysis reaction. The kind and quantity of alkali used in the precipitation of the copper compounds is varied, depending on whether the ammonium chloride remaining in the mixture is desired as such or is to be decomposed for recovery of ammonia. Figure 8-19 illustrates an order in which the various steps of the process can be carried out.

This process permits conversion of half or more of the chlorobenzene in each pass through the reaction vessel with formation of aniline in yields of 95 per cent or higher, based on the consumed chlorobenzene. It also permits carrying out of the ammonolysis reaction and most of the liquor-handling steps in a closed system. It is less laborious and involves less possibility of workmen becoming exposed to the toxic reaction mixture or its vapor than the older batch method of carrying out the reaction.

Preparation of N-Methylaniline from Chlorobenzene.

$$C_6H_5Cl + 2CH_3NH_2 \xrightarrow{Cu_2Cl_2} C_6H_5NHCH_3 + CH_3NH_2{\cdot}HCl$$

The aminolysis of chlorobenzene with methylamine occurs under approximately the same conditions as ammonolysis to give N-methylaniline. Hughes et al.[1] have found the optimum conditions to be (1) cuprous chlo-

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[1] Hughes, Veatch, and Elersich, *Ind. Eng. Chem.*, **42**, 787 (1950).

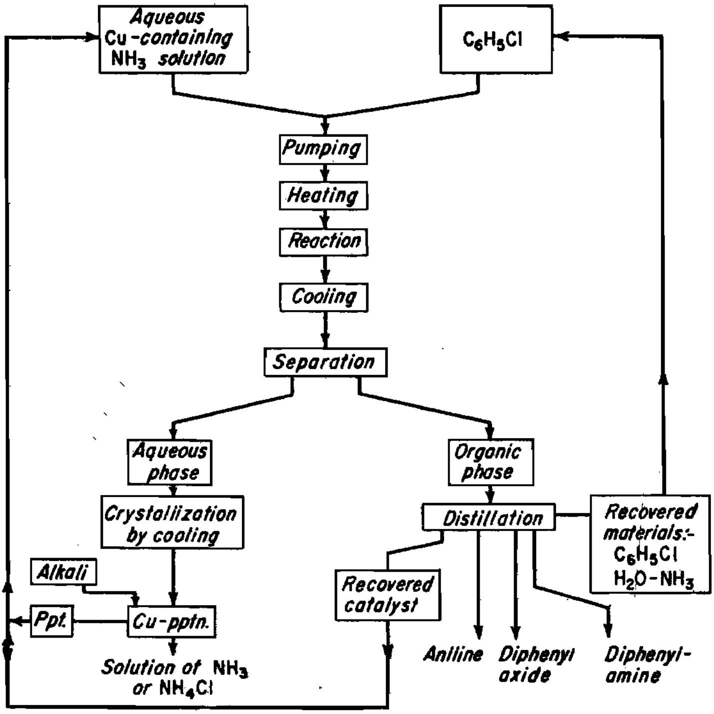

FIG. 8-19. Aniline via continuous ammonolysis of chlorobenzene: process steps.

ride as catalyst, in a concentration of 0.4–0.6 mole per mole chlorobenzene; (2) reaction temperature, 215°C; (3) reaction pressure (not an independent variable) about 900–1,100 psi under conditions noted; (4) methylamine concentration, 60 per cent in aqueous phase; (5) mole ratio of methylamine to chlorobenzene, 5:1; and (6) reaction time, about 30 min.

Hughes and coworkers have proposed a continuous process (Fig. 8-20) and have suggested its use for the production of aniline as well as methylaniline.[1] The salient features pertain to the continuous partial elimination of the sodium chloride, stemming from the treatment of part of the aqueous portion of the reaction mass with alkali, for the recovery of methylamine without precipitation and filtration of the copper catalyst.

Operations. The charge to the reactor consists of 500 parts by weight of 60 per cent aqueous methylamine (saturated with NaCl at room temperature) and 240 parts by weight of cuprous chloride. Chlorobenzene, 220 parts, is delivered to the reactor by a separate line and the mixture

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[1] Hughes, U.S. 2,455,931; 2,455,932 (1948); Hughes and Veatch, U.S. 2,490,813 (1949).

stirred for 30 min, the temperature being kept at 215°C. The product goes through a condenser to a "settler," where the lower organic layer is drawn off and sent to a fractionating column. Here, unconverted chlorobenzene (about 10 per cent) is separated and recycled.

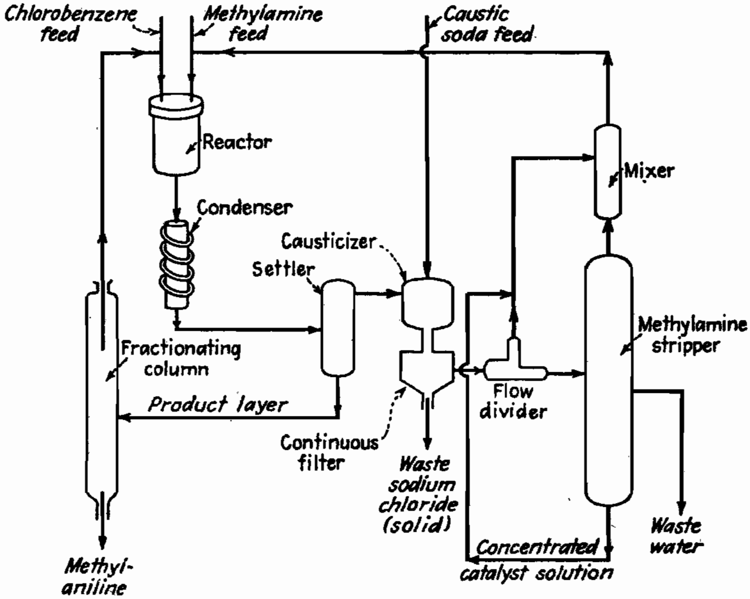


FIG. 8-20. Flow diagram: continuous production of N-methylaniline.

The aqueous layer in the causticizer is treated with stoichiometric quantities of sodium hydroxide to decompose the methylamine hydrochloride with the precipitation of salt. If vigorous agitation is employed in this step, the copper catalyst remains in solution and can readily be recycled. The salt is removed in a continuous filter.

To maintain the desired methylamine concentration, the filtrate is divided into two streams. One stream is sent to a methylamine stripper where the amine is removed overhead and blended with the untreated stream. The catalyst solution remaining in the stripper is drawn off at the base, with just enough water to maintain desired concentrations, and delivered to the mixer. The recycled aqueous methylamine-catalyst mixture is fortified with fresh reactants before entering the reactor.

As would be expected, the presence of sodium chloride in the recycled reactants causes an appreciable reduction in the conversion rate (Fig. 8-21). Notwithstanding this effect, the rates under optimum conditions are practical, and the per-pass conversion of 90 per cent is relatively high.

Vacuum distillation of the product gives two fractions: (1) comprising 92 per cent of the material boiling above chlorobenzene, which contains more than 96 per cent methylaniline, and 3 per cent (±1.5 per cent) phenolic impurity; (2) comprising 8 per cent higher-boiling-point material, which is chiefly a compound of the diphenylamine type, possibly N-methyldiphenylamine, $CH_3 \cdot N(C_6H_5)_2$. The presence of so much tertiary amine suggests that methylaniline is more basic and hence more reactive than aniline under reaction conditions.

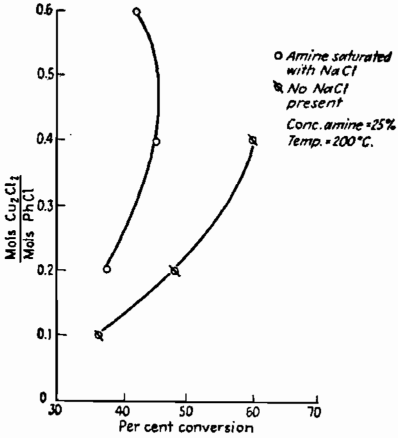


FIG. 8-21. Effect of sodium chloride on aminolysis of chlorobenzene.

2-Aminoanthraquinone from 2-Chloroanthraquinone. By the use of potassium chlorate and ammonium nitrate as oxidants, it is possible to obtain directly a 2-aminoanthraquinone of 97.5–98.5 per cent purity. A copper catalyst is not essential but is sometimes used to moderate the conditions of the reaction. The only treatment required is a thorough washing of the 2-aminoanthraquinone with hot dilute aqueous ammonia or dilute sodium hydroxide.

By employing 7.5 parts of 28 per cent ammonia liquor per part of 2-chloroanthraquinone (molar ratio 25:1) and heating at 200°C, the reactions can be completed in 24 hr; at 210°C, only 15 hr is required. It is advisable to fill the autoclave up to 75 per cent of its capacity with the aqueous ammonia in order to ensure against excessive freeboard.

At the completion of the reaction, the ammonia vapor is vented to the absorbers until the residual pressure is about 200 lb. The charge is then delivered to a steel vessel containing dilute sodium hydroxide, to decompose the combined ammonia. When the hot reaction product is brought in contact with the caustic solution, a finely divided brown product is obtained. When the product crystallizes out from its mother liquor in the autoclave, fine, long, purple-brown needles are obtained.

The ammonia is removed by distillation with steam, most of the by-product hydroxy compounds going into solution as the sodium salt during this operation. The aminoanthraquinone is then filtered hot and washed with hot dilute alkaline solutions. Generally, no purification operation is required. The results obtained by the foregoing procedure are set forth in Table 8-15.

Table 8-15. Effect of $KClO_3$-NH_4NO_3 Mixtures in Ammonolysis of 2-Chloroanthraquinone

2-Chloroanthraquinone, 36.375 G. 28 Per Cent Aqueous NH_3, 315G. Capacity of Autoclave, 500 Cc.

Expt.	Binary mixture		Temp, °C	Time, hr	Yield, %	Purity, %	Net yield, %
	Materials	G					
1	$KClO_3$	1.0	195	24	96.5	95.5	92.1
2	$KClO_3$ NH_4NO_3	1.0 8.0	195	24	96.5	97.7	94.3
3	$KClO_3$ NH_4NO_3	0.5 6.0	200	18	97.8	97.6	95.5
4	$KClO_3$ NH_4NO_3	0.5 6.0	200	18	97.8	98.0	95.8
5	$KClO_3$ NH_4NO_3	1.0 8.0	200	18	97.4	98.5	95.9

Preparation of *p*-Nitroaniline in Jacketed Autoclaves. A batch consisting of 500 lb of molten *p*-chloronitrobenzene and 2,600 lb of 26°Bé ammonia (mole ratio NH_3:PCNB, 15:1) is introduced into a 500-gal autoclave provided with an efficient stirrer. The ammonia liquor is run in first in order to prevent the formation of a mass of fused nitro compound at the base. The heating is at first very gradual, so that the operating temperature of 175°C, corresponding to a pressure of 530–580 psi, is not reached until after the expiration of 3 hr.

The heating of the autoclave is continued for 16 hr at 175°C, at which time the conversion to amine is practically complete. Some of the ammonia gas is vented to the absorption system, and when the residual pressure on the autoclave has dropped to 200 lb, the pressure-relief line is closed, as it is then safe to effect a transfer of the charge from the autoclave to the ammonia still (containing the calculated quantity of hydrated lime) by means of the residual autoclave pressure (see Fig. 8-22).

The still is usually a large steel vessel of 1,500-gal capacity, which can conveniently hold two autoclave charges under ordinary conditions and a third one in case of an emergency. It is provided with an agitator, injector pipe for live steam, gas line to the ammonia absorbers, and vent to the atmosphere, the latter enabling the operator to determine when the removal of ammonia is complete.

When all the ammonia has been removed from the still, the lines to the absorbers are closed, and the steam pressure on the kettle is brought up to 60 lb. The charge is then passed through a pressure filter.

The crystallizing tubs are large wooden vats provided with wooden

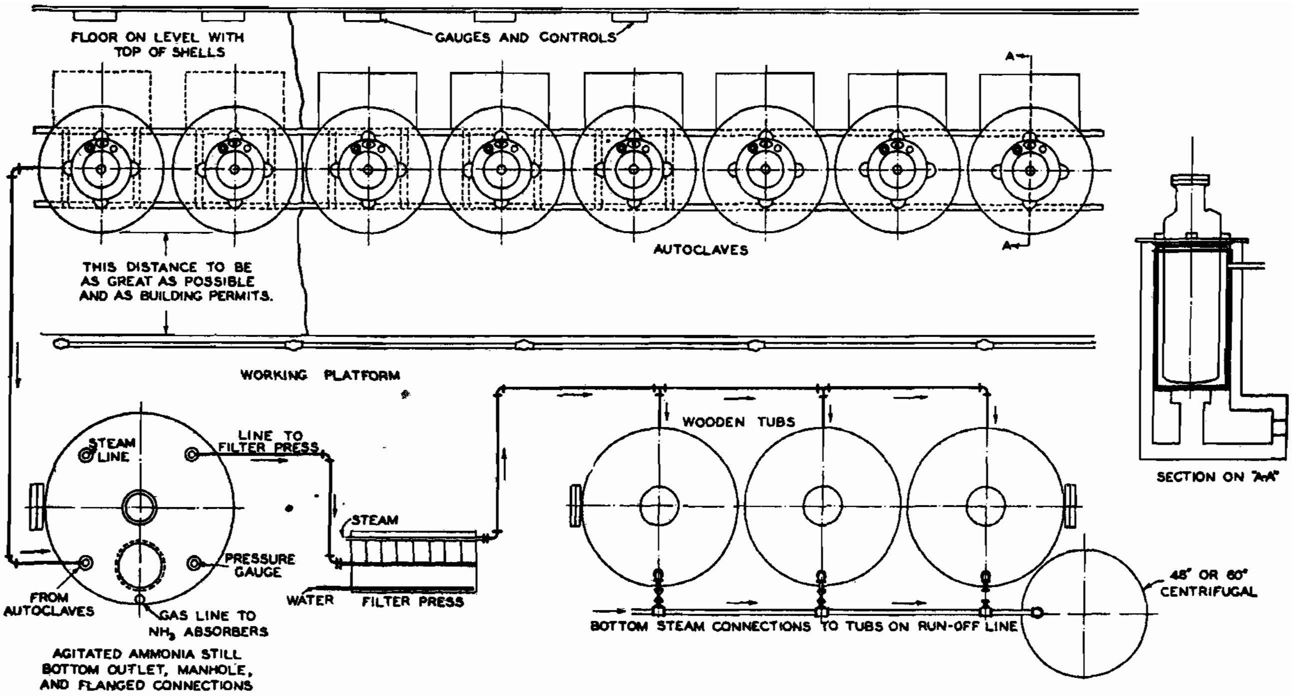


FIG. 8-22. Plant assembly for preparation of water-soluble amines.

stirrers. They are tightly covered and provided with wooden flumes which serve to remove the toxic vapors. As a result of the sudden drop of both temperature and pressure, the *p*-nitroaniline, on entering the tub, immediately crystallizes out of solution as a very finely divided canary-yellow product.

Through a process of condensation, 4,4′-dinitrodiphenylamine is produced as an impurity. Being a secondary amine, it does not diazotize; consequently, when the *p*-nitroaniline made by this process is diazotized in the course of preparing lakes or dyestuffs, it will be observed that a flocculent precipitate consisting of approximately 0.3 per cent of the total product will remain in suspension as an inert solid impurity. This characteristic at one time was a powerful influence militating against a universal acceptance of this product, despite the fact that its purity averages 99 per cent, as well as the knowledge that the diazonium solution can be easily filtered. In order to remove this objectionable characteristic, recourse may be had to the use of mild reducing agents such as sodium sulfide. The reductoactive material is placed in the crystallizing tubs prior to the entry of the charges from the filter press. These agents, by acting on the small amount of dinitrodiphenylamine that is present, serve to effect a distinct

TABLE 8-16. *p*-NITROANILINE OPERATING BUDGET
Steam-jacketed Autoclaves

Operations involved	*Loss in yield, %*
Sources of loss of *p*-nitroaniline:	
Impurities in *p*-nitrochlorobenzene, including losses in transfer	1.0
Charging, autoclaving, filtering	0.5
Wash waters and centrifugal operations	1.0
Mother liquor and cleaning catch boxes	2.0
Drying and packaging	0.5
Total calculated loss in yield	5.0
Per cent yield of theory for good operations	95.0*
	Total used, loss, %
Sources of loss of ammonia liquor:	
Delivery to operation system, including storage losses	0.5
Charging and discharging of autoclaves	0.5
Free and combined NH_3 left in mother liquor	1.0
Losses in absorber system	2.0
Leaky stuffing boxes and operating losses	2.0
Total operating loss of NH_3	6.0†

* Small-scale operations show that yields of 96–97 per cent of the theoretical are possible.

† This figure does not, of course, include the ammonia entering into the reaction. The NH_3 consumed in the reaction is usually based on the *p*-nitroaniline delivered. This is obviously high, for the preceding data on *p*-nitroaniline losses show that some of the amine that consumed NH_3 in its preparation was lost in process.

improvement in the clarity of the diazonium solution of the *p*-nitroaniline thus treated. A similar improvement can be effected by recrystallizing the amine under pressure from weakly ammoniacal solutions, the enolized dinitro compound staying in solution.

The charge in the crystallizing tub is cooled to 30°C and is then delivered by gravity to a centrifugal. The mother liquor leaving the centrifugal flows to an elaborate system of catch boxes, where it is cooled. Periodically, the water in the catch boxes is siphoned out to permit removal of the settled *p*-nitroaniline.

Continuous Preparation of Nitroanilines. The I.G. Farbenindustrie developed a continuous process for the ammonolysis of *o*-chloronitrobenzene, *p*-chloronitrobenzene, 2,5-dichloronitrobenzene, and 3,4-dichloronitrobenzene to *o*-nitro-, *p*-nitro-, 4-chloro-2-nitro-, and 2-chloro-4-nitroanilines, respectively. The facilities are shown diagrammatically in simplified form in Fig. 8-23.

The optimum conditions for the preparation of the related nitroanilines with aqueous 40 per cent NH_3 are set forth in Table 8-17.

TABLE 8-17. AMMONOLYSIS DATA ON AROMATIC HALIDES

	Feed rate, kg/hr	Moles of NH_3/mole of compound	Temp, °C, reaction zone	Space velocity/hr (reaction chamber)
o-Nitroaniline	28.8	12:1	225–230	6.1
p-Nitroaniline	21.3	17:1	237–240	5.7
4-Chloro-2-nitroaniline	38.5	10:1	205–208	7.3
2-Chloro-4-nitroaniline	36	12:1	230–236	8.1

Operating Procedure. The chloronitrobenzene, liquid ammonia, and aqueous ammonia (to give a 40 per cent NH_3 solution) from the respective storage vessels pass through measure vessels to the Balke pumps (*B*), which in turn force the liquids at 200 atm pressure to the mixing nozzle. The mixture then flows through the preheater, where it is heated with steam to 180°C, and then to the steel (2.5 per cent Cr, 0.5 per cent Mo, 0.5 per cent W) reaction coil immersed in an oil bath which is of the hairpin type. It is there heated to the required temperature. The completion of the reaction takes place in the insulated finishing towers (T_1 and T_2) which are not heated during operation. The pressure (200 atm) in the reaction space is held through regulation of the expansion valve (*EV*) immediately before the expansion vessel into which the mixture of nitroaniline, water, ammonium chloride, and excess ammonia is released through an inlet pipe set tangentially, so that atmospheric pressure is attained. In the expansion

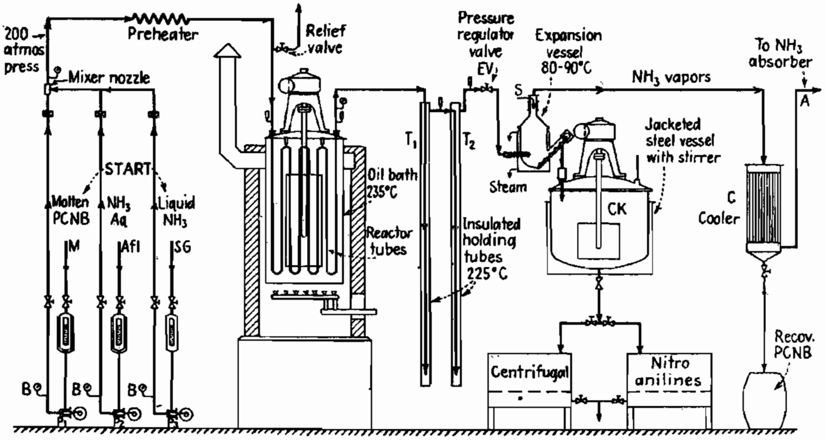
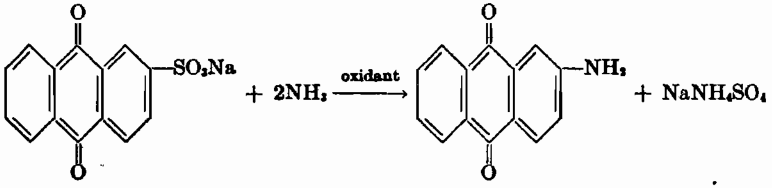


Fig. 8-23. Flow diagram: continuous production of nitroanilines.

vessel, which is sprayed from above by hot condensed water from a jet (*S*), the magma released from pressure rises to an average temperature of 75°C and the majority of the excess ammonia passes off in the exit gases through the cooler (*C*) to the ammonia absorption system (*A*). To vaporize as much ammonia as possible, the magma in the expansion vessel is heated to 80–90°C with external circulation of hot water and by the injection of steam. The magma consist of finely divided nitroaniline and ammonium chloride solution. It is carried from the bottom of the expansion vessel by an inclined eccentric screw to the runoff pipe, down which it flows into the water-cooled agitated vessel (*CK*), from which it is run as required to filters or centrifugals.

The preceding scheme was blueprinted by I.G. Farbenindustrie for large-scale operations, in which the ammonium chloride in the *p*-nitroaniline mother liquor was liberated by the addition of lime, and recovered. The German product was frequently dark and contained acetone insolubles. This handicap could in all probability be remedied by the insertion of a set of small-pressure filters in the line between the holding tubes and the expansion vessel. Experience has shown that such a technique leads to a canary-yellow, finely divided product.

2-Aminoanthraquinone from Sodium Anthraquinone-2-sulfonate.



The preparation of 2-aminoanthraquinone from "silver" salt presents no particularly difficult technical problems. Compared with the preparation of the amine from 2-chloroanthraquinone, this reaction may be carried out under distinctly milder conditions. The reactants NH_3 and anthraquinone-2-sulfonic acid (Na salt) are both present in aqueous solution, and the conversion to amine takes place readily.

As the reaction progresses, the amino compound separates out as a light, golden-brown product. The 2-aminoanthraquinone obtained by this process generally averages 99 per cent pure, by titration with sodium nitrite. The yields range from 90–94 per cent of the theoretical. Copper and its salts are not necessary, the best results being obtained by employing the technique involving the use of oxidants and the ammonium salts of oxidizing acids.

A number of important technical and economic considerations are involved in the use of sodium anthraquinone-2-sulfonate (silver salt) for the preparation of 2-aminoanthraquinone. The cost of chloroanthraquinone is approximately the same as anthraquinone when they are prepared according to the Friedel-Crafts reaction. The former lends itself to the direct production of an amine of 97–98.5 per cent purity. The product from silver salt is, however, of a higher purity and can, furthermore, be prepared at a lower operating temperature (viz., 170–180°C) so that steam-jacketed equipment can be employed. Consequently, despite economic handicaps, the silver-salt process is firmly entrenched and is used to a considerable extent.

When anthraquinone-2-sulfonic acid is made by the sulfonation of anthraquinone according to traditional methods, its cost is distinctly higher than that of 2-chloroanthraquinone because of extra operating steps and the fact that disulfonic acids are formed during the sulfonation process. The cost of production may be somewhat lowered by cyclizing the intermediate benzoylbenzoic acid with 96 per cent sulfuric acid at 130°C and then sulfonating the anthraquinone thus formed by the addition of oleum. Another and more economical method involves the conversion of 4′-chloro-2-benzoylbenzoic acid to the sulfonic acid derivative by treatment with sodium sulfite under pressure and then cyclizing the sulfobenzoylbenzoic acid to anthraquinone-2-sulfonic acid. It is clear that this process results solely in the formation of "silver salt," and experience shows that the yields are good and that it can be converted to 2-aminoanthraquinone of high purity.

Conversion of Methanol to Methylamines

Mono-, di-, and trimethylamines are obtained by the reaction of methanol with ammonia under a pressure of 50 atm at about 380–450°C, over an aluminum oxide catalyst. It is difficult and often uneconomical and impracticable to arrange operating conditions for the production of only one of the amines. It is customary, therefore, either to rework the products under suitable conditions or to reintroduce them into the amination system along with fresh reactants.[1] Swallen and Martin have shown that primary methylamine can be converted to dimethylamine and trimethylamine by repassing it through the catalytic chamber in the absence of ammonia. The results obtained when methylamine and various mixtures of it were passed over a partially dehydrated aluminum trihydrate catalyst are set forth in Table 8-18.

TABLE 8-18. EQUILIBRIUM STUDIES: PREPARATION OF METHYLAMINES*

Composition of feed	Temp, °C	Space velocity, $\frac{\text{cc gas}}{\text{cc catalyst}}$	Composition of product, %			
			NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
100% CH_3NH_2	450	550	33.2	31.8	31.4	3.6
	450	550	31.8	31.3	32.6	4.3
87.0% CH_3NH_2 13.0% $(CH_3)_3N$	425	400	27.0	25.3	33.1	15.6
	425	400	25.4	29.8	27.7	17.1
	450	670	35.2	27.6	24.4	12.9
	450	630	39.0	33.6	16.3	11.1
	450	550	29.2	26.5	29.8	14.5
	450	550	30.4	26.4	28.6	14.6
	475	510	40.0	28.2	16.4	15.3
	475	420	38.0	26.6	17.4	18.0
65.0% CH_3NH_2 20.2% $(CH_3)_2NH$ 14.8% $(CH_3)_3N$	450	680	38.6	23.6	17.4	20.4
	450	350	32.0	25.8	26.2	15.9

* Swallen and Martin, U.S. 1,926,691 (1933).

Operating Procedure.[2] Methanol and ammonia are delivered at an hourly rate of 250 and 650 liters to a mixer (Fig. 8-24) and passed to a holding tank. The mixture is pumped through a heat exchanger where it is vaporized, then brought to the reaction temperature, 380°C, in a preheater, and finally led over the catalyst at 50–60 atm. The reaction product is passed through a pressure-reducing valve and heat exchanger and collected in a receiver maintained at 25 atm. The mixture of methylamines is first separated from water in a column at 18 atm and 180°C. The dehydrated ammonia-amine mixture is injected by a pump into a

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[1] Herold and Smeykal, U.S. 2,068,132 (1937); Swallen and Martin, U.S. 1,926,691 (1933).

[2] *F.I.A.T. Final Rept.* 716, operations at Ammoniak Merseburg at Leuna.

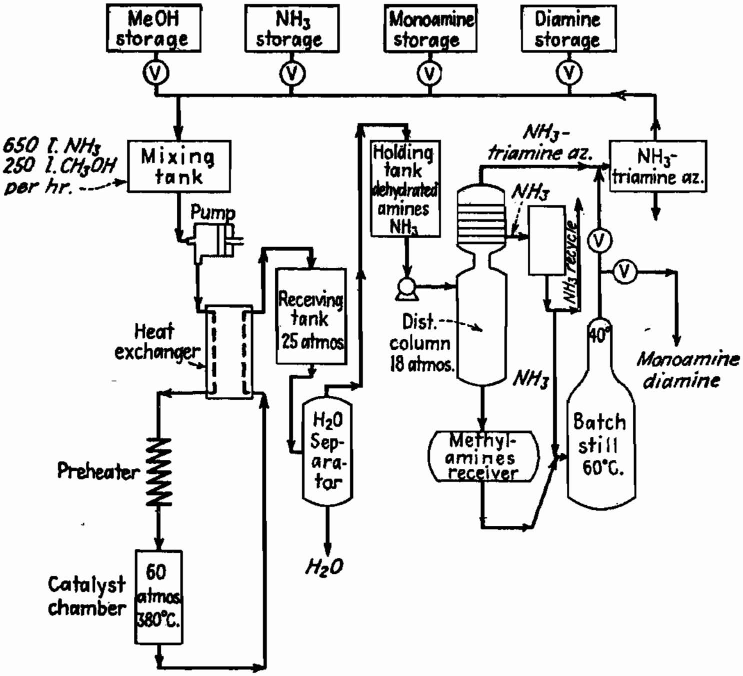

FIG. 8-24. Flow diagram: preparation of methylamines.

distilling column where the ammonia-triamine azeotrope is largely removed at the top, ammonia for recycling is bled off at the upper middle of the column, and the bottoms comprising mono-, di-, and some trimethylamines are drawn off at the base.

The final treatment depends on the industrial demands for particular amines. Unlike the higher alkylamines which can be separated from one another by careful fractionation, the methylamines, because of the closeness of boiling points (Table 8-19), have to be separated by involved azeotropic

TABLE 8-19. PROPERTIES OF ETHYL- AND METHYLAMINES

Substance	Bp, °C	Sol.: H_2O, g/100 cc	Dissociation constants
$C_2H_5NH_2$	16.5	∞	0.00056
$(C_2H_5)_2NH$	55.9	81.5	0.00126
$(C_2H_5)_3N$	89.5	1.5	0.00064
CH_3NH_2	−6.8	Sol.	0.00047
$(CH_3)_2NH$	7.4	Sol.	0.00102
$(CH_3)_3N$	3.5	V. sol.	0.00055

distillations. Because of its minor importance, the trimethylamine as an azeotrope with ammonia is frequently returned to the initial mixing tank with fresh methanol as described below, resulting in the establishment of an equilibrium favoring the formation of mono- and dimethylamines. When both mono- and triamines are returned, practically all the added methanol is converted to dimethylamine, as can be seen from Table 8-20.

TABLE 8-20

Constituent	Charge, wt %	Products, wt %
Ammonia	28.4	25.7
Monomethylamine	12.0	10.6
Dimethylamine	0	18.0
Trimethylamine	39.7	38.2
Methanol	19.9	0

According to Bogrow,[1] the practice of Ammoniak Merseburg at Leuna is to deliver the mixture of amines from the distilling column to batch stills (Fig. 8-24). Here, the residual trimethylamine is removed as an azeotrope at 15 atm by repeated introduction of recovered ammonia. The still pressure is then lowered to 6 atm to separate the monoamine, and finally to 4 to 2 atm to recover dimethylamine. The ammonia-trimethylamine fraction may be recycled as noted above or may be treated separately by compressing to 60 atm and heating at 430°C. Under these conditions and in the presence of an aluminum oxide catalyst, approximately 60 per cent of the triamine content of the azeotrope is converted to mono- and dimethylamines.

Using an NH_3:CH_3OH ratio of 2.6:1 and a feed rate of 900 liters per hour (as noted above), this procedure leads to the production of 40 tons monomethylamine and 25 tons dimethylamine per month. Approximately 100 tons methanol and 35 tons liquid ammonia are required.

Physical Processes for Separating Methylamines. Since the cost of separating methylamines is a major item, much effort has been put into developing separation processes. There are numerous patented separation procedures based on the differences in the physical and chemical properties of these products. For example, Babcock found that the vapor-pressure curve of trimethylamine does not parallel the practically parallel curves of NH_3, mono- and dimethylamine.[2] It intersects the dimethylamine curve at about 55 psia, and furthermore, when a mixture of trimethylamine and dimethylamine is distilled above this pressure, a dimethylamine-rich

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[1] BOGROW, *F.I.A.T. Final Rept.* 716, *O.P.B.* 88,843.

[2] Babcock, U.S. 2,049,486 (1936).

azeotrope (about 72 per cent di-) distills over, leaving trimethylamine behind. However, at atmospheric or pressures well below 55 psia, the situation is reversed and a trimethylamine-rich azeotrope (about 75 per cent tri-) distills over, leaving dimethylamine behind. Thus, when a 60 per cent trimethylamine, 40 per cent dimethylamine mixture is distilled under 122 psia, the dimethylamine-rich azeotrope comes over at 73.2°C, and 95–100 per cent trimethylamine is left behind for recycle to the reactor. When the dimethylamine-rich azeotrope is next distilled at atmospheric pressure (15–25 psia is preferred), the trimethylamine-rich azeotrope comes over at 3.1°C, and pure dimethylamine remains. Returning the trimethylamine-rich azeotrope to the first distillation completes the cycle.

Several processes are based on the solubility relationships and partial-pressure differences of the amines in water and certain organic solvents. The advantage of such procedures is that repeated distillations of trimethylamine azeotropes can be eliminated. When it is recalled that trimethylamine forms a binary azeotrope not only with NH_3, but with mono- and dimethylamines as well, and that mono- and dimethylamine mixtures, boiling about 14°C apart, can be conveniently separated by fractional distillation, it can be seen why much effort has been put into developing processes to separate trimethylamine more conveniently than by fractional distillation alone.

A unique process, involving extractive distillation, using water as the solvent, is based on the following facts.[1] In water at working temperatures between about 25–90°C, trimethylamine is the least soluble of the three methylamines. At 70°C, for example, trimethylamine is only one-eighth as soluble as monomethylamine and less than one-fifth as soluble as dimethylamine. In this case, the solubility relationship remains about the same when the pressure on the system is increased, thereby permitting condensation of NH_3 and amine gases with cooling water when the entire system is operated under sufficient pressure. An operation using water is carried out as follows. Ammonia is distilled from the reactor mixture under about 200–250 psi. The amine mixture is fed to the extractive distillation column operating at 150–175 psi. In this step, heated water is fed to the top of the column sufficient to dissolve the mono- and dimethylamine from the amine mixture fed to a lower part of the column. The water:amine ratio is such that only undissolved trimethylamine gas is evolved from the top of the column and an aqueous solution of mono- and dimethylamines flows from the bottom. Mono- and dimethylamine mixture is stripped from the water at 125–150 psi and then fractionally distilled at 100 psi. All the gases evolved in the entire operation are condensed in water-cooled condensers.

Since the development of the above process, extraction processes using

[1] Spence, U.S. 2,119,474 (1938).

organic solvents have been patented. Solvents such as aniline, mono- and diethanolamine, carbitol, ortho-dichlorobenzene, and monomethylformamide, among others, are mentioned. In these solvents dimethylamine is considerably more soluble than NH_3 and the other amines. For example, at 20 and 40°C, respectively, one volume of liquid aniline dissolves the following gas volumes: NH_3, 40 and 27; mono, 271 and 122; di, 520 and 183; tri, 300 and 98. An extraction process employing aniline at atmospheric pressure is described by Tyerman.[1] The NH_3-amine mixture, stripped from water and methanol, is fed to a packed column countercurrent to aniline. Aniline solution of dimethylamine flows from the bottom of the column at 35°C. NH_3, mono-, and trimethylamine gas mixture from the top of the column passes into an aniline presaturator kept at 20°C. Saturated aniline overflows from the presaturator via a U seal to the top of the column, and the NH_3, mono-, and trimethylamine gas evolved from the presaturator is absorbed in water, from which it can be stripped, and returned to the aminator. Dimethylamine is stripped from the aniline solution, and the aniline is returned to the aniline presaturator, which feeds the column. Part of the free dimethylamine is fed back to the bottom of the extraction column to maintain the replacement of the other components in the mixture.

A process which takes advantage of both the solubility characteristics and chemical properties of the amines is one which employs selective absorption in weakly acidic compounds such as cresols.[2] Solubility is influenced not only by the solvent, but by the different basicities of the amines, as indicated under dissociation constants in Table 8-19. According to this process, mono- and dimethylamine are separated from trimethylamine by countercurrent extraction of the mixture with cresol saturated with water. The undissolved trimethylamine overhead is the least soluble in various solvents and is more weakly basic than dimethylamine. Prior to extraction, NH_3 can be removed, under specific conditions, from the three amines by countercurrent extraction with 17 per cent NaOH solution. This operation gives a mixed amine gas overhead and an NaOH solution of NH_3. Under another set of conditions employing 10 per cent NaOH solution in lower volumes, 100 per cent trimethylamine is the overhead gas.

Separations Involving Chemical Reaction. One process is based on the fact that reaction rates of NH_3, mono-, and dimethylamine with methylformate, which is converted to a mixture of formamides, are quite different.[3] The order is as follows: di $>$ mono $>$ NH_3. Therefore, when less than the theoretical quantity of methylformate is continuously reacted under specific conditions with a mixture of NH_3 and the three amines, most of the di-

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[1] Tyerman, U.S. 2,570,291 (1951).

[2] Knust, U.S. 2,705,246 (1955); Brit. 686,500 (1953).

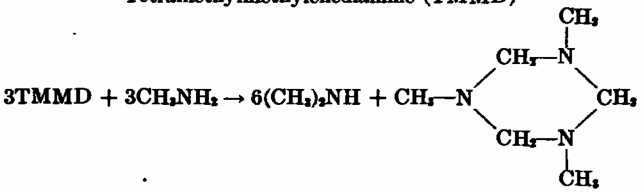
[3] Tyerman, U.S. 2,310,478 (1941).

methylamine, about half the monomethylamine, and a minor amount of NH_3 are converted to formamides. Ammonia, unconverted monomethylamine, and unreactive trimethylamine can be distilled easily from the higher-boiling mono- and dimethylformamides. Hydrolysis of the formamide mixture yields mono- and dimethylamines which are readily separated by fractional distillation.

A later procedure involves the formation and transformation of formaldehyde reaction products.[1] The chemistry of this process is as follows:

$$2(CH_3)_2NH + CH_2O \rightarrow H_2O + (CH_3)_2N{\cdot}CH_2{\cdot}N(CH_3)_2$$

Tetramethylmethylenediamine (TMMD)



Trimethyltrimethylenetriamine (TMTMT)

$$\text{TMTMT} + \text{heat in presence of } H_2 \rightarrow 3CH_3N{=}CH_2 \text{ (transient monomer)} \xrightarrow[\text{Ni catalyst}]{H_2} 3(CH_3)_2NH$$

According to this scheme, dimethylamine is produced without recycling monomethylamine to the aminator, since the monomethylamine is converted to dimethylamine by hydrogenating the transient aldimine. The advantages claimed for this dimethylamine process are that only the unreactive trimethylamine is recycled and that it does away with fractional distillations under pressure.

Hydroammonolysis of Ketones, Aldehydes, and Acids

In general, the products of conversion of low-molecular-weight ketones and aldehydes by hydroammonolysis are similar to those obtained by the ammonolysis of alcohols. Acetone thus yields a mixture of mono-, di-, and triisopropylamines, and isobutyraldehyde gives similar isobutylamines.[2] Equipment of the type shown in Fig. 8-24, for the conversion of alcohols, or that shown in Fig. 8-25, for the hydroammonolysis of stearic acid, may be used with slight modification. The reactions are exothermic, and while the catalyst is fresh, the reaction velocity is very high. The catalytic reactor temperature is maintained by water-cooling coils within the desired temperature range, 80–160°C, depending on the specific carbonyl compound undergoing reaction. Only a slight hydrogen-ammonia pressure (2–3 atm) is required. An ammonia ratio of about 10:1 is used, the excess being

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[1] Isham, U.S. 2,657,237 (1953).

[2] *F.I.A.T. Final Repts.* 716 and 1081.

continuously recovered and recycled with fresh material. A large excess of hydrogen is cycled through the system along with necessary make-up gas. The catalysts for hydroammonolysis are a mixture of 1 part tungsten and 2 parts nickel sulfides. For the preparation of stearylamines, as described below, equal parts of molybdenum and nickel sulfides are used.

Stearylamine Manufacture. Distilled technical stearic acid is melted in a kettle and pumped through heated lines to the receiving tank, Fig. 8-25, from which it flows to a sprayer and vaporizer before being injected into the stainless-steel catalytic reaction chamber. To avoid plugging, hydrogen is introduced into the feed line, which enters the top of the reactor and extends down to the lower third of the free space above the catalyst.

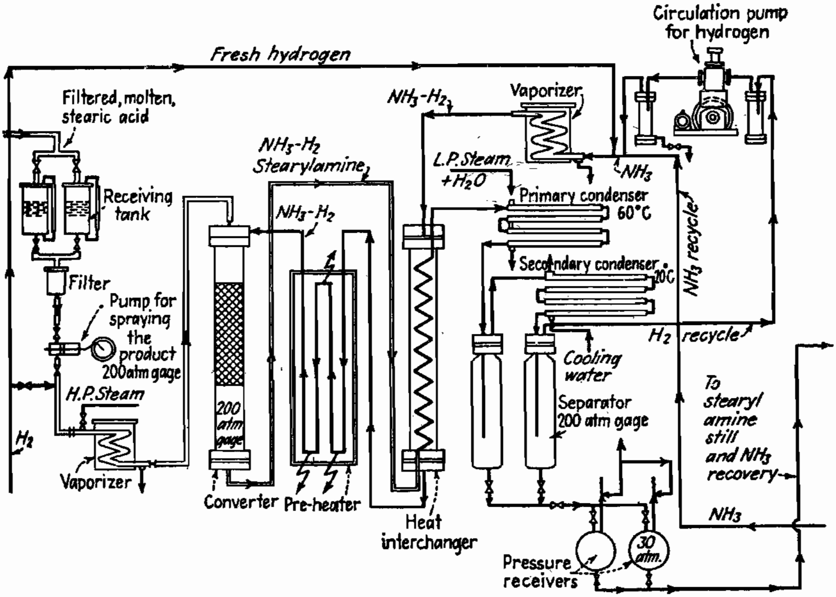

FIG. 8-25. Preparation of stearylamines by hydroammonolysis.

Before starting operations, the NiS-MoS catalyst, in the form of 8-mm pellets, is reduced with 200 cu m of hydrogen until the sulfur content of the reaction water is less than 50 mg per cu m. About 8 days is required for this operation, the reduction temperature being raised slowly from 300–400°C.

Stearic acid is fed at a rate of 0.3 vol. per vol. of catalyst per hour and passes concurrently with preheated ammonia and hydrogen downward through the catalyst. Hydrogen is circulated at a rate of 10,000 liters per vol. fatty acid per hour, while the supply of gaseous ammonia is 10 times theoretical.

The reaction temperature is controlled at 300–330°C, while the NH_3-H_2 pressure is maintained at 200 atm gauge. The stearylamine and gases leave at the base of the reactor and pass through a heat exchanger and then a primary condenser and receiver at 60°C and 200 atm and a secondary condenser and receiver at 20°C and 200 atm, from which the excess hydrogen is released to the circulation pump. The stearylamine, water, and ammonia are directed and expanded into receiving cylinders at 30 atm gauge, from which they are led to a pressure column operating at 16 atm to effect the separation of ammonia, which goes overhead, from the hydrous amine that is drawn off at the base. The stearylamine and water pass to a steam-heated vaporizer for removal of water.

The yield of stearylamine is 90–92 per cent of theory. Some tar with about 50 per cent fatty acid content is found in the vaporizer and is removed at 8-hr intervals from a bottom vent until gas emerges.

Urea Manufacture: Urea is produced from ammonia and carbon dioxide, which first react to form ammonium carbamate:

$$CO_2 + 2NH_3 \rightarrow H_2N{\cdot}CO{\cdot}ONH_4$$

The ammonium carbamate is then converted to urea:

$$H_2N{\cdot}CO{\cdot}ONH_4 \rightarrow H_2N{\cdot}CO{\cdot}NH_2 + H_2O$$

As stated previously (Class 5, Addition Reactions) the conversion of carbamate to urea is not complete, and equilibrium depends on the excess of ammonia used. Unconverted materials can be recycled to the process or used in the manufacture of other products, particularly fertilizers. Several schemes have been developed for recycling NH_3 and CO_2 obtained by the decomposition of ammonium carbamate. Tonn[1] and Cook[2] describe the operational differences and give simplified flow diagrams to explain the mode of operation of several processes which employ recycling. The reaction is run under pressures varying from 1,750–6,000 psi and temperatures from 160–210°C. Depending on the operating technique, conversions vary from 40–76 per cent. A little over 2 (stoichiometric) to 6 moles of ammonia is used per mole of CO_2. Yields of 90 per cent or better on NH_3 and CO_2 are obtained in most cases. Older processes recirculate the unconverted CO_2 and NH_3 to the reactor as a hot-gas mixture or as an ammonia solution of ammonium carbamate. A disadvantage of the hot-gas procedure is that the compressors and feed lines must be kept hot to prevent clogging with solid ammonium carbamate. The second procedure is plagued with corrosion difficulties to the extent that even silver-lined reactors are attacked. To increase conversion, lessen corrosion, and improve heat transfer in the reactor, some improved processes use a large excess of practically anhydrous

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[1] TONN, *Chem. Eng.*, **62** (10), 186 (1955).

[2] COOK, *Chem. Eng. Progr.*, **50**, 327 (1954).

liquid ammonia, with varying ratios of solution recycle. Some of the newer processes separate unconverted CO_2 and NH_3 by preferential absorption using a solvent, such as urea nitrate solution, which dissolves NH_3 (Inventa and Montecatini processes), or monoethanolamine solution, which dissolves CO_2 (Chemico process). The Inventa process (Swiss) feeds practically pure liquid ammonia and compressed CO_2 to the reactor. The excess ammonia is recovered as a gas and put through a liquefaction unit. The Montecatini process (Italian) recycles recovered liquid ammonia containing some aqueous ammonium carbamate. The Chemico process (American)[1] uses 200 per cent excess ammonia, most of which is recovered under the reactor let-down pressure by condensation in a water-cooled condenser. CO_2 for recycle is separated from the remaining ammonia in a monoethanolamine

TABLE 8-21. COMPARISON OF UREA PROCESSES

Technical Data

Process	Solution recycle	Pechiney	Inventa*	Chemico	Montecatini
Moles NH_3/CO_2 in reactor	5/1	2/1	2–3/1	6/1	3/1
Pressure, psi	6,000	3,000	3,000	2,500	2,275–2,560
Temperature, °F	390–410	360	360	245–355	320–360
Conv., carbamate to urea, %	70	50	50	50	68.5
NH_3 used, ton/ton urea	0.58	0.58	0.58	0.58	0.83
CO_2 used, ton/ton urea	0.75	0.75	0.75	0.77	0.89

Economic Data

Raw materials	$/ton	48.00	48.00	48.00	48.00	48.00
Utility: Power		2.80	1.30	3.64†	1.62	1.39
Utility: Water		0.50	0.75	0.73	0.33	0.20
Utility: Steam		2.50	2.00	2.16	1.80	1.20
Labor and supervision		3.40	4.64	4.13	3.60	5.86
Maintenance		6.06	2.00	3.81	4.00	2.41
Depreciation and taxes		16.00	13.00	10.90	9.20	7.3§
Manufacturing costs‡		79.26	71.69	73.37	68.55	66.40§
Investment, $1,000/ton/day		20–40	15–25	30–40	12–30	21
Economic size, tons/day		100	100	100–150	150	50–100

Licensees: Pechiney, Foster Wheeler Corp.; Inventa, Vulcan Copper and Supply Co.; Chemico, Chemical Construction Co.

* Based on earlier European plants; data not available on improved installations.

† Reduced to $1.16 by using gas-engine drives for compressors (i.e., $0.69 for gas and $0.47 for electrical energy).

‡ Urea (delivered crystals) sold at $120 per ton at the time costs were estimated.

§ Based on partial liquid recycle process. Total liquid recycle process has just been developed.

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[1] *Ibid.*

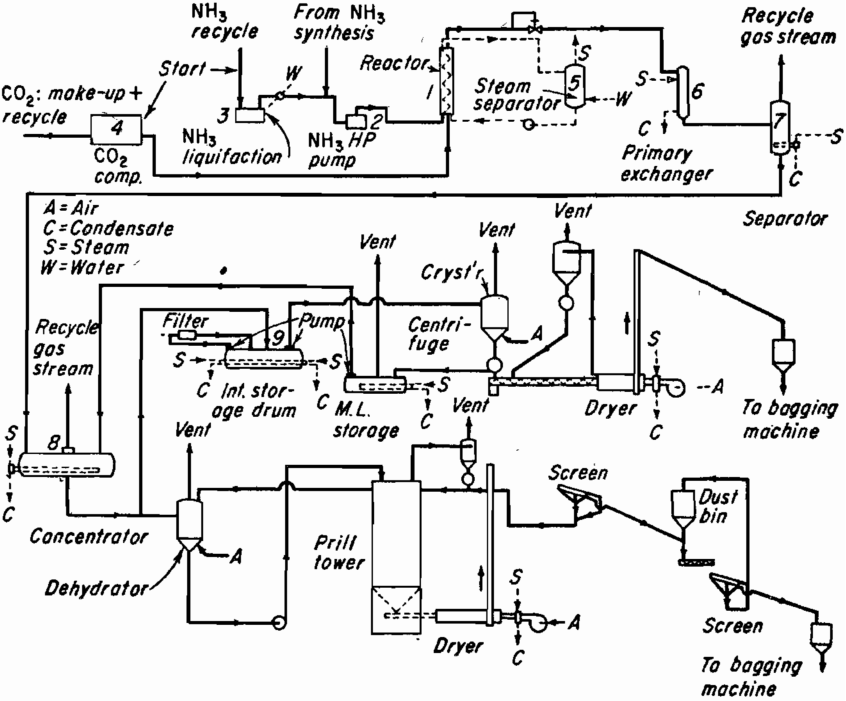

FIG. 8-26. Urea synthesis section.

scrubbing unit. A silver-lined reactor with no internal heat exchanger is used. In the Pechiney process (French) the recycle feed to the reactor is an oil suspension of finely divided ammonium carbamate, formed by passing the gases from an ammonium carbamate decomposer into agitated oil. The oil acts as a heat-transfer agent and a corrosion protectant. Together with make-up gases, the $NH_3:CO_2$ ratio in the reactor is kept close to the theoretical 2:1 ratio. Therefore, no purge recovery is necessary. Urea as a water solution is separated from the circulated oil and discharged from the ammonium carbamate decomposer. A lead-lined reactor is used. It also has no internal heat exchanger. Yields of 93 per cent on CO_2 and NH_3 are obtained. Tonn, Jr., has tabulated technical and cost data for various processes. Table 8-21 shows the data for five processes.

Synthesis Operation. The Inventa process, together with flow diagrams (Figs. 8-26 and 8-27) showing the flow to the reactor, gas separation, and urea finishing sections, has been described by Bland.[1] In this installation, high-purity CO_2 goes to reactor (1) made of a special corrosion-resistant alloy. Liquid ammonia in slight excess over the stoichiometric quantity is

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[1] BLAND, *Petroleum Processing*, 7, 1457 (1952).

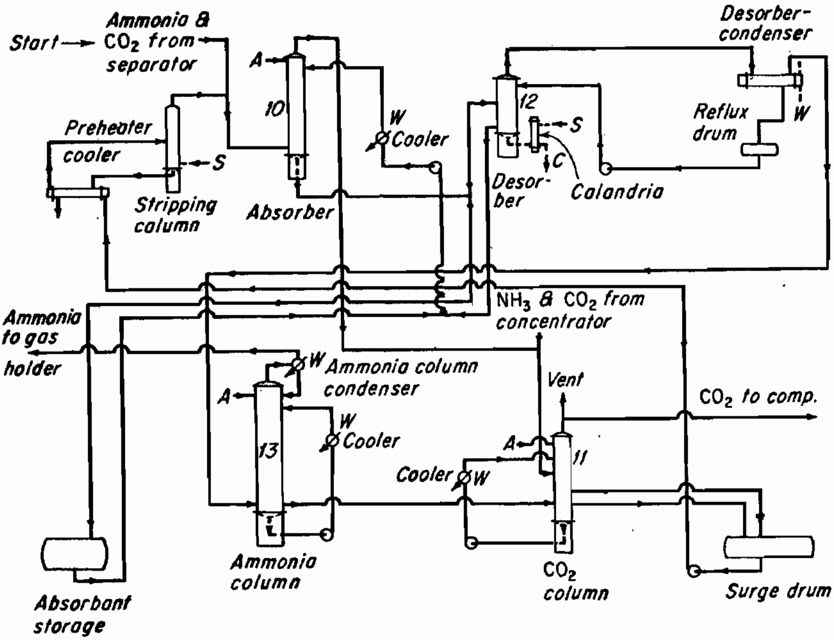


FIG. 8-27. NH_3 and CO_2 recovery and recycle section.

pumped in separately. The reactor operates under about 200 atm pressure at about 180–200°C. The conversion to urea is about 50 per cent per pass. The over-all reaction heat (the conversion of carbamate to urea is slightly endothermic) is used to produce steam in the shell-and-tube type of reactor. About 1,700 lb of steam per ton of urea is produced. The reacted mixture flows from the reactor through a pressure let-down valve, which reduces the pressure below 10 atm, and then into the steam-heated primary exchanger (6). Here under the reduced pressure, the carbamate dissociates to CO_2 and NH_3. The mixture then flows to the steam-heated separator (7) where the gases are flashed off and residual carbamate is decomposed. About 90 per cent of the unconverted CO_2 and NH_3 is removed at (7). From the separator (7) the crude urea solution goes to the concentrator (8), where the remaining gases are removed together with part of the water formed during the reaction. The crude urea from the concentrator is either prilled or purified by crystallizing from water. If it is to be crystallized, it goes from the concentrator (8) to the intermediate storage drum (9), from which it is delivered to a continuous crystallizing and drying unit. A bypass filter is used when plastic or pharmaceutical-grade urea is produced. For fertilizer-grade urea, the crude urea solution from the concentrator (8) is dehydrated and prilled.

Recycle Operation. NH_3 and CO_2, flashed from the separator (7) (90 per cent comes off here) is fed to the countercurrent absorber (10), using urea nitrate solution to dissolve NH_3. The overhead gas from (10), mainly CO_2, joins the NH_3 and CO_2 gas flashed from the concentrator (8). The gas mixture now flows to the CO_2 purification column (11), which removes the last traces of NH_3 before the CO_2 is recycled. NH_3 solution from the bottom of the absorber (10) is desorbed in (12), and the absorbent is returned to the absorber (10). NH_3 from the desorber (10) goes through a condenser to the NH_3 column (13) for final purification before it is collected in a gas holder which feeds the NH_3 liquefaction unit (3) in the synthesis section. The NH_3 and CO_2 in the liquid effluents from the CO_2 column (11) and the NH_3 column (13) are removed in the stripping column ahead of the absorber (10) and added to the gases entering (10).

XI. CONTROL OF THE AMMONIA-RECOVERY SYSTEM

The successful industrial preparation of amines by the ammonolysis of aromatic halides, alcohols, and sulfonic acids depends largely upon the proper functioning of the ammonia system. This matter derives its importance from the fact that 5–15 moles of NH_3 is employed per mole of organic compound undergoing treatment. A large capital investment is, therefore, involved. It is essential, furthermore, that the excess of the ammonia be recovered and delivered to the reaction system at a constant and optimum strength. This is absolutely necessary to ensure a maximum conversion to amine of uniform quality. In properly conducted operations, the recovery is efficiently and almost automatically carried out. This is accomplished by the choice of suitable equipment and the installation of mechanically controlled devices.

The type of apparatus that can be used for the recovery of the excess ammonia may be varied within wide limits. The physical properties of the amine and the compound from which it is derived, along with the means utilized to effect the separation of the amine, are the principal guides in the selection of the proper apparatus.

Absorption Systems. When anhydrous ammonia is used, the essentials of a refrigeration assembly will serve for the recovery of the excess ammonia (Fig. 8-28). In recent years, the use of liquid ammonia, frequently in conjunction with an organic solvent, has increased markedly, and the use of high-pressure ammonia-recovery systems is destined to become more prevalent.

In liquid-phase ammonolysis with aqueous ammonia, the ammonia-recovery system may consist of a number of submerged coils, or double-pipe condensers, followed by a series of vertical absorbers. The submerged coils are cooled by circulating water, and the temperature of the vapors is brought down to 60–80°C. This practice makes it possible to condense and recover, in a preliminary separator tank, the weak liquor, which is returned continuously by gravity flow to the still, or to the tail end of the absorption system, while the free ammonia travels forward to effect the concentration of the liquor in the following vertical absorbers.

The vertical absorbers contain aqueous ammonia of varying concentrations, and a standpipe suspended from the top supplies the NH_3 gas, which is distributed at the base by means of suitable perforated fittings. Any unabsorbed gas escapes at the top and is then led to the bottom of the following absorber. The heat of solution is removed either by internal cooling coils or by an outside spray system.

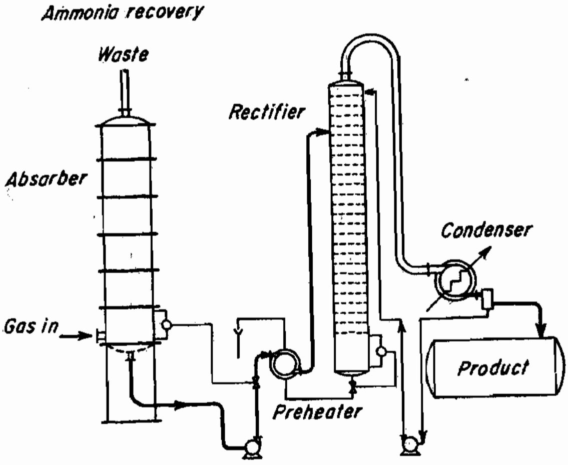


FIG. 8-28. Ammonia recovery system. Absorbers operate at atmospheric pressure. Rectifiers operate at approximately 200 psi.

The absorbers are set on a heavy foundation of masonry, at a sufficiently high level to permit bottom connections for cleaning and transfers incidental to operations. The piping can be so arranged that the ammonia vapor is led to the absorber containing the strongest solution and is then made to pass into absorbers containing liquor of progressively decreasing strength. When a sufficient number of absorbers are employed, the ammonia vapors are led in a direct manner through the absorbers. In properly conducted systems, practically no ammonia gas escapes at the exhaust from the final absorber. The over-all efficiency in recovery should be at least 96 per cent of that theoretically possible.

The absorption tanks may be arranged in a tier so that there is a constant overflow of liquid from the final absorber, which contains almost pure water, to the lowest tank, which holds the most concentrated liquor. A pump removes the strong solution, which should be ready for reuse, to a storage tank where it is cooled prior to delivery to the pressure system.

Description of Recovery System. In the preparation of 2-aminoanthraquinone, the excess ammonia can be recovered in the following manner (Fig. 8-29): at the end of the reaction, the gaseous constituents of the reaction mixture are gradually released through the line (2) by means of the needle valves (3 and 4) and allowed to expand to a pressure of about 50 psi. The expansion causes a considerable drop in temperature, and heat is eliminated as the gaseous products flow through the cooling coil (5), resulting in a concentrated ammonia condensate. The condensate remains substantially in the separator (6). The partly dehydrated gases pass from the separator (6) to the first solution tank or absorber (7) and are further expanded to a pressure of about 5 psi in their passage through the needle valve (8), thus being further cooled. Sufficient pressure is maintained on the gases to give a desired velocity and an injector action in the first solution tank, or absorber (7), which is preferably charged with a measured quantity of water or dilute aqueous ammonia. The weak liquor or water is drawn by the injector through the pipe (9), in contact with the ammonia in the gases, and the ammonia-water mixture is diffused into the balance of the ammoniacal solution. The ammonia absorption releases heat, which is removed by the cooling coil (10), a sufficient amount of cooling medium being circulated through the coil to maintain a temperature commensurate with

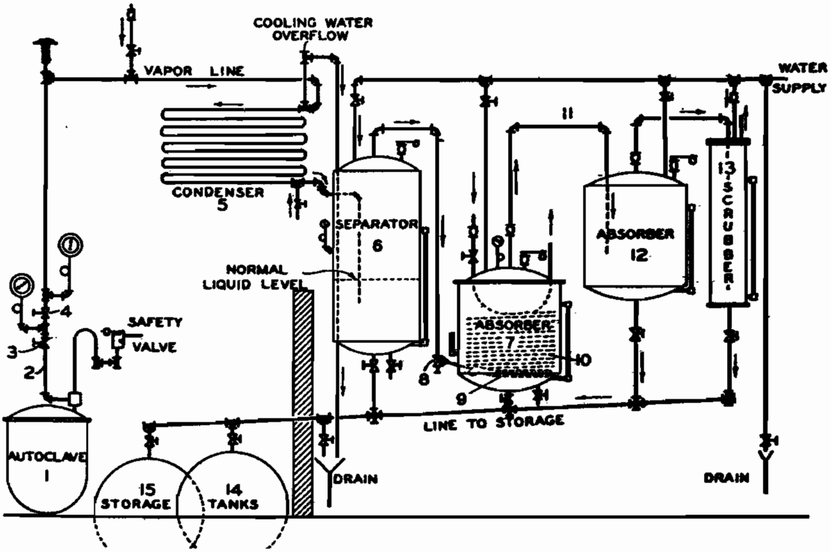


FIG. 8-29. NH_3 recovery system.

the concentration of aqueous ammonia that is desired; thus, a temperature of 35°C or thereabouts, with a proper charge of water and a pressure of the entering ammonia of about 5 psi, gives an aqueous ammonia of about 28 per cent concentration. Unabsorbed gases pass through the line (11) into the second solution tank, or absorber (12), which is nominally at atmospheric pressure, and what gas escapes from this tank passes through the liquid in the tower (13) and out of the vent.

A number of modifications of the preceding system have given eminently satisfactory service in practical operations on a large scale. Generally, it is not advisable to release all the pressure from the autoclave. If all but 150–200 lb pressure is allowed to escape, it is possible then to blow the charge under its own pressure to a vessel of lighter construction in which the amino compound undergoes subsequent treatment. The receiving vessel (still) may be prepared with an alkaline solution to decompose the combined ammonia. In this vessel, the residual ammonia is effectively removed by distillation, and the ammoniacal vapors are led to the recovery system. The residual amino compound can then be treated in any desired manner most advantageously to effect its removal.

CHAPTER 9

OXIDATION

By L. F. Marek

I. TYPES OF OXIDATIVE REACTIONS

In the organic chemical industry, oxidation constitutes one of the most powerful tools used in the synthesis of chemical compounds. The oxidation processes are many and varied and are manifested in a variety of net effects. The principal types of oxidative reactions may be set forth as follows:

1. **Dehydrogenation** is illustrated in the transformation of a primary alcohol to an aldehyde:

$$C_2H_5OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O$$

or a secondary alcohol to a ketone:

$$CH_3{\cdot}CHOH{\cdot}CH_3 + \tfrac{1}{2}O_2 \rightarrow CH_3{\cdot}CO{\cdot}CH_3 + H_2O$$

2. **An atom of oxygen may be introduced** into a molecule, as is illustrated by the oxidation of an aldehyde to an acid:

$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH$$

or of a hydrocarbon to an alcohol:

$$(C_6H_5)_3CH + \tfrac{1}{2}O_2 \rightarrow (C_6H_5)_3COH$$

3. **A combination of dehydrogenation and introduction of oxygen** may occur, as in the preparation of aldehydes from hydrocarbons:

$$CH_4 + O_2 \rightarrow CH_2O + H_2O$$

or the preparation of benzoic acid from benzyl alcohol:

$$C_6H_5{\cdot}CH_2OH + O_2 \rightarrow C_6H_5{\cdot}COOH + H_2O$$

4. **Dehydrogenation may also be accompanied by molecular condensation,** as is the case when two molecules of benzene form diphenyl or two molecules of toluene form stilbene or when methylanthraquinone is converted to anthracene yellow C.

$$2C_6H_6 + \tfrac{1}{2}O_2 \rightarrow C_6H_5{-}C_6H_5 + H_2O$$
$$2C_6H_5{\cdot}CH_3 + O_2 \rightarrow C_6H_5{\cdot}CH{=}CH{\cdot}C_6H_5 + 2H_2O$$

5. Dehydrogenation, oxygen introduction, and destruction of carbon linkages may all occur in the same process of oxidation, e.g., in the oxidation of naphthalene to phthalic anhydride:

$$C_{10}H_8 + 4.5O_2 \rightarrow C_8H_4O_3 + 2H_2O + 2CO_2$$

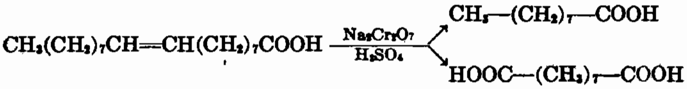
6. Oxidation may be accomplished indirectly through the use of intermediate reactions:

$$C_6H_5{\cdot}CH_3 \rightarrow C_6H_5{\cdot}CCl_3 \xrightarrow{H_2O} C_6H_5{\cdot}COOH$$
$$C_6H_6 \rightarrow C_6H_5{\cdot}SO_3H \xrightarrow{NaOH} C_6H_5OH$$
$$CH_3OH + CO \rightarrow CH_3COOH$$

7. Olefins may be oxidized under mild conditions to hydroxy derivatives and may be converted to aldehydes and carboxylic acids of lower molecular weight when stronger oxidizers are employed. Thus, oleic acid can be converted to dihydroxystearic acid with alkaline potassium permanganate:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow[\text{alkali}]{KMnO_4} CH_3(CH_2)_7CHOH{-}CHOH(CH_2)_7{-}COOH$$

When sodium dichromate in acid solution is employed, fission as well as oxidation occur and pelargonic and azelaic acids are produced:

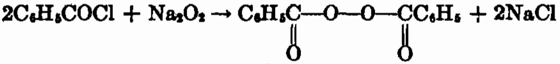


$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} \begin{cases} CH_3{-}(CH_2)_7{-}COOH \\ HOOC{-}(CH_2)_7{-}COOH \end{cases}$$

8. Peroxidation occurs readily under certain conditions. Thus, some reactions occur directly with air when catalyzed by ultraviolet irradiation:

$$\text{Isopropylbenzene} \xrightarrow[\text{UV}]{\text{air}} \text{isopropylbenzene peroxide}$$

Others require the interaction of an inorganic peroxide:



$$2C_6H_5COCl + Na_2O_2 \rightarrow C_6H_5\underset{\displaystyle \overset{\|}{O}}{C}{-}O{-}O{-}\underset{\displaystyle \overset{\|}{O}}{C}C_6H_5 + 2NaCl$$

Benzoyl Chloride Benzoyl Peroxide

9. Amino compounds may be oxidized to azobenzene, *p*-amino-phenol, or nitrobenzene under moderate conditions, or the N-containing radical may be completely removed under drastic conditions. In this way, quinone is derived from aniline.

10. Sulfur compounds may be oxidized by acid permanganate, as in the preparation of sulfonals, trionals, and tetranals from $(CH_3)_2C(S{\cdot}C_2H_5)_2$ or $(CH_3)(C_2H_5)C(S{\cdot}C_2H_5)_2$ or $(C_2H_5)_2C(S{\cdot}C_2H_5)_2$, in which the sulfide sulfur is oxidized to sulfonic groups. It should be noted that the mercaptans behave differently toward oxidizing agents from the alcohols, in that the action of strong oxidizing agents increases the valence of the sulfur atom instead of removing hydrogen, as in the case of the alcohols. Thus:

$$\underset{\text{Ethyl Alcohol}}{CH_3CH_2OH} \xrightarrow{\text{oxidation}} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

$$\underset{\text{Ethyl Mercaptan}}{CH_3CH_2SH} \longrightarrow \underset{\text{Ethanesulfonic Acid}}{CH_3CH_2SO_2OH}$$

On the other hand, mild oxidation of mercaptans may result in the formation of disulfides. Thus:

$$\underset{\text{Ethyl Mercaptan}}{2CH_3CH_2SH} \xrightarrow{\text{oxidation}} \underset{\text{Diethyl Disulfide}}{C_2H_5S{-}SC_2H_5} + H_2O$$

II. OXIDIZING AGENTS

The principal problem involved in oxidation reaction is the induction of the desired reaction coupled with a satisfactory control of the extent of reaction. Since this is so, a study of the processes employing oxidation would best be founded on an inspection of the *materials* and *methods* used to solve these problems.

In the case of liquid-phase oxidations, it is possible to use either gaseous oxygen or compounds having oxidizing power. To illustrate the methods that are used, the processes will first be examined from the standpoint of the oxidizing agent, and the character of the action of each agent will be pointed out later by the use of exemplary reactions.

Permanganates

The solid salts of permanganic acid are powerful oxidizing agents. Calcium permanganate induces such rapid oxidation of ethanol that inflammation may result. Aqueous solutions of the permanganates also possess powerful oxidizing properties. One of the commonest and most useful of the agents employed in organic oxidations is potassium permanganate. The potassium salt is available in the form of stable crystals, whereas the sodium salt is deliquescent; consequently, the former is almost invariably used. It functions as an oxidizing agent of different strengths in alkaline, neutral, and acid solutions.

The calcium and barium salts have been used for the oxidation of complex proteins. The calcium salt has the advantage in that it forms insoluble products. The calcium oxide combines with the manganese dioxide to form the insoluble $CaO:MnO_2$, thus simplifying recovery of products.

Alkaline Solution. When potassium permanganate alone is used in aqueous solution, the solution becomes alkaline through the formation of potassium hydroxide:

$$K_2Mn_2O_8 + H_2O \rightarrow 2MnO_2 + 2KOH + 3O$$

Three atoms of oxygen are released per molecule of permanganate, and manganese dioxide in the hydrated form is precipitated.

Kinetic studies of the oxidation of aromatic hydrocarbons with potassium permanganate show that reaction is first order with respect to each reactant.[1] With toluene, oxidation takes place almost exclusively at the methyl group to give successively benzyl alcohol, benzaldehyde, and benzoic acid; with ethyl benzene, attack is predominantly at the alpha carbon atom to yield acetophenone; and with *n*- and isopropylbenzene, the products are propiophenone and acetophenone, respectively, plus benzoic acid. These results are of interest primarily for mechanism studies.

When the products are organic acids, the potassium salts usually form. After the removal of MnO_2 by filtration, the carboxylic acid may be recovered by acidification with a mineral acid. Very dilute aqueous solutions are used in the oxidation of toluene derivatives to the corresponding acids. Loss of color shows the end point. Excess of reagent is easily remedied by the addition of ethanol or other harmless reducing agent. Thus, *p*-chlorotoluene is oxidized to *p*-chlorobenzoic acid, naphthalene to phthalonic acid, maleic acid to mesotartaric acid, *o*-nitrophenol to dinitrodihydroxydiphenyl. In general, however, hydroxy and amino groups must be protected by alkylation or acylation to prevent oxidation of such substituents.

An excess of alkali may be added at the start, in which condition potassium permanganate is used for oxidizing ortho-substituted derivatives of toluene. Thus, *o*-toluic acid yields phthalic acid. Substituted cinnamic acids are oxidized to the corresponding benzoic acids. Triphenylmethane is oxidized to the corresponding alcohol, diphenylmethane to the ketone, and oleic acid to dihydroxystearic acid.

Potassium hypomanganate, K_3MnO_4, made by fusion of manganese dioxide, KOH, and sodium nitrite or by fusion of potassium permanganate with KOH at high temperatures, reacted in strongly alkaline solutions is specific in its oxidizing action. It does not oxidize olefins but slowly oxidizes primary and secondary alcohols and ketones.[2]

Neutral Solution. To avoid the alkalinity produced by the use of potassium permanganate alone as an oxidizing agent, resort may be had to the introduction of carbon dioxide to neutralize the alkali or to the use of magnesium sulfate for the formation of neutral potassium sulfate and insoluble magnesium oxide. These expedients are necessary in very few cases, however.

In such a neutralized oxidizing solution, acet-*o*-toluidide gives a yield of 80 per cent of the oxidation product acetanthranilic acid; whereas in the alkaline solution, a yield of only about 30 per cent is obtainable.

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[1] CULLIS and LADBURY, *J. Chem. Soc.*, **1955**, 555–560, 1407–1412, 2850–2854, 4186–4190.

[2] PODE and WATERS, *J. Chem. Soc.*, **1956**, 717–725.

Acid Solution. The addition of acetic or sulfuric acid to potassium permanganate solutions yields a powerful oxidizing agent useful only in the preparation of very stable compounds. The powerful action of this agent markedly restricts its applicability. In use, the oxidizing solution is added gradually to the substance undergoing oxidation, since in this way the action is limited and controllable. Each molecule of permanganate yields five atoms of oxygen.

$$K_2Mn_2O_8 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 3H_2O + 5O$$

Acid solutions may be used for the preparation of certain naphthalenesulfonic acids incapable of formation by other means. Both aliphatic and aromatic sulfides or hydrosulfides are oxidized to corresponding sulfonic acids. *o*-Iodobenzoic acid is oxidized to *o*-iodosobenzoic acid.

Dichromates

The usual form of oxidation with dichromates is in the presence of sulfuric acid and with the sodium or potassium salt. Although the dichromates exert an oxidizing tendency in the absence of acid, the oxidation reaction can be made to occur much more quickly in the presence of acid, and acid solutions are almost invariably used. Such mixtures react to give oxygen as follows:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

2 moles of chromic acid (1 mole of dichromate) giving three atoms of oxygen. The sodium salt is the cheaper, is much more soluble in water, and is consequently more often used.

Chromic Acid Solution. Chromic anhydride, CrO_3, dissolved in glacial acetic acid, is sometimes used as an oxidizing agent. Two moles of the anhydride yields three atoms of oxygen: $2CrO_3 \rightarrow Cr_2O_3 + 3O$. In practice, only the theoretical amount of the oxidizing agent is added, and this is usually introduced gradually as the oxidation proceeds. Aromatic alcohols may be oxidized to aromatic aldehydes, provided a primary amine is present to form a Schiff's base with the aldehyde as soon as it is formed. Quinoline homologues are oxidized to quinoline carboxylic acids. If acetic anhydride is used, benzene homologues may be oxidized to aldehydes, since the formation of the acetyl derivatives prevents further oxidation.

12-Hydroxystearic acid, derived from ricinoleic acid from castor oil, may be oxidized with chromic acid, CrO_3, dissolved in acetic acid to form 12-ketostearic acid. The esters of this keto acid are useful stabilizers and plasticizers for lacquers, plastics, and resins.[1] Catalytic dehydrogenation in the presence of active catalysts, such as nickel-on-kieselguhr or copper-

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[1] Cox, U.S. 2,180,730 (1939).

cadmium-chromite, may also be used to convert 12-hydroxystearic acid derivatives to the keto acids.[1]

Chromic acid in hot glacial acetic acid oxidizes anthracene quantitatively to anthraquinone in a very smooth reaction, but the method is too expensive for commercial application in competition with synthetic anthraquinone made from cheap phthalic anhydride and benzene by means of the Friedel-Crafts reaction. Prior to the development of the present methods of phthalic anhydride manufacture, the process was used extensively for anthraquinone production in Europe. The method has been recommended for anthracene analysis.

Chromic acid and the dichromates find numerous other applications as oxidizing agents in the organic chemical industry. In the manufacture of perfumes, they may be used to oxidize anethole to anisic aldehyde, isosafrol to piperonal (heliotropin), etc. The dichromates may be used to effect the condensation of α-naphthol with dimethyl-p-phenylenediamine to form indophenol. They are used in the preparation of methylene blue, safranine, and other dyestuffs.

Hypochlorous Acid and Salts

The lithium,[2] sodium, and calcium salts of hypochlorous acid are known in the solid state. Although they decompose easily when wet, they are stable if thoroughly dry. Bleaching powder, formed by reacting chlorine with dry calcium hydroxide, is related to the hypochlorites and depends upon the presence of the hypochlorite radical for its characteristic action. Chlorinated solutions of zinc and aluminum hydroxides are more active oxidizing agents than are comparably treated solutions of the alkalies or alkaline earths because of greater hydrolysis and consequent more rapid decomposition of hypochlorous acid. But the sodium salt has the advantage of ease of preparation and handling.

Hypochlorous acid is unstable and decomposes very easily to liberate oxygen. Decomposition rate is not violent, however, and for some purposes may even be increased by the use of a cobalt or nickel salt to act as a catalyst. The action of the salts, especially those of the alkalies or alkaline earths, may be increased by the addition of carbon dioxide or acids because of the more rapid liberation of the hypochlorous acid caused thereby. This property furnishes a method of control when these substances are used for oxidation.

Calcium hypochlorite is used to a large extent for bleaching linen and cotton textile materials and paper pulp. The sodium salt is used in bleaching rayon yarn. Both salts are used for "sweetening" uncracked gasolines by the oxidation of the mercaptans to sulfides and disulfides.

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[1] Lazier, U.S. 2,178,760 (1939).

[2] Laue, U.S. 2,384,629 (1945).

Sodium Chlorite and Chlorine Dioxide

Sodium chlorite, $NaClO_2$, is marketed as an 80 per cent dry powder for use in bleaching. When reacted with chlorine, sodium chlorite releases chlorine dioxide, ClO_2, a gas at normal temperatures and soluble in water. Chlorine dioxide is a powerful oxidizing and bleaching agent; but because of its instability, it cannot be produced and stored.[1] The aqueous solutions are decomposed by light to perchloric and chloric acids, oxygen, and water.

There is a trend toward increasing use of chlorine dioxide for bleaching wood pulp. Consumption in 1955 was 25 per cent greater than in 1954, and by the middle of 1956 some 36 United States pulp mills were using chlorine dioxide bleaching, with some 20–30 others giving it consideration. First use was in 1946 in Canada and Sweden and in 1952 in the United States on kraft pulps. Use is being extended now to sulfite and dissolving pulps. Chlorine dioxide is useful because it bleaches paper pulp without loss of strength, oxidizing lignin substances to colorless, water-soluble compounds, and giving whiter pulps with fewer stages than other agents.[2]

Chlorine dioxide has also been found to have utility in bleaching and maturing flour, treating water, checking blue mold in fruits, and bleaching textiles.

There are some seven processes available for generation of chlorine dioxide at point of use, of which three are based on methods developed in the United States. *The Solvay method* is based on the reduction of sodium chlorate with methanol in sulfuric acid solution. Three stages of packed towers are used and an air stream is blown countercurrent to the solution to strip out ClO_2, which is then absorbed in water. Conversion of chlorate to ClO_2 is 85–90 per cent. In the *Olin-Mathieson* method, streams of concentrated solutions of sodium chlorate and sulfuric acid are fed to the top of a lead-lined tank, and SO_2 in an inert gas stream is blown in at the bottom through diffuser plates. The ClO_2 generated is stripped from the inert gas carrier by absorption in water. Yield is also 85–90 per cent. The *Brown Company process* involves the reaction of strong $NaClO_3$-$NaCl$ liquor from an electrolytic cell with HCl in an air stream. The partially spent chlorate liquor is recycled to the cells, and ClO_2 is scrubbed from the air stream. This process is not yet used commercially, but the high experimental yields of 91–94 per cent indicate potential commercial interest.

Chlorates

Chloric acid, $HClO_3$, is a powerful oxidizing agent. It may be obtained in aqueous solutions at concentrations up to about 40 per cent and is stable

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[1] WOODWARD, PETROE, and VINCENT, *Am. Inst. Chem. Eng.*, **40**, 271 (1944); HUTCHINSON and DERBY, *Ind. Eng. Chem.*, **37**, 813 (1945); Hanford and Salzberg, U.S. 2,436,256 (1948); Hutchinson, U.S. 2,475,285; 2,475,286 (1949); *Rev. Paper Trade J.*, Jan. 6, 1949, p. 21.

[2] *Chem. Eng.*, **63** (7), 134–136 (1956).

at temperatures up to 40°C. Such a solution will ignite paper immersed in it. When the oxidizing action of this agent is controlled, it is possible to effect the oxidation of ethanol or ethyl ether to acetic acid, of ethylene to glycol, of allyl alcohol to glycerine, of fumaric acid to racemic acid, etc. In conjunction with mineral acids, chloric acid oxidizes aniline to aniline black. However, since its aqueous solutions must be obtained by double decomposition from its salts, its industrial usefulness is very limited, and it is more often used in the form of the soluble salts.

Potassium chlorate is a powerful oxidizing agent. However, its solubility in water is limited, being only 3.3 g per 100 g of water at 0°C and 56.5 g per 100 g of water at 100°C. It has been widely used in the dry, finely divided state as an oxidizing agent and in the laboratory as a source of pure oxygen. Mixed with reducing agents such as carbon, sulfur, sugar, and cellulose, it is used in the manufacture of powder, fireworks, explosives, matches, etc. In solution, it has been used in the oxidation of aniline in the production of aniline black. When heated to above its melting point (357°C), the dry salt tends to decompose to potassium chloride and oxygen, each molecule of chlorate giving 1½ molecules of oxygen. Concurrently with the above decomposition, potassium chlorate decomposes to give the perchlorate and the chloride. The relative speed of the two reactions varies with the temperature and is markedly affected by catalysts. Thus, the decomposition to oxygen may completely outrun the other reaction in the presence of a manganese dioxide catalyst.

The solubility of sodium chlorate in water is far greater than that of the potassium salt. Also, it is less expensive, and large amounts are used annually in the United States as a herbicide.

Peroxides

The principal peroxides used as oxidizing agents are those of lead, manganese, and hydrogen.

PbO_2. Lead peroxide is used as an oxidizing agent in conjunction with acetic, sulfuric, or hydrochloric acids, usually the first. One mole yields one atom of oxygen, and a salt of the acid is formed during the process. It must be used in a finely divided form and, for this reason, is best prepared by precipitation from a solution of lead nitrate by the addition of sodium hypochlorite or bleaching powder.

MnO_2. Manganese dioxide is widely used as an oxidizing agent in both its natural and prepared forms. It is employed in conjunction with sulfuric acid and during the reaction is reduced to manganese sulfate, releasing one atom of oxygen per mole. One of its principal uses is in the oxidation of methyl groups to aldehyde groups, in which role it has been largely used to convert toluene to benzaldehyde.

H_2O_2. The production of hydrogen peroxide has shown tremendous increases since the end of the World War II. Thus, from a volume of 7.44

million lb (100 per cent H_2O_2 basis) in 1943, production increased to an estimated 40 million lb in 1955. Capacity is expected to reach 100 million lb and production about 80 million lb by 1960.

There has been an increasing volume of production by nonelectrolytic processes. Since the power requirement of the electrolytic process is only 8 kwhr per lb of (100 per cent) H_2O_2, the main saving by the newer processes is in elimination of the expensive electrical equipment. Most of the nonelectrolytic developments are based on modifications of the I.G. Farbenindustrie's Pfleiderer process, using the anthraquinone type of oxidation-reduction cycle.[1]

Hydrogen peroxide is manufactured, marketed, and used as an aqueous solution, the strength of which is customarily designated in terms of the volume of free oxygen equivalent. Although hydrogen peroxide is generally marketed industrially as the 100-vol. product (31.3 g H_2O_2 per 100 cc solution, or 28.5 per cent H_2O_2 by weight) in glass carboys, aluminum drums, and aluminum tank cars, some 130-vol. material is shipped in tank cars where long hauls make the freight saving an advantage. The wartime importance and the peacetime growing interest in high-concentration hydrogen peroxide have resulted in commercial-scale manufacture and shipment of 90 per cent and higher concentrations. Thus, 90 per cent hydrogen peroxide free of impurities is stable, may be stored in high-purity (99.6 per cent) aluminum containers, but requires intelligent handling.[2]

Very pure 85–90 weight per cent hydrogen peroxide has a high order of stability, the temperature coefficient being reported as 2.2 ± 0.1 for any 10°C interval in the 50–100°C range. Thus, at 30°C pure concentrated hydrogen peroxide decomposes to the extent of 1 per cent per year; at 66°C, 1 per cent per week; at 100°C, 2 per cent per 24 hr; and at 140°C, very rapidly. Vigorous stirring is without effect on decomposition, and aluminum and tin ions have no effect. The catalyst effect of zinc, ferric, cupric, and chromic ions is positive and increasing in the order named.

By means of a process of continuous fractional crystallization in which a solid phase of progressively higher H_2O_2 content moves in one direction and a liquid of progressively lower H_2O_2 moves in the opposite direction, it has become commercially feasible to manufacture[3] 98–100 per cent H_2O_2. The process starts with a 90 per cent H_2O_2 solution feed and rejects most of the impurities while increasing the concentration to a practical maximum of 99.6 per cent H_2O_2. This concentrated material is of extreme purity and

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[1] *Chem. Week*, Nov. 5, 1955, p. 75; Apr. 4, 1956, p. 96; *Chem. Eng.*, **62** (8), 108 (1955); Corey and Harris, U.S. 2,739,042 (1956); SCHUMB, SATTERFIELD, and WENTWORTH, "Hydrogen Peroxide," Reinhold Publishing Corporation, New York, 1955.

[2] GREENSPAN, *J. Am. Chem. Soc.*, **68**, 907 (1946); INDUSTRIAL INTELLIGENCE STAFF, C.W.S., *Chem. Eng. News*, **23**, 1519, 1626 (1945); SHAMLEY and GREENSPAN, *Ind. Eng. Chem.*, **39**, 1536–1543 (1947); WHITE, *Chem. Eng. News*, **23**, 1626 (1945).

[3] Crewson and Ryan, U.S. 2,724,640 (1955).

exceedingly high stability, decomposing at ambient temperatures at a rate corresponding to less than 1 per cent loss in concentration per year. The material is packaged in pure aluminum containers and may be shipped in drums or tank cars.

The pattern of hydrogen peroxide use in 1955 and 1959 are estimated to be as shown in the accompanying table.

Use	Million lb H_2O_2	
	1955	1959
Textile	18.5	40.0
Pulp and paper	7.5	12.0
Plasticizers and stabilizers	3.2	4.0
Foam rubber	1.4	3.0
Military	1.4	8.0
Miscellaneous	8.0	13.0
Total	40.0	80.0

Thus, about half of the hydrogen peroxide is consumed in textile bleaching and some 15 per cent more in pulp and paper bleaching, hydrogen peroxide having displaced chlorine and hypochlorites in portions of these fields because of use advantages. Substantially all silk and woolen goods, rayon fabrics, and light cotton goods are now bleached with hydrogen peroxide.[1]

Liquid-phase oxidation of isopropanol with oxygen at superatmospheric pressure and temperatures in the range of 90–140°C gives almost quantitative yields of hydrogen peroxide and acetone in the ratio 1 lb H_2O_2 per 1.7 lb acetone.[2] A commercial operation has been established in which the above reaction is used for captive production of H_2O_2 for conversion of allyl alcohol to glycerol. Allyl alcohol is obtained by reaction of isopropanol with acrolein, which in turn is obtained from the oxidation of propylene with oxygen. Such developments of low-cost production of hydrogen peroxide will open the way to wider use in chemicals manufacture.

Still other approaches to methods for cost reduction have been patented for the formation of hydrogen peroxide by direct oxidation of hydrogen[3] and of hydrocarbons,[4] such as propane, *n*-butane, and isobutane and for its recovery from the aqueous solutions thus formed.

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[1] Slater, *J. Soc. Chem. Ind.* (*London*), **6**, 42–46 (1945), for a general discussion of peroxides and uses.

[2] Hatch, *Petroleum Refiner*, **35** (3), 198–199 (1956); Harris, U.S. 2,479,111 (1949); N. V. de Bataafsche Petroleum Maatschappij, Brit. 708,339 (May 5, 1954).

[3] Cook, U.S. 2,368,640; 2,368,806 (1945).

[4] Lacomble, U.S. 2,376,257 (1945); Kooijman, U.S. 2,461,988 (1949); Harris, U.S. 2,533,581 (1950).

Hydrogen peroxide catalytically decomposed is effective as a monopropellant. The German "buzz bombs" were launched by use of a hydrogen peroxide–permanganate system.[1] Hydrogen peroxide is also effective in bipropellant systems and is used as a source of oxygen with such fuels as hydrazine hydrate, gasoline, and diesel oil. Torpedoes and submarines were driven by the bipropellant systems, using hydrocarbons as fuels. Various substances such as alcohols and crotonaldehyde were tested as fuels.[2]

The reactions of oxidation, epoxidation, hydroxylation, ring cleavage, quinone formation, and free radical reactions foretell increasing commercial interest in hydrogen peroxide as a reagent chemical. In alkaline solutions, H_2O_2 may be used in the preparation of organic peroxides such as benzoyl peroxide and diethyl peroxide. A 3 per cent solution oxidizes piperidine to glutaric acid by rupture of the ring. Phenols are converted to dihydric phenols or quinones. By the action of hydrogen peroxide in the presence of small amounts of ferrous salts, hydroxy acids are converted to aldehydo or keto acids. Very small amounts of selenium oxychloride markedly accelerate the rate of reaction of hydrogen peroxide in oxidizing aldehydes to acids. In the presence of catalysts, such as the oxides of ruthenium, vanadium, chromium, or molybdenum, hydrogen peroxide adds to unsaturated organic compounds as two hydroxyls giving glycols.[3] The chief addition compound of commercial importance is urea hydrogen peroxide, a solid material containing 36.17 per cent hydrogen peroxide.

The commercial availability of H_2O_2 of high concentration has permitted the preparation of concentrated peracid solutions applicable to the oxidation of organic substances such as aniline to azoxybenzene, β-naphthol to *o*-carboxycinnamic acid, anthracene to anthraquinone, and hydroxylation of unsaturated fatty acids.[4] Newer peracid techniques of oxidizing nitrogen-containing heterocyclics has set off a flood of research among drug companies in search of new drugs containing the heterocyclic nitrogen oxide grouping.[5]

The principal peroxy hydrates of commerce are sodium perborate and sodium percarbonate, which are used to replace hydrogen peroxide where a dry substance is desired. Sodium perpyrophosphate has limited use as a bleaching and dyeing auxiliary.

Na_2O_2. Sodium peroxide is used in only a limited way industrially for oxidizing organic substances, partly because of the hazards associated with

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[1] BELLINGER, FRIEDMAN, BAUER, EASTES, LADD, and ROSS, *Ind. Eng. Chem.*, **38**, 160–169 (1946).

[2] WHEELER, WHITTAKER, and PIKE, *Chem. Age (London)*, **56**, 367–374 (Mar. 29, 1947).

[3] MILAS, *J. Chem. Soc. Ann. Rept.*, 1943, p. 107; Brit. 508,526 (July 3, 1939).

[4] GREENSPAN, *Ind. Eng. Chem.*, **39**, 847–848 (1947); Milas, *loc. cit.*; U.S. 2,402,566 (1946); SHAMLEY and GREENSPAN, *loc. cit.*; See SWERN, *Chem. Revs.*, August, 1949, for review on peracids.

[5] *Chem. Week*, June 18, 1955, pp. 74–76.

its storage and use. After considerable research effort, sodium peroxide is being utilized in the commercial production of bleached groundwood pulp.[1]

By the action of sodium peroxide, phenanthraquinone in aqueous suspension changes smoothly to diphenic acid (biphenyl-2,2′-dicarboxylic acid). By the action of a cooled solution of sodium peroxide on the acid chloride, it is possible to form benzoyl peroxide, $C_6H_5 \cdot CO \cdot O \cdot O \cdot CO \cdot C_6H_5$.

Silver Oxides. Silver has the capacity to act as an oxygen carrier or oxidation catalyst, presumably because it can form oxides other than the common Ag_2O. Although not extensively used as such, the oxide, Ag_2O, acts as a mild oxidation agent. Moist, freshly prepared silver oxide is frequently used in the organic chemical laboratory for the replacement of halogen atoms by the hydroxyl group.

Silver oxide, Ag_2O, acts as a mild oxidizing agent and oxidizes glycerol to glycolic acid, aldehydes to acids, *o*-dihydroxybenzene to *o*-benzoquinone being reduced to metallic silver. The oxide is fairly readily reduced by hydrogen gas. Silver oxide made alkaline with sodium or ammonium hydroxide oxidizes $=CHOH$ and $=CO$ groups when these are attached to two $—CH_2OH$ or $—COOH$ groups or combinations. Thus, alkaline Ag_2O is reduced by tartaric acid, glycerol, mannitol, etc. Neutral or acid Ag_2O is reduced by glycolic, lactic, or malic acids.

Silver oxide is an excellent oxidation catalyst for vapor-phase reactions and is used commercially, notably in the oxidation of ethylene to ethylene oxide.

Nitric Acid and Nitrogen Tetroxide

The principal disadvantage of nitric acid as a partial oxidizing agent arises from the tendency to act as a nitrating agent. Even when dilute solutions are used, the products of oxidation may contain nitro derivatives. The method of Krafft uses the concentrated acid (sp gr, 1.5) and is particularly effective in the partial oxidation of substances that are already nitrated. A temperature of 0–5°C is used for mixing the acid and organic compound; this is gradually raised to 50°C and the product poured into water. Dinitroxylene is oxidized in this way to dinitrophthalic acid. Oxidation with dilute acid is slow when applied to the benzene homologues. Carboxylic acids are formed. Thus, pentamethylbenzene dissolved in benzene is converted to tetramethylbenzoic acid by boiling for 60 hr with dilute nitric acid.

Nitric acid and nitrogen oxides are assuming new significance as oxidizing agents. Toluic acids may be made by the nitric acid oxidation of xylenes; *p*-toluic acid is obtained from oxidation of *p*-cymene through the oxidation of the isopropyl group.[2] Nitric acid in the presence of sulfuric acid and a

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[1] *Chem. Eng. News*, **23**, 1540 (1945).

[2] *Chem. Eng. News*, **27**, 1892 (1949).

catalyst compound of mercury, copper, or selenium is effective in the oxidation of heterocyclic aromatic nitrogen compounds having an oxidizable organic grouping attached to the N-containing aromatic nucleus by one or more C-C bonds for formation of pyridine carboxylic acids as in the production of nicotinic acid,[1] for conversion of 4-picoline to isonicotinic acid or of 8-hydroxy quinoline to quinolinic acid.

Nitric acid oxidation with 50–60 per cent acid of the hydrocarbon-free mixture of cyclohexanol and cyclohexanone, obtained from a first-step air oxidation of cyclohexane, in the presence of catalysts of dissolved salts of copper, vanadium, or manganese, results in commercial yields of adipic acid.[2]

Purification of these oxidation products of cyclohexane for the second-stage nitric acid oxidation to adipic acid is not necessary but is advantageous from the viewpoint of yield and purity of product. The preferred commercial practice is to treat the product obtained by air oxidation of cyclohexane in pressure autoclaves with a controlled amount of water to permit an oil-water separation. The cyclohexanol and cyclohexanone dissolved in the water phase are removed by steam distillation and added to the oil phase. Succinic and glutaric acids which occur as by-products are recovered from the water phase. The combined oil is stripped to remove dissolved cyclohexane for recycle to the stage 1 air oxidation. The oil is then steam distilled and freed of water.[3]

The refined product from this treatment is oxidized by nitric acid in two stages at different temperatures, in the presence of catalysts and at pressures of 35–50 psi. First-stage oxidation is in the presence of an ammonium vanadate–copper oxide catalyst, and the exothermic reaction is maintained at 60–80°C by cooling. Reaction time of 5 min is controlled by continuously bleeding off a stream to the second stage. The second oxidation stage is performed at about 105°C. Total nitric acid requirement is about 1 lb per lb of adipic acid made.

Adipic acid yields for the combined air–nitric acid process are as high as 80 per cent. Cyclohexyl nitrate is recovered from the off-gas from the oxidizers and may be oxidized to recover adipic acid.[4]

Oxidation of cyclohexanol alone by means of 67 per cent nitric acid at 55–60°C results in 90 per cent yields of adipic acid when vanadium is used as a catalyst. Ratios of 1–3 moles cyclohexanol per mole nitric acid were used. Without a catalyst, 82 per cent yields are obtained.[5]

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[1] Larrison, U.S. 2,475,969 (1949); Mueller, U.S. 2,513,099 (1950).

[2] Hamblet and McAlevy, U.S. 2,557,282 (1951).

[3] Goldbek and Johnson, U.S. 2,703,331 (Mar. 1, 1955); *Chem. Week*, Oct. 27, 1956, pp. 114–116.

[4] Hamblet and Hanson, U.S. 2,750,415 (June 12, 1956).

[5] GODT and QUINN, *J. Am. Chem. Soc.*, **78**, 1461–1464 (1956).

Nitric acid oxidation of ethylene chlorohydrin has been developed to produce monochloracetic acid, an important chemical intermediate. With nitric acid strengths of around 60 per cent and temperatures of about 60°C, yields of over 90 per cent monochloracetic acid based on ethylene chlorohydrin are claimed.[1]

The commercial inexpensiveness of nitrogen tetroxide should stimulate research in its use as an oxidation agent. Nitrogen tetroxide, containing about 70 per cent oxygen, has been advocated as an oxidizer to supply the oxygen needed for combustion in rocket motors. Riebsomer has reviewed the literature and pointed to the need for repetition under carefully controlled conditions of much of the earlier work because of conflicting reports of results achieved by previous workers.[2] A great many substances have been oxidized by nitrogen tetroxide, including various hydrocarbons and substituted hydrocarbons. In most cases, the products have been reported to be complex mixtures and have not been well characterized. Reaction of nitrogen pentoxide with cyclohexane in carbon tetrachloride solution at 0 or 20°C results mainly in formation of nitrocyclohexane and cyclohexyl nitrate.[3]

Polyolefins and acetylenic hydrocarbons react with almost explosive violence with white fuming nitric acid, and olefins react vigorously. Saturated hydrocarbons, however, such as *n*-decane react slowly with concentrated nitric acid.[4] Cyclo-monoolefins, e.g., cyclohexene, may be nitrated with nitrogen tetroxide to mixtures of 1,2-dinitrocyclohexane and nitritonitrocyclohexane.[5]

Reaction of cyclohexene with nitrous oxide at temperatures between 200 and 350°C and high pressures of several hundred atmospheres results in oxidation to cyclohexanone.[6] Similarly, nitrous oxide can be used to oxidize propylene to propionaldehyde.

Nitric acid oxidation of coal, with or without oxygen, leads to the formation of complex mixtures of the benzenoid or aromatic type of organic acids. Nitric acid oxidation of carbohydrates yields oxalic acid.[7] Nitric acid of 50–75 per cent concentration at temperatures of 20–40°C oxidizes tetrahydrofuran to good yields of succinic acid.[8] Oxidation with nitric acid of a secondary aliphatic alcohol or an aliphatic ketone results in fission of the aliphatic chain at the point of attachment of the functional group accom-

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[1] Burrows and Fuller, U.S. 2,455,405 (1948).

[2] Riebsomer, *Chem. Revs.*, **36**, 157–233 (1945); Pollard, *Trans. Faraday Soc.*, August, 1949, p. 760.

[3] Brand, *J. Am. Chem. Soc.*, **77**, 2703–2707 (1955).

[4] Trent and Zucrow, *Ind. Eng. Chem.*, **44**, 2668–2673 (1952).

[5] Doumani, Coe, and Attane, U.S. 2,621,205 (1952).

[6] Buckley, U.S. 2,636,898 (1953).

[7] Brooks, U.S. 2,322, 915 (1943).

[8] Ebel, U.S. 2,312,468 (1943).

panied by oxidation to yield two molecules of carboxylic acid.[1] α, ω-Dicarboxylic acids result from nitric acid oxidation of the product of polymerizing ethylene with a vinyloxy compound.[2]

Copper Salts

Copper is capable of existing in two states of oxidation and of passing readily from one to the other of these states by oxidation or reduction. In its higher state of oxidation, it is capable of acting as an oxidizing agent and, in its lower state, as a reducing agent. This property makes the metal a useful material as an oxygen carrier or oxidation catalyst. It is more frequently used in the latter capacity than in the capacity of an oxidizing agent alone in organic chemical synthesis. When used as an oxidizing agent in solution, it is generally reduced from the cupric to the cuprous state.

In the determination of sugars and in their study, use is made of the relative ease of oxidation. Both aldoses and ketoses are capable of oxidation, the ketoses the more readily. Hydroxy ketones resemble aldehydes in their ease of oxidation. Fehling's solution consists of an aqueous solution of sodium potassium tartrate, sodium hydroxide, and copper sulfate, essentially an alkaline solution of cupric hydroxide. The sugar reduces the cupric ions to the cuprous form, and red cuprous oxide is precipitated. This solution has a rather weak oxidizing power and acts only on substances that are easily oxidized. Alcohols, acids, and simple ketones are not oxidized. Aldehydes, hydroxy ketones, and di- and triphenols are oxidized readily by this solution. When, for example, glucose is heated with Fehling's solution, a precipitate of cuprous oxide rapidly forms, and reaction is complete in a few minutes. Neither sucrose nor glycol is oxidized by Fehling's solution, and either one prevents the undesired precipitation of cupric hydroxide that would normally occur in the alkaline solution. An alkaline solution is used, since oxidation is more rapid.

Substantial quantities of sour gasoline are being sweetened by oxidation of mercaptan sulfur by means of oxygen and copper chloride solution.

Alkali Fusion

Fusion with alkali in the presence of air (oxygen) often accomplishes oxidations impossible to obtain otherwise. For instance, the formation of oxyacids from substituted phenols by direct oxidation of side chains is difficult of accomplishment because of the much greater susceptibility of the hydroxyl group to attack and consequent tendency for the breakdown of the molecule. Alkali fusion accomplishes the desired reaction but with poor yields. Xylenols yield the corresponding mono- and dibasic acids by

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[1] Olin, Fritsch, and Hinds, U.S. 2,267,377 (1941).

[2] Hanford, U.S. 2,360,673 (1944).

the reaction. Thus, *p*-xylenol is successively oxidized to *m*-homosalicylic acid and to hydroxyterephthalic acid.

The alkali fusion is of importance in the formation of certain anthraquinone vat dyes. Thus, fusion of β-aminoanthraquinone with two or three parts of potassium hydroxide at 250°C for ½ hr yields Bohns' Indanthrene blue RS (N-dihydro-1,2:1′,2′-anthraquinoneazine). Similarly, benzanthrone yields Bally's Indanthrene dark blue BO.

A mixture of caustic soda and potassium nitrate or chlorate possesses oxidizing powers, whereas caustic soda alone acts as a condensing and dehydrating agent. A good example of the use of the oxidizing mixture is in the formation of the dye alizarin from anthraquinone-β-sulfonic acid, sodium salt.

Fuming Sulfuric Acid (Oleum)

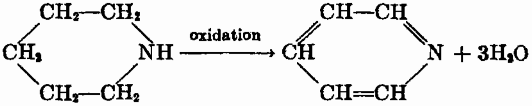
Fuming sulfuric acid, $H_2SO_4 + SO_3$, in the presence of mercury salts is a powerful oxidizing agent. It was formerly used extensively in this way for the oxidation of naphthalene to phthalic anhydride but has been displaced in this operation by the newer air-oxidation processes.

Fuming sulfuric acid attained importance as an oxidizing agent for the introduction of hydroxyl groups in anthraquinone derivatives in the production of a variety of alizarin dyes. Thus, fuming sulfuric acid at low temperatures may be used to convert alizarin and other hydroxy derivatives of anthraquinone to trihydroxy or up to hexahydroxy derivatives.

An early use of sulfuric acid as an oxidizing agent was in the oxidation of ethyl mercaptan to diethyl disulfide. However, to effect this reaction, the

$$2C_2H_5SH \xrightarrow{\text{oxidation}} C_2H_5S{-}SC_2H_5 + H_2O$$

oxidation must be mild and controlled, since with strong oxidizing agents the sulfonic acid is formed. Also, piperidine (hexahydropyridine) may be oxidized to pyridine. The



pyridine ring is very stable to oxidation, not being attacked by nitric or chromic acids and yielding a sulfonic acid only at high temperatures. 7

Ozone

The use of ozone for the oxidation of oleic acid to azelaic plus pelargonic acids has reached commercial practicability in a multimillion-dollar plant.[1]

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[1] *Chem. Eng.*, **59** (9), 246–248 (1952); Cannon, *ibid.* **62** (6), 138–142, (1955); *ibid.* **62** (6), 314–316 (1955).

Here the ozone is produced from oxygen in ozonizers designed and manufactured by Welsbach Corporation. Such ozonizers working on air to give a product stream containing 1 per cent by weight of ozone and an output of 60 lb of ozone per day have double this capacity, with oxygen as feed in place of air. Power requirement at 15,000 volts potential amounts to 8–9 kwhr per lb of ozone from air at 1 per cent concentration and to 4–4.5 kwhr per lb of ozone from oxygen. Ozone plant costs in 1955 for a 3,000-lb-per-day ozone unit were on the order of $250 per pound daily capacity with air feed, about $150 per pound daily capacity with recycled oxygen feed, and about $115 with once-through oxygen feed. Larger units have lower unit costs, and smaller units may have substantially higher unit costs. Ozone costs may range from about 8–10 cents per pound under favorable circumstances to as much as 50 cents per pound where conditions are not favorable.

Ozone is being promoted for use in the conversion of tertiary amines to amine oxides, of α-pinene to pinonic and pinic acids, of olefins to ozonides and these in turn to aldehydes and oxy-peroxides, of sulfides to sulfoxides and sulfones, and of various other organic substances. Such reactions are of practical interest in drug manufacture, and several drug companies are now commercially using ozone in their manufacturing operations, specifically in oxidation of sterols in hormone syntheses.

The powerful oxidizing potential of ozone has been made use of in textile bleaching in Italy, experimentally in paper bleaching, for destruction of phenolic bodies in coke-oven waste liquors,[1] and in limited ways for water purification.

Ozone in oxygen mixtures reacts slowly with lower-molecular-weight paraffinic hydrocarbons at room temperatures. At temperatures above 260°C, the ozone reaction merges with normal slow combustion.[2]

Vapor-phase reaction between ozone and olefins is quite rapid, the overall reactions become complicated, and stoichiometry varies with the reaction pressures.[3] A 3 mole per cent mixture of ozone in oxygen reacts with methane, propane, *n*-butane, and isobutane at 25–50°C.[4] The reaction of ozone with isobutane resulted in formation of *tert*-butanol plus one-third to one-half as much acetone, the combined yield being about equivalent to ozone reacted. Acetone was formed from propane oxidation.

A comprehensive bibliography of ozone technology is being undertaken, and two of the projected six volumes have appeared in print.[5]

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[1] Niegowski, *Ind. Eng. Chem.*, **45**, 632–634 (1953).

[2] Shubert and Pease, *J. Chem. Phys.*, **24**, 919–920 (1956).

[3] Cadle and Schadt, *J. Am. Chem. Soc.*, **74**, 6002–6004 (1952).

[4] Schubert, Pease, and Pease, *J. Am. Chem. Soc.*, **78**, 2044–2048 (1956).

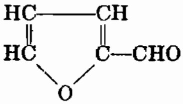
[5] Thorp, "Bibliography of Ozone Technology:" vol. 1, "Analytical Procedures and Patent Index;" vol. 2, "Physical and Pharmacological Properties," Armour Research Foundation, Chicago, 1955.

III. LIQUID-PHASE OXIDATION WITH OXIDIZING COMPOUNDS

The oxidation of aniline furnishes an example for comparison of a number of oxidizing agents. Results obtained by conducting the reaction under conditions best suited for the particular agent are shown in the accompanying tabulation:[1]

Oxidizing agent	*Product*
Manganese dioxide in sulfuric acid	Quinone
Potassium dichromate in dilute sulfuric acid at 0–10°C, for 24 hr.	Quinone
Potassium permanganate:	
Acid	Aniline black
Alkaline	Azobenzene plus ammonia
Neutral	Azobenzene plus nitrobenzene
Alkaline hypochlorite	Nitrobenzene
Hypochlorous acid	*p*-Aminophenol

Another substance exhibiting a variety of actions toward oxidizing agents is furfural:



The aldehyde group normally behaves like that of acetaldehyde toward oxidation, but in the presence of certain agents, the ring structure is destroyed and polybasic acids are formed.[2]

Oxidizing agent	*Product*
Sodium chlorate in neutral solution with V_2O_5 catalyst	Fumaric acid
Sodium chlorate in dilute acid with OsO_4 catalyst	Mesotartaric acid
Caros' acid, $HO{\cdot}O{\cdot}SO_3H$, a strong oxidizing agent	Succinic acid
Hydrogen peroxide in presence of ferrous salts	δ-Hydroxyfurfural
Bromine water at 100°C	Mucobromic acid
Potassium permanganate (diluted solution)	Pyromucic acid

The action of oxidizing agents on organic compounds depends not only upon the nature of the agent or the compound but also upon such factors as concentration, temperature, hydrogen-ion concentration, and method of mixing. Consequently, any comparison of the variety of effects obtainable by varying the oxidizing agent or organic compound cannot be pursued too far.

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[1] Bernthsen, "Textbook of Organic Chemistry," rev. trans., p. 664, D. Van Nostrand Company, Inc., New York, 1922.

[2] Milas, *J. Am. Chem. Soc.*, **48**, 2005 (1927).

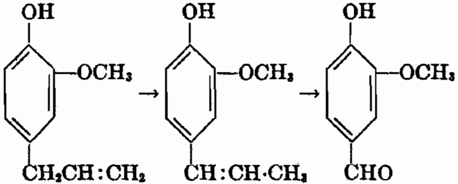
Ethylenic Bonds to Dihydroxy Groups. The oxidation of olefins and olefin derivatives with dilute aqueous potassium permanganate may be used for the formation of dihydroxy compounds. With 2 per cent permanganate solution, cinnamic acid yields phenyl-glyceric acid through the formation of a glycol derivative. Dilute permanganate oxidizes ethylenic bonds of fatty acids to dihydroxy groups, thus oleic acid to dihydroxystearic acid.

Hydrogen peroxide in the presence of catalysts of the oxides of Ru, V, Cr, or Mo also oxidizes organic unsaturated compounds to glycols.

More drastic oxidation of the ethylenic bonds of oleic, linoleic, and similar unsaturated fatty acids causes the action to go beyond the formation of oxygenated groups and to result in rupture of the bond as well as in oxidation. Such agents as the dichromates, permanganates, and nitric acid may be used to obtain the effect. Thus, oleic,[1] dihydroxystearic, and sterolic acids[2] yield azelaic and pelargonic acids, products that may be further oxidized if the reaction is forced.

Isoeugenol to Vanillin. The formation of vanillin from eugenol is an example of an oxidation of a side chain to an aldehydic group in which it is convenient to protect one substituent against oxidation. Eugenol obtained from oil of cloves is heated with an alkali such as sodium hydroxide to convert it to isoeugenol, the hydroxyl group is protected by acetylation, and the substance is oxidized and then saponified to vanillin.

The relatively slight difference in susceptibility to oxidation of the hydroxyl and propylene side chains makes it difficult to oxidize the propylene chain without affecting to some extent the hydroxyl substituent, unless it has been protected. Dichromates have been used to accomplish the oxidation step in this process of manufacture but are open to the objection that oxidation tends to go beyond the easily oxidized aldehyde stage, with resultant formation of acids. The same is true of oxidation with permanganate. Less potent agents, such as nitrobenzene, have consequently been used for the direct oxidation of isoeugenol to vanillin.



Eugenol Isoeugenol Vanillin

Nitrobenzene has an advantage over more powerful oxidizing agents, such as the dichromates and permanganates, in the oxidation of isoeugenol

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[1] Green and Hilditch, *J. Chem. Soc.*, **1937**, 764.

[2] Grün and Wittka, *Chem. Umschau*, **32**, 257–259 (1925).

to vanillin, as it does not induce such far-reaching oxidation of the desired aldehyde group to the undesired carboxylic group. Technically, the process may be conducted as follows: Eugenol from oil of cloves is dissolved in dilute sodium hydroxide solution and the whole heated to 160°C under pressure in an autoclave. This treatment converts the eugenol to isoeugenol and forms the sodium salt. For oxidation, 1 mole of nitrobenzene is added for each mole of eugenol originally transferred to the autoclave. Nitrobenzene is added slowly as the oxidation proceeds. After the reaction is complete, pressure on the autoclave is released, and the gaseous by-products are permitted to blow off. Vanillin may be recovered from the alkaline solution by precipitation with hydrochloric acid. The yield approximates 80 per cent of theory.

Isoborneol to Camphor. Nitric acid has been widely used in the production of synthetic camphor from turpentine. The commonly accepted general practice for this manufacture (the one adapted by Gubelmann for use in this country) involves the following steps: (1) distillation of turpentine to obtain pinene, (2) saturation with HCl gas to obtain bornyl chloride, (3) hydrolyzing this to obtain camphene, (4) esterifying camphene to isobornyl acetate, (5) saponification to isoborneol, and (6) oxidation to camphor.

The oxidation is performed as follows: 20 parts of isoborneol is dissolved in 100 parts of 1.32 sp gr nitric acid to which has been added 5 parts of 50 per cent sulfuric acid, and the mixture is heated with stirring at 80–90°C (176–194°F) for 10 hr. Other oxidizing agents, such as potassium permanganate, chromic acid, and nitric acid under other conditions, have not been found to be satisfactory.[1]

Isoborneol dissolved in benzene or chloroform is readily oxidized to camphor with chlorine. Thus, a solution of 15.4 parts of isoborneol dissolved in 16 parts of benzene is shaken violently with a solution of 7.1 parts of chlorine dissolved in 900 parts of water by weight. Violent agitation is necessary to secure intimate contact of the two immiscible solutions. Camphor is recovered from the benzene solution after reaction is complete, in almost quantitative yield, and contains only traces of chlorine. Use of alkaline aqueous solutions of chlorine results in the formation of sodium chloride as a by-product.

Aniline to Quinone. Sodium or potassium dichromate may be used to oxidize aniline to quinone, but a low temperature and slow addition of the oxidizing agent must be employed in order to restrict the action. Although the high stability of the quinone structure toward further oxidation makes possible the use of so powerful an oxidizing agent as sodium dichromate in acid solution, care must still be exercised in order to prevent destructive reaction. An instance of the method is as follows: A mixture of 25 parts of

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[1] Beri and Sarin, *Chemistry & Industry*, 1936, 605.

aniline, 200 parts of water-white sulfuric acid, and 600 parts of water, contained in a wooden or corrosion-resistant vat, is cooled by ice or refrigeration. A solution of 25 parts of sodium dichromate in 100 parts of water is then slowly added with agitation and stirring is continued for 12 hr. A solution of 50 parts of sodium dichromate in 200 parts of water is then added, and stirring is continued until the reaction is complete. During the whole operation, the temperature is maintained below about 5°C through the addition of ice or by refrigeration. Quinone is recovered by skimming from the surface of the solution and is purified by steam distillation.

Oxidation of aniline with MnO_2-H_2SO_4 mixtures is claimed to give 73 per cent yield of quinone.[1]

Quinone is readily reduced to hydroquinone, and much of the quinone that is manufactured is sold in the form of the hydrogenated product. Hydroquinone, in turn, is readily oxidized to quinone by such agents as chlorine, nitric acid, persulfuric acid, chromic acid, ferric chloride, and permanganates. The reduction of quinone to hydroquinone and the reoxidation of hydroquinone to quinone are very rapid processes and are strictly reversible. This reaction is one of the rare oxidation and reduction reactions of organic chemistry that are rapid and reversible, like the oxidation and reduction of inorganic ions. Quinhydrone, $C_6H_4O_2 \cdot C_6H_4(OH)_2$, is formed as an intermediate in the process but is largely dissociated in solution. The dissociation is so rapid that quinhydrone acts like a mixture of quinone and hydroquinone, and an inert electrode in a solution of quinhydrone can be made to serve as a reference electrode, or half cell, if connected to another half cell. This property has led to the use of quinhydrone in the potentiometric determination of hydrogen-ion concentrations in unknown solutions.

Oxidation of Toluene. The use of manganese dioxide for the oxidation of toluene to benzaldehyde and benzoic acid was formerly extensive.[2] With manganese dioxide, the principal product is benzaldehyde; for high yields of benzoic acid, a stronger oxidizing agent such as chromic acid is required. For benzaldehyde production, the reaction is usually carried to the point where about 50 parts of benzaldehyde and 250 parts of toluene are recovered from a batch operation starting with 300 parts of toluene. In order to prevent extensive oxidation to benzoic acid, oxidation is not carried further than this. The method is as follows: 300 kg of toluene and 700 kg of 65 per cent sulfuric acid are mixed with intense stirring, and then 90 kg of finely powdered manganese dioxide is added while the temperature

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[1] FIERZ-DAVID, "Grundlegende Operationen der Farbenchemie," 2d ed., p. 153, Springer-Verlag OHG, Berlin, 1922; "Dye Chemistry," p. 145, trans. by Mason, Churchill, London, 1921.

[2] RASCHIG, *Chem. Ztg.*, **24**, 346 (1900); MONNET, *ibid.*, **22**, 929 (1898); **23**, 872 (1899); Fr. 276,258 (1898).

is held at 40°C. Benzaldehyde is recovered by steam distillation and constitutes a chlorine-free product. Benzoic acid forms as a by-product.

IV. LIQUID-PHASE OXIDATION WITH OXYGEN

The oxygen of the air is the cheapest available oxidizing agent but, at the same time, perhaps the most difficult to control. Although atmospheric oxygen is constantly reacted with organic substances at ordinary temperature, the rates of the reactions are too slow, generally, to be of any significance from the standpoint of usefulness in chemical synthesis. To induce molecular oxygen to react at commercially useful rates, it is usually necessary to provide a catalyst, to elevate the temperature, or to use a catalyst in conjunction with elevated temperatures. In many cases, the temperature must be elevated to the point where vapor-phase processes only are practicable. These will be dealt with later. In liquid-phase processes, catalysts may be either dissolved or suspended in finely divided form to ensure contact with bubbles of gas containing oxygen which may be caused to pass through the liquid undergoing oxidation. To speed up production, means must be provided for initially raising the temperature and for later removing reaction heat. Where low temperatures and slow reaction rates are indicated, natural processes of heat flow to the atmosphere may suffice for temperature control.

Acetaldehyde to Acetic Acid. The formation of acetic acid furnishes an excellent example of liquid-phase oxidation with molecular oxygen. Acetic acid may be obtained by the direct oxidation of ethanol, but the concentrated acid is generally obtained by oxidation methods from acetaldehyde that may have been formed by the hydration of acetylene or the oxidation of ethanol.[1] The oxidation usually occurs in acetic acid solution in the presence of a catalyst and at atmospheric or elevated pressures. Temperatures may range up to 100°C, depending upon conditions, but are usually lower.

Figures 9-1 and 9-2 show the general type of apparatus used. The reaction vessel consists principally of an aluminum-lined steel vessel fitted with aluminum coils for heating and cooling, inlet and outlet openings, and an air distributor.[2] In operation, about 4,500 kg (about 10,000 lb) of 99.0–99.8 per cent acetaldehyde previously cooled to 0–5°C is first introduced, and then 18–22 kg (about 39.6–48.4 lb) of manganese acetate is added either in the form of a saturated acetic acid solution or as a powder ground to pass a 200-mesh sieve. Air is introduced through the distributor head, and at

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[1] See "Vapor-phase Oxidation of Aliphatic Compounds," p. 517; see also Hale and Haldeman, Brit. 287,064 (1927); Fr. 650,771 (1928); *Chem. Age,* **23**, 272–276 (1930).

[2] Cadenhead [*Chem. Met. Eng.*, **40**, 184–188 (1933)] states that 1,000-gal kettles are used.

the same time, steam is passed through the aluminum coils to raise the temperature gradually to the operating point. When reaction starts, oxygen absorption from the incoming air is almost complete, and the heat of reaction must be removed by cooling water, which is substituted for the initial steam. The temperature is so controlled that after 1 hr it approximates 27°C; after 2 hr, 28–30°C; and after 4 hr, 60°C. The most satisfactory operating temperature is about 60°C. Reaction is complete in about 12–14 hr. The pressure is not allowed to exceed 5 kg per sq cm (65.3 psi), the nitrogen being vented through a series of condensers attached to the dome. Condensed aldehyde is returned to the kettle. Before being released, the nitrogen is passed through water scrubbers to remove the last of the aldehyde, which is later recovered. A concentrated acetic acid, exceeding 96 per cent in strength, results. Distillation is used for final concentration and purification of acid. The yield varies from 88–95 per cent of the theoretical. A retort of this size will produce about 60 tons of 99 per cent acid per month when operated normally or about 80–100 tons per month when forced.

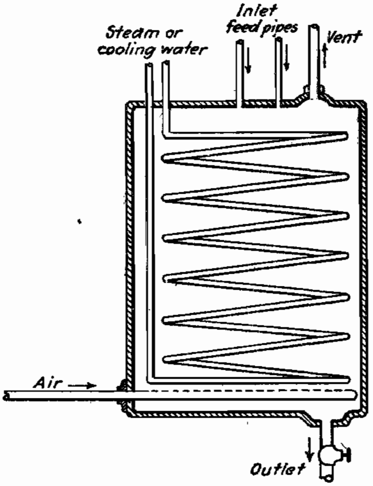

Fig. 9-1. Apparatus for batch liquid-phase oxidation of acetaldehyde to acetic acid.

Through study of the mechanism by which the catalyzed liquid-phase oxidation of acetaldehyde to acetic proceeds, it has been found that at temperatures below 15°C and in suitable solvents the acetaldehyde forms an unstable compound, acetaldehyde monoperacetate.[1] At controlled low temperatures this compound can be made to yield peracetic acid and acetaldehyde. Salts of the metals cobalt, copper, and iron catalyze the first-stage reaction, in a manner used in acetic acid manufacture.

This process is significant in that it is now in pilot-plant operation, and commercial production of peracetic acid is being planned. Previously, *in situ* use of this peracetic oxidation of unsaturated natural fatty acids to epoxy derivatives has been demonstrated.[2] It is to be expected that the commercial availability of low-cost peracetic acid will open many new areas of epoxidation reaction since almost any olefinic double bond is capable of

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[1] Carbide and Carbon Chemicals Co., Brit. 735,974 (1956); *Chem. Week*, Apr. 14, 1956, pp. 92–94.

[2] Findlay and Swern, U.S. 2,567,930 (1951).

epoxidation by peracetic acid. Because of the resulting coproduction of acetic acid, it is possible that custom epoxidation by a user of acetic acid might be a logical result or that an added incentive will be given for product diversification by acetic acid users.

Oxidation of fatty oils by peracetic acid results in products which are epoxidized, hydroxylated, and acetylated and have properties of value for use in vinyl plasticizers and greases.[1]

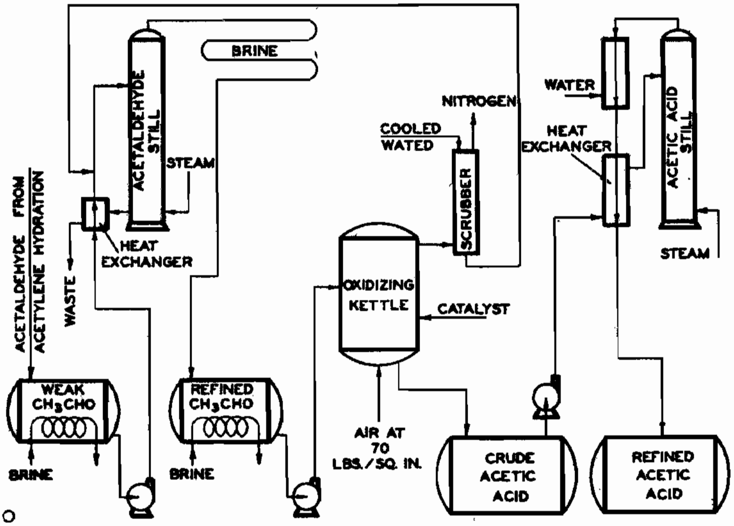

FIG. 9-2. Flow sheet for oxidation of acetaldehyde to acetic acid.

In the presence of catalysts, such as the acetates of the eighth group of metals, particularly cobalt, oxidation of acetaldehyde by air to acetic anhydride is claimed to occur directly at temperatures of 30–35°C and to result in 85–95 per cent conversions per pass.[2]

Ethanol to Acetic Acid. The liquid-phase oxidation of ethanol by the quick-vinegar process has been widely practiced. In this case, the presence of *Mycoderma aceti* is used to convey oxygen to the alcohol and effect oxidation. In the early practice of the quick-vinegar process, wooden tanks about 3–4 ft in diameter and 8–10 ft high filled with beechwood shavings, other cellulosic material, or even coke which carry the microorganism *Mycoderma aceti* have been used. A dilute alcohol solution containing up to 12–15 per cent ethanol is allowed to trickle down over the packing material. Oxygen, as air, introduced at the bottom of the vat becomes heated

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[1] *Chem. Eng.*, 60 (8), 118–122 (1953).

[2] Hull and Marshall, U.S. 2,367,501 (1945); Elyce, Stanley, and Turck, U.S. 2,622,098 (1952).

from the heat of the reaction, rises, and passes out at the top. Functioning of the microorganism is best in a dilute acid solution and ceases at acid concentrations of about 12 per cent. A temperature of about 35°C is most satisfactory. The product consists of a dilute acetic acid solution containing up to about 10 per cent acid. The best modern practice makes use of earthenware towers filled with beechwood shavings and fitted at the top with automatic spray devices for feeding in the dilute alcohol mixture or fermented mash solution.

Theoretically, 100 parts by weight of C_2H_5OH yields 130 parts of CH_3-COOH by oxidation, equivalent to slightly over 1 kg of acid per liter of alcohol. In practice, such 100 per cent yields are never obtained. Yields of 80–90 per cent of theory have been obtained in careful laboratory work, and 70 per cent yields are normally obtained in good industrial practice.

The catalyzed oxidation of ethanol to acetic accompanied by acetaldehyde oxidation may be accomplished by use of acetic acid solutions with a cobalt acetate catalyst. In an example, 252 g of acetaldehyde is fed to the catalyst solution for activation, and then 85.4 g of 100 per cent ethanol together with air is introduced. Conversion of ethanol is 94.2 per cent to acetic acid, 3.5 per cent unchanged, and 2.3 per cent to ethyl acetate.[1] Temperatures below 145°C were used. Various other metal acetates have been patented for the above process, including the salts of alkali and alkaline-earth groups,[2] salts of the platinum metals group,[3] and salts of the chromium metals group.[4] A solid palladium-on-alumina catalyst is active in promoting air oxidation of ethanol to acetic acid.[5]

Oxidation of Aliphatic Hydrocarbons and Derivatives. The use of dissolved catalysts, promoters, and initiators in a solvent of both the products and the hydrocarbon being oxidized facilitates the air (oxygen) oxidation of the lower aliphatic hydrocarbons. Such a technique permits the use of liquid-phase conditions, simplifies the problem of maintaining uniformity of temperature and removal of reaction heat, and permits regulation of the oxidation by control of pressure and rate of air or oxygen introduction. In such a process, Loder makes use of various liquids as solvents, preferably organic acids relatively inert to oxidation; catalysts such as salts of Ce, Co, Cu, Mn, V, U, Fe; plus promoters such as salts of Ba, Mg, K; plus "initiators" such as peroxides, peracids, aldehydes, ketones, olefins, or organic substances forming peroxides.[6] As an example of the above process, with a cobalt acetate catalyst, diethyl ketone initiator, and acetic acid

[1] Hull, U.S. 2,287,803 (1942).

[2] Hull, U.S. 2,353,157 (1944).

[3] Hull, U.S. 2,353,159 (1944).

[4] Hull, U.S. 2,353,160 (1944).

[5] KLASSEN and KIRK, *J. Am. Inst. Chem. Eng.*, **1**, 488–495 (1955).

[6] Loder, U.S. 2,265,948 (1941).

solvent, the air oxidation of isobutane at 100–155°C and 50 atm pressure resulted in the reaction of 338.3 g out of 1,131.8 g of isobutane charged to give a product containing acetone, 68.8 g; methyl acetate, 48.2 g; isobutyl acetate, 31.1 g; isobutanol, 47.1 g; unidentified, 18.1 g; water, 40.1 g; and a net gain of 13 g acetic acid. Similarly, *n*-butane is oxidized predominantly to acetic acid, but reaction conditions may be so modifed that methyl ethyl ketone yield is increased. Propane likewise yields either acetone or acetic acid.[1] A single plant operating at Pampa, Tex., is reported to have been designed for a capacity of 1,800,000 lb of glacial acetic acid per week.[2]

Similarly, the oxidation of olefins with or without functional groups results in the formation of useful compounds.[3] Thus, oxidation of allyl acetate or chloride results in formation of glycerol, of mixed octylenes in formation of octylene glycols, of ethyl crotonate in methyl glycerol, etc. Oxidation of olefins of various structures by oxygen at 85–125°C in the presence of a cobalt naphthenate catalyst and a mild alkali-like magnesium oxide results in epoxidation at the double bond with yields up to 50 per cent in all but the case of 2,2,5,5-tetramethyl-3-hexene, which is structurally incapable of forming hydroperoxide at the allyl position.[4] Unsaturated or hydroxylated long-chain fatty acids and their esters may also be oxidized by this process, with resultant simultaneous oxidation and chain cleavage to yield aliphatic dibasic acids and aliphatic monohydroxy-monocarboxylic acids.[5]

The oxidation mass in processes such as the above applied to either aliphatic- or alkyl-substituted aromatics is extremely corrosive and, in the experimental work, use was made of tantalum-lined reaction vessels. It has been found possible to use chromium-bearing steel for the reaction vessel if suitable proportions of lead or barium salts are present in the reaction mixture.[6]

Oxidation of Liquid Petroleum Hydrocarbons. The use of soluble salts of metals such as manganese, copper, iron, chromium, and vanadium permits operating temperatures of 100–160°C in liquid-phase processes in which air or gaseous oxygen is contacted with the liquid hydrocarbon. Interest in such oxidations has centered quite largely in the formation of fatty acids suitable for the production of soaps, fats, esters, solvents, etc., or capable of hydrogenation to high-molecular-weight alcohols, which after

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[1] Powers, *Oil Gas J.*, **54**, 74–76 (Aug. 29, 1955); Mitchell, *Petroleum Refiner*, **35** (7), 179–182 (1956).

[2] Thornton, *Petroleum Processing*, **8** (7), 1041–1044 (1953); Farrar, *Oil Gas J.*, **52**, 119–122 (Aug. 10, 1953).

[3] Loder, U.S. 2,316,604 (1943).

[4] Hawkins and Quin, *J. Appl. Chem. (London)*, **6**, 1–11 (1956); Millidge and Webster, U.S. 2,741,623 (1956).

[5] Loder and Salzberg, U.S. 2,292,950 (1942).

[6] Henke and Benner, U.S. 2,276,774 (1942).

sulfonation are, in turn, suited for use as detergents. Sodium and lithium soaps of these acids have been described as promising for the manufacture of lubricating greases.[1] Much of this work has centered on the oxidation of paraffin wax and hydrocarbons of comparable molecular weight.[2] It is reported that some 100,000 tons per year of fatty acids was produced by oxidation of various hydrocarbons in Germany during World War II.[3]

The acids tend to be aldehydic or hydroxylated in character; undesirable esters and other oxygenated compounds are formed; gums tend to be deposited; polymerization and condensation reactions that occur during the subsequent saponification operations give undesirable colors and odors to the product; separation of unoxidized hydrocarbons from the products is often difficult; etc. Volatile compounds, other than carbon oxides and steam, also form and may be recovered from the gases leaving the oxidation zone. Small quantities of the lower fatty acids, such as formic, acetic, and propionic, are produced and may be recovered with the water-soluble volatile products by scrubbing the exit gases with water or by extracting the oxidation mass with water.

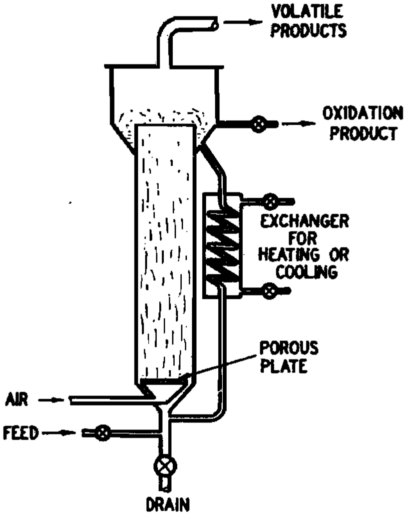

FIG. 9-3. Arrangement of apparatus for liquid-phase oxidation of hydrocarbons to fatty acids.

Very intimate contact between air and the hydrocarbon oil to be oxidized is desired. One method proposed for this is shown in Fig. 9-3. Admission of air through a porous diaphragm, properly placed, is used to induce a frothy condition in the material being oxidized, and a portion of the reacting material is recirculated through an external heat exchanger for temperature control. By continuously admitting unoxidized material and withdrawing oxidized product in regulated streams, the process may be made continuous. Either dissolved catalysts or solid catalysts fixed in place with fluid passing over them may be used.[4]

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[1] KIRK and NELSON, *Oil Gas J.*, **52** (37), 97–98 (1954).

[2] *Oil Gas J.*, **164** (7), 130–139; (8), 145–151; (9), 69–77 (1945); *Soap Sanit. Chemicals*, **XXI** (8), 38–39, 70, 78 (1945); NAMETKIN and ZVORYKINA, *Natl. Petroleum News*, **33** (40), R702–708; *C.I.O.S. Rept.* XXVI-50, Item 22 (Combined Intelligence Objectives Subcommittee).

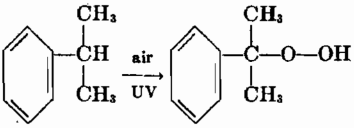
[3] *Chem. Eng. News*, **23**, 1520 (1945); *Rept.* 44 (Technical Oil Mission).

[4] Luther and Goetze, U.S. 2,015,347 (1936); 2,095,338 (1937); Keunecke, U.S. 2,095,473 (1937).

Liquid-phase oxidation with air of hydrocarbons such as low-melting scale waxes, waxy cracking stocks, and paraffinic gas oils in the presence of dissolved catalysts like manganese naphthenate has been found to give difunctional acids.[1] Temperatures in the range of 150–160°C, over-all time of 6–15 hr, and air at 150 psi resulted in products having no more than 5 per cent unsaponifiable and high proportions of water-soluble acids, believed to be mostly glutaric. The products from this process have been tested in alkyd resins, polyester resins, plasticizers, diester lubricants, and the like with good results.

Separation and recovery of the desired fatty acids are difficult from such mixed products, and many recovery processes have been patented. The use of morpholine soaps in separating the acids has been patented.[2] One practical procedure is based on the removal of unreacted hydrocarbons at high temperatures (320°C for soap acids and 380°C for edible acids) by flashing from pressure systems.[3]

Under certain controlled conditions, it is possible to obtain substantial yields of peroxides and hydroperoxides from the air oxidation of hydrocarbons. Commercially available peroxides obtained from liquid-phase air oxidation of hydrocarbons are sold under the name Uniperox and find use as diesel-fuel additives and polymerization catalysts.[4] Thus the autoxidation of isopropylbenzene (cumene) at elevated temperatures and with brief ultraviolet irradiation is comparatively rapid, occurring at the labile H atom of the isopropyl group.



Isopropylbenzene peroxide is a liquid comparatively stable to heat, decomposition beginning to set in at 165–175°C. The following peroxides also are described: *p*-menthane-hydroperoxide,[5] diphenyl-methane-hydroperoxide, autoxidation of indene, and cleavage of tetralin-peroxide.[6]

Cyclohexane. Petroleum-derived cyclohexane is the significant commercial raw material for adipic acid manufacture.[7] Cyclohexane may be converted by oxidation to adipic acid by either of two basically different processes. One of these, direct single-step oxidation, has received con-

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[1] Zellner and Lister, American Chemical Society, Minneapolis, Minn., September, 1955.

[2] Zellner, U.S. 2,342,028 (1944).

[3] Described in *C.I.O.S. Rept.* XXVI–50, Item 22.

[4] Farkas, Smith, and Stribley, presented before Petroleum Division, 109th American Chemical Society Meeting, Atlantic City, N.J., Apr. 8–12, 1946.

[5] Fisher, Goldblatt, Kniel, and Snyder, *Ind. Eng. Chem.*, **43**, 671 (1951).

[6] Hock and Lang, *Ber. deut. chem. Ges.* **76B**, 1130–1131 (1943); **77B**, 257–264 (1944).

[7] Sherwood, *Petroleum Processing*, **11** (5), 74–79 (1956).

siderable attention and has been variously described in the patent and technical literature.[1] This single-step method, however, has not attained commercial success, largely because of inadequate yields and operating problems.

The present commercially important method is a two-step route, by which cyclohexane is first oxidized to a mixture of cyclohexanol and cyclohexanone and then these intermediate products are subsequently oxidized to adipic acid.

The first step is performed in liquid phase with air as oxidizing agent under pressures of 3.5–5 atm to maintain liquid conditions. With a cobalt naphthenate-catalyst, temperatures in the range of 120–130°C are adequate, whereas without catalyst the temperatures need to reach 145–150°C.[2] An important feature of the process is the relatively low per-pass conversion of about 15 per cent of the cyclohexane charge. Water formed by the oxidation reaction and impurities in the feedstock such as sulfur-containing compounds and other hydrocarbons are removed azeotropically as reaction proceeds. Unless reaction water is removed, the air-oxidation ceases after about 25–30 per cent conversion. Removal of feed impurities and oxidation by-products results in a clean recycle stream.

The intermediates, cyclohexanol and cyclohexanone, are obtained as a still residue after steam distillation of unconverted cyclohexane, and this impure bottoms mixture may then be subjected to second-step oxidation without further purification. Yield of pure cyclohexanol plus cyclohexanone by this process is on the order of 60–75 per cent, but the yield of products convertible to adipic acid in the impure bottoms is on the order to 80–85 per cent of theory, indicating the presence also of adipic acid itself plus other oxidation products, which oxidize to adipic acid. The preferred commercial practice, however, is to autoclave the reaction product with water first in order to separate lower-molecular-weight oxidation products. This process is described earlier in this chapter.

The second-step oxidation is normally by means of nitric acid, but catalytic air oxidation results in good yields of adipic acid.[3] In recent practice, the refined first-step product of cyclohexane oxidation freed of unconverted hydrocarbon and a 50–60 per cent nitric acid solution containing copper-vanadium catalyst are separately and continuously fed to a jacketed reaction vessel at a ratio such that weight ratio of 100 per cent nitric acid to organic feed is between 2.5 and 6. The reaction mixture is rapidly recirculated through a tubular reactor at 60–80°C, and fresh feed is admitted to give about 5 min time of contact. Yields are improved by reheating the continuously withdrawn effluent stream to 95–100°C for a

[1] Loder, U.S. 2,223,493 (1940); Wadsworth, U.S. 2,589,648 (1952).

[2] Loder, U.S. 2,223,494 (1940); Hamblet and Chance, U.S. 2,557,281 (1951).

[3] Hamblet, et al., U.S. 2,557,282 (1951); Hamblet and McAlevy, U.S. 2,439,513 (1948).

period of about 7 min. Heat must be removed during the exothermic reactions, and a recovery system is employed to recover the gaseous nitrogen oxides for reconversion to nitric acid. For operations at an annual capacity of 8–15 million lb of adipic acid, batchwise operation may be economical in comparatively simple apparatus.

The liquid product from the 100°C reactor is countercurrently stripped with 90°C air to remove nitrogen oxide gases. The more volatile oxidation by-products such as valeric and butyric acids are removed by steam distillation and the liquors concentrated for adipic acid recovery. Adipic acid is crystallized from the liquors at about 40–50°C and is recovered by centrifugal separation. Mother liquor is then recycled to the process.[1] Two-step crystallization may be used to improve recovery and reduce the proportion of succinic acid impurity in the recycle.

Single-stage vapor-phase air oxidation of cyclohexane in presence of solid catalysts results in complete combustion, whereas without catalysts aldehydes constitute the major products.[2]

Isopropylbenzene (Cumene). Oxidation of isopropylbenzene, cumene, to cumene hydroperoxide and the subsequent decomposition to phenol and acetone have become of significant commercial importance in recent years and have, furthermore, pointed the way as a generally useful new route for potential commercial manufacture of other important chemicals.[3] For use in the phenol-plus-acetone process, cumene is usually obtained by the phosphoric acid–catalyzed alkylation of benzene with propylene.

Economic comparison with traditional phenol processes shows the commercial significance of this newest process.[4]

The acid-catalyzed decomposition of cumene hydroperoxide in a homogeneous medium, 50 per cent acetic acid at 60°C, gives yields of 92 per cent phenol and 81 per cent acetone.[5] Over-all phenol yield is about 80 per cent, and total product ratio is about as follows:[6]

Product	Weight Per Cent
Phenol	57
Acetone	34
α-Methylstyrene	6
Acetophenone	3

Minor amounts of mesityl oxide are also produced.

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[1] Hamblet and Gee, U.S. 2,713,067 (1955).

[2] Hoot and Kobe, *Ind. Eng. Chem.*, **47**, 776–781 (1955).

[3] O'Connor, *Chem. Eng.*, **58** (10), 215–218 (1951); Nieuwenhuis, *Chem. Week*, May 2, 1953, pp. 30–39; Stormont, *Oil Gas J.*, **51** (40), 106–107 (1953).

[4] *Can. Chem. Processing*, **37** (8), 26 (1953); Foster, *Petroleum Engr.*, **25** (12), C3–C4 (1953); Salt, *Chemistry and Industry*, **1953**, S46–S49; Sherwood, *Petroleum Processing*, **8**, 1348–1354, 1543–1545, 1722–1728 (1953).

[5] Seubold and Vaughan, *J. Am. Chem. Soc.*, **75**, 3790–3792 (1953).

[6] *Chem. Eng. News*, **31** (12), 1114 (1953); *Petroleum Refiner*, **33** (4), 164 (1954); *Chem. Eng.*, 62 (10), 122 (1955).

Treatment of *p*-cymene, *p*-methylisopropylbenzene, by the peroxidation-decomposition process yields *p*-cresol and acetone. Starting with diisopropylbenzene, either the mono- or dihydroperoxide may be obtained[1] and from these a variety of products including isopropylphenol, isopropylacetophenone, hydroquinone, diacetylbenzene, and others, depending on the decomposition technique.

When air or oxygen is bubbled through or otherwise contacted with liquid cumene at temperatures in the range of 100–130°C, oxidation occurs with resultant formation of cumene hydroperoxide, which is comparatively stable under these conditions. The usual oxidation catalysts, such as salts of the transition metals, cannot be used for the reaction since they tend to cause decomposition of the cumene hydroperoxide. Purity of the charge material is important since small amounts of certain impurities such as sulfur compounds, phenols, aniline, unsaturated hydrocarbons, and the like act as inhibitors to break the chain reaction and thereby slow down the reaction. The maximum reaction rate is attained after a portion of hydroperoxide is formed in fresh cumene charge.[2]

In laboratory, batch, noncatalytic experiments with cumene oxidized with oxygen at 120°C during a period of 6 hr, the moles of products found per 100 moles of cumene converted were as follows:

Product	Moles per 100 Moles
Cumene hydroperoxide	80.1
Dimethyl phenyl carbinol	14.7
Water	3.4
Acetophenone	0.4
Methanol	0.5
Carbon dioxide	0.3

The copper catalyzed reaction at 120°C showed about 11.6 weight per cent conversion per hour at a yield of near 98 per cent.

It has been shown that the presence of metallic copper gives rise to a substantially increased rate of reaction. Thus, experiments performed in a copper reaction vessel gave a rate of cumene hydroperoxide formation of 22.3 relative to a rate of 4.1 in an exactly comparable stainless-steel vessel. Continuous preparation of hydroperoxide from cumene in a long tubular copper vessel filled with copper turnings at 120°C using oxygen gas gave a production rate of 74 g of cumene hydroperoxide per hour per liter of volume, with a product stream averaging 21 weight per cent of cumene hydroperoxide.[3]

Two general commercial processes have been described.[4] In one of these,

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[1] Hawkins, Quin, and Salt, U.S. 2,715,646 (1956).

[2] FORTUIN and WATERMAN, *Chem. Eng. Sci.*, **2**, 182 (1953); Special Supplement to *Chem. Eng. Sci.*, **3**, 60–66 (1954).

[3] *Ibid.*

[4] *Chem. Eng.*, **60** (2), 104 (1953).

cumene in liquid phase is contacted with oxygen at 100–130°C until not over 5 per cent by weight of the reaction mixture of cumene hydroperoxide is formed. Cumene is then treated with a strong base and reoxidized with oxygen at about 110°C until the hydroperoxide concentration in the liquid reaches at least 11 per cent. Pretreatment of cumene with aqueous bases like potassium hydroxide solutions, intermediate treatment of partially oxidized cumene with a strong base, or suspending finely divided calcium carbonate in the liquid results in improved yields and higher oxidation rates.[1]

In another of the commercial processes, cumene is also oxidized in liquid phase with oxygen at 105–135°C in the absence of any added catalyst. Steam is used in the gas-vapor zone of the reactor to prevent explosions.

Xylenes. The dicarboxylic acids resulting from side-chain oxidation of *p*- and *m*-xylenes do not yield anhydrides as phthalic acid does, and liquid-phase oxidation conditions have proved necessary in conversion of these isomers.

Para-xylene may be oxidized to terephthalic acid by means of nitric acid. Liquid-phase oxidation of *m*- and *p*-xylene is complicated by the increased resistance to oxidation of the second methyl group after the first has been oxidized to the carboxyl group. As a consequence of experience with this difficulty, development has been toward oxidation in two steps, a first to the toluic acid stage and a second to the dicarboxylic acid. Esterification of the first carboxyl group results in much easier oxidation of the second methyl to a carboxyl group. Other *p*-substituted benzenes such as *p*-diisopropylbenzene are oxidized by air in the presence of a cobalt catalyst to terephthalic acid.[2] Use is made of this in a recent new approach which permits the use of catalyzed air oxidation of *p*-xylene and results in formation of dimethyl terephthalate. A four-step process has attained commercial importance: air oxidation of *p*-xylene to toluic acid using oil-soluble catalysts of cobalt or manganese, esterification with methanol to methyl *p*-toluate, a second air oxidation to monomethyl terephthalate, and finally esterification with methanol to dimethyl terephthalate.

This method is reported to function satisfactorily also with *m*-xylene and leads to the formation of dimethylisophthalate. Coproducts to be expected include benzoic and toluic acids, both of which have commercial use.

V. VAPOR-PHASE OXIDATION OF ALIPHATIC COMPOUNDS

Almost without exception, the vapor-phase processes employed in the partial oxidation of organic compounds use molecular oxygen as the oxidizing agent and require catalysts and elevated temperatures for opera-

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[1] Joris, U.S. 2,621,213; 2,619,509; 2,613,227 (1952).

[2] Fortuin and Rumscheidt, U.S. 2,746,990 (1956).

tion at industrially useful rates. Only certain substances are fitted for vapor-phase processing. These must have sufficiently high vapor pressures at the temperatures required for oxidation to make it possible to mix them with air (oxygen) and pass them in the gaseous state over the catalyst material. They must be of sufficient thermal stability to resist undesired decomposition and give rise to products of comparable thermal stability. Furthermore, the products must be reasonably stable to continued oxidation and must be readily recoverable from the gaseous products.

These various restrictions limit the materials capable of economic processing by vapor-phase oxidation to the simpler aliphatic and the aromatic series of compounds. Because the methods applied to these two classes of compound are characterized by consideration for group properties, they will be treated separately.

Oxidation of Methanol.[1] Consideration of the reactions involved in the synthesis and decomposition of methanol shows that only low conversions to formaldehyde may be obtained by the direct catalytic decomposition of the alcohol.

$$CH_3OH \rightarrow H_2CO + H_2 \rightarrow CO + 2H_2$$

Catalysts and temperatures conducive to the dehydrogenation of methanol are also conducive to the decomposition of the formaldehyde to hydrogen and carbon monoxide. Furthermore, the reaction is endothermic, and heat must be supplied.

However, if oxygen, in the form of air, is furnished to the reaction and the process conducted in the vapor phase in the presence of suitable catalysts, industrially practicable yields of formaldehyde are obtained and the process is made exothermic. Although the oxidation of methanol process appears simple, it requires regulation of temperature, air-to-alcohol ratio, and time of contact to ensure continuous high yields at high efficiency. A simple, practical method consists in mixing air with methanol, passing the resulting air-methanol mixture over a suitable catalyst (see Fig. 9-4), condensing the gaseous reaction mixture, and recovering the product.

For oxidation to formaldehyde, 1 lb of pure methanol theoretically requires 26.7 cu ft of dry air measured under standard conditions (2.18 lb). Exact control of the ratio is made possible by the use of separate, controlled streams of air and liquid methanol introduced to a vaporizing chamber, which is supplied with heat to vaporize the liquid. Cleaned, dry air is supplied through a storage tank by a compressor, and methanol enters the mixing chamber as a liquid. Only small amounts of mixed air and vapor

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[1] Walker, "Formaldehyde," *Am. Chem. Soc. Monograph* 98, Reinhold Publishing Corporation, New York, 1944; Neidig, *Chem. Inds.*, **56** (2), 242 (1944); Olive, *Chem. Eng.*, **56** (2), 130–133 (1949); *B.I.O.S. Final Repts.* 978, Item 22, and 1331, Item 22 (British Intelligence Objectives Sub-committee).

are present at any time; the mixture passes immediately to the catalyst chamber and thence to the recovery system.

Large amounts of formaldehyde have been made with a catalyst consisting of copper arranged in the form of gauze rolls supported in concentrically arranged bundles of copper tubes, which, in turn, are held by headers on each end. Such a catalyst chamber may consist of six or eight copper tubes 24 in. long and 2 in. in diameter containing rolled-up copper gauze for about 4 or 5 in. of their length, fitted into suitable headers at each end and enclosed in a cover. Means are provided for heating the catalyst mass at the start of operation. Reaction occurs at a temperature of 400–450°C, and operation is conducted at a temperature of about 550–600°C in the catalyst mass. The rate of feed and the air:methanol ratio are maintained so as to make operation autothermal. The gaseous mixture passes from the catalyst chamber to a rectifying and recovery system, where rapid countercurrent cooling is obtained by contact with the relatively cool aqueous formaldehyde solution that passes down the column. Formaldehyde solution is withdrawn at the bottom of the column, and fixed gases containing the vapor of unreacted methanol are passed out of the top to a condenser where the methanol is partly recovered. The fixed gases from this condenser are scrubbed with water or dilute methanol solution for complete methanol recovery. Condensed methanol and methanol recovered from the aqueous solution by rectification are fed back to the mixing chamber for recirculation over the catalyst. Methanol containing very little formaldehyde may be obtained by the rectification of solutions containing as much as 38 per cent of formaldehyde so as to leave very little methanol in the residual aqueous solution.

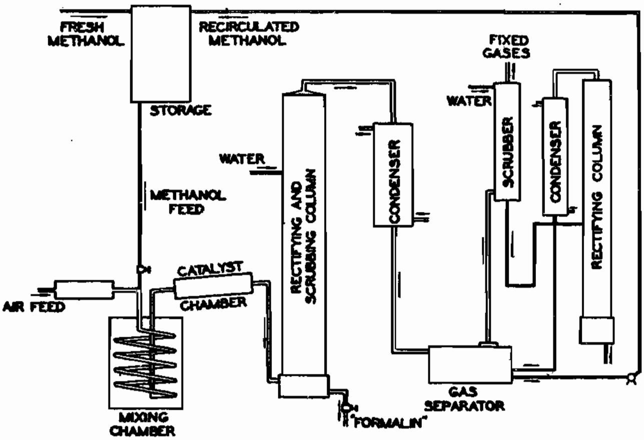

FIG. 9-4. Schematic layout for oxidation of methanol to formaldehyde.

The German plants at Leverkusen and Ludwigshafen[1] made use of a silver catalyst for oxidation of methanol to formaldehyde. Operation is conducted with a methanol vapor-air mixture of about 50 per cent methanol vapor by volume, well on the rich side of the explosive limits. At the preferred operating temperature of 635°C, a conversion of about 65 per cent methanol per pass is obtained, obviating substantial recycle ratios. Under proper conditions of operation, about 55 per cent of the formaldehyde results from exothermic oxidation and about 45 per cent from the endothermic dehydrogenation, with side reactions resulting in carbon monoxide, carbon dioxide, formic acid, and methylol. The fouling of silver catalysts used in this process is reported to be due to the formation of a layer of spongy silver on the catalyst surface, greatly accelerated by water vapor and fluctuating temperatures.[2]

The water formed by reaction is not sufficient to bring the formaldehyde solution to the 37.0–37.5 per cent by weight concentration at which it is generally sold, and some water must be added. Water may be added to the methanol feed for purposes of control and improvement of yield.[3] Commercial formaldehyde contains some 37 per cent H_2CO, about 9 per cent methanol, and 54 per cent water. This solution will not deposit polymer on standing, whereas one containing no methanol will deposit solid on slight cooling. Large commercial formaldehyde producers have now developed stabilizers that will permit production of full-strength stable formaldehyde without the use of methanol.

Formaldehyde also appears on the market as the hydrated solid polymer *paraformaldehyde*, containing about 95 per cent formaldehyde, which is prepared by the evaporation of formaldehyde solution.

According to theory, 100 g of pure methanol should yield 93.75 g of pure formaldehyde, but, in practice, only about 82–85 per cent of theoretical yield is obtained. Conversions as high as 96 per cent are possible with laboratory methods and have been approached for short periods in commercial apparatus. At the ordinary conversion efficiency, 100 lb of methanol yields between 190 and 200 lb of commercial formaldehyde solution.

Oxidation of Ethanol. Ethanol may be dehydrogenated or oxidized to acetaldehyde in the vapor phase with good yields. Shreve[4] reports yields of 85–95 per cent by air oxidation of ethanol to acetaldehyde with a silver catalyst at 550°C and per-pass conversions of 50–55 per cent. Dehydrogenation of ethanol to acetaldehyde over an asbestos-supported copper catalyst activated by small additions of cobalt and chromium has been re-

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[1] *B.I.O.S. Final Repts.* 978, Item 22, and 1331, Item 22.

[2] BREWSTER, *Chem. Eng. News*, 26, 2877 (1948).

[3] Uhl and Cooper, U.S. 2,465,498 (1949).

[4] SHREVE, "The Chemical Process Industries," p. 918, McGraw-Hill Book Company, Inc., New York, 1945.

ported to result in maximum yields of 85 per cent acetaldehyde plus 9.6 per cent ethyl acetate at 275°C and a per-pass conversion of 50 per cent.[1] In the commercial air-oxidation process, about a fifth of the acetaldehyde may arise from dehydrogenation.

The direct oxidation of ethanol to acetic acid in a continuous catalytic vapor-phase process is more difficult since losses to formaldehyde, carbon oxides, etc., occur. Simultaneous oxidation of mixtures of acetaldehyde and ethanol in the vapor phase is claimed to give good conversions of acetaldehyde to acetic acid and of ethanol to acetaldehyde, which latter is then recycled in the process. The greater the proportion of acetaldehyde to alcohol, the lower may be the temperature for reaction.[2] Reaction of a mixture of 1 part by weight of ethanol, 1.077 parts of acetaldehyde, 1.055 parts of air, and 0.196 part of steam by passage through a 60-ft by 0.75-in. tube at 525°F is said to yield a product containing 0.182 part by weight of acetic acid, 1.078 parts of acetaldehyde, and 0.855 part of ethanol. By recycling and introducing fresh ethanol, there is obtained 1.086 parts by weight of acetic acid, 0.091 part of acetaldehyde, and 0.095 part of ethanol for each part of ethanol fed to the system.

Oxidation of Other Alcohols, Glycols, Carbonyls, and Esters. The processes described for ethanol have also been found generally applicable to the oxidation of propanol and butanol to the corresponding acids, particularly those using dissolved cobalt catalysts in acid solutions.

In recent years, methyl vinyl ketone has received considerable attention as a possible component of various polymer products. Almost all the information regarding uses, preparation, methods of polymerization, stabilization, etc., of methyl vinyl ketone is contained in the patent literature.[3]

Catalytic dehydrogenation of methyl vinyl carbinol at temperatures above 250°C in presence of a brass spelter catalyst is claimed to give a 33 per cent yield of methyl vinyl ketone, $CH_3{\cdot}CO{\cdot}CH{=}CH_2$. Catalytic vapor-phase oxidation of the unsaturated alcohols to form unsaturated carbonyl compounds has been found to give considerably higher yields. Temperatures in the range of 360–550°C and use of a metallic silver catalyst are described.

Glyoxal used in a newly developed process for the shrinkproofing of viscose rayon may be produced by the direct oxidation of ethylene glycol.[4]

A variety of organic substances when catalytically oxidized result in the formation of maleic anhydride. The usual vanadium or molybdenum

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[1] Church and Joshi, paper before Unit Process, Symposium, Division of Industrial and Engineering Chemistry, American Chemical Society, Chicago, Sept. 4, 1950.

[2] Bludworth, U.S. 2,263,607 (1941).

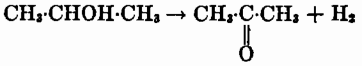
[3] See Breuer, "Review of German Patent Literature Relating to Synthetic Rubber," *Rubber Age*, **54**, 229–234 (1943); 336–340 (1945); Yale and Hearne, U.S. 2,398,685 (1946).

[4] Field, *Chem. Inds.*, **60**, 960 (1947).

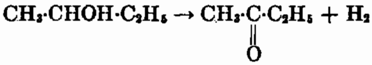
mixed, supported oxidation catalysts are effective in the oxidation of furfural to maleic anhydride. Yields of over 75 per cent at conversions of over 95 per cent per pass are reported.[1] A catalyst composed of 1 part V_2O_5 plus 6 parts MoO_3 supported on an aluminum base is effective in the oxidation of crotonaldehyde to maleic acid and anhydride. Reaction mixtures of 30–85 parts by weight of air, 3–25 parts of steam per part of crotonaldehyde result in over 40 per cent per-pass conversions at a catalyst temperature of 350°C, with over 80 per cent of the reacted aldehyde converted to maleic acid.[2]

Oxidation via Dehydrogenation

Catalytic vapor-phase processes for the dehydrogenation of isoalcohols and side-chain aromatics are of great industrial importance. Examples of such processes are the preparation of acetone and methyl ethyl ketone from isopropanol and secondary butanol:



$$CH_3\cdot CHOH\cdot CH_3 \rightarrow CH_3\cdot \underset{\underset{O}{\|}}{C}\cdot CH_3 + H_2$$



$$CH_3\cdot CHOH\cdot C_2H_5 \rightarrow CH_3\cdot \underset{\underset{O}{\|}}{C}\cdot C_2H_5 + H_2$$

as well as the production of styrene from ethylbenzene;

$$C_6H_5\cdot C_2H_5 \rightarrow C_6H_5\cdot CH{:}CH_2 + H_2$$

Acetone and Methyl Ethyl Ketone. The raw materials for these syntheses are the olefins propene and 2-butylene which are converted to alcohols by sulfation and hydrolysis (see Chap. 13).

The same plant (Fig. 9-5) may be used to ketonize either isopropanol or *sec*-butanol.[3] Hydrogen is passed up through the dry alcohol kept at such a temperature that the hydrogen leaving the saturator carries with it an equal volume of alcohol vapor. The hydrogen flow is adjusted to evaporate 128 lb per hr of the alcohols, whichever is used.

The mixed vapors then pass to the catalyst chamber which consists of 130 tubes of ⅝-in. bore and 4 ft 6 in. in length, arranged in 13 rows each containing 10 tubes. The tubes are of N.C.T. 3 steel and are carried between mild-steel tube plates, the tube plates being attached to a mild-steel casing so that flue gas can be circulated at high velocity in a direction normal to the axis of the tubes. The flue gases are circulated by a fan, and heat is supplied to them by the products of combustion of a gas burner feeding into the stream, the excess gas being bled to atmosphere. The rate of circulation is such that the temperature of the flue gases does not drop

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[1] Nielsen, U.S. 2,464,825 (1949).

[2] Bludworth and Pearson, U.S. 2,462,938 (1949).

[3] *B.I.O.S. Final Rept.* 131, Item 22.

by more than 5°C during passage across the tubes. The temperature difference between flue gases and maximum temperature attained in the tubes is 20°C.

The tubes are filled with pumice of 2–4 mm size, which has been soaked in zinc acetate solution so that on drying and heating to 500°C in the air the zinc oxide content is 7–8 per cent of the weight of the catalyst. The catalyst tubes are vertical and have plugs screwed into their bottom ends carrying orifices to equalize the gas flow through all the tubes. The plugs also support the catalyst in the tubes.

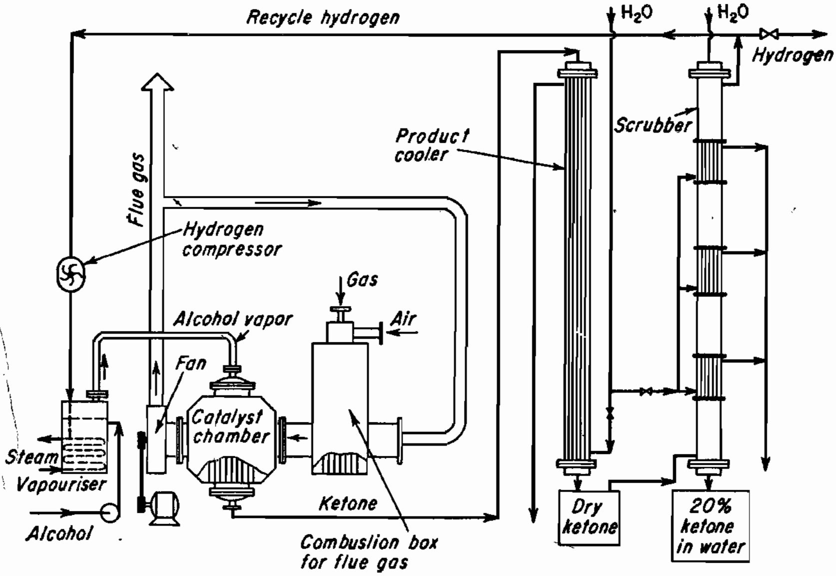


FIG. 9-5. Ketonizing system: conversion of secondary alcohols to ketones.

The saturated vapors pass downward through the tubes, the first 18 in. acting as a preheating section. The temperature attained in the last 3 ft depends on the alcohol being fed. When isopropanol is used the temperature is 380°C, when secondary butanol is used the temperature is 350°C. These temperatures give 98 per cent conversion of the alcohol fed, higher conversions resulting in impurities in the resultant ketones.

The catalyst achieves this performance for 10 days without necessity for raising the temperature. After this period, the degree of decomposition tends to decrease and the flow of gases is stopped, the temperature is raised to 500°C, and nitrogen containing about 2 per cent of oxygen is passed until carbon dioxide can no longer be detected in the exit gas. This, normally, is after a period of 4–5 hr.

The vapors leaving the catalyst chamber can be heat exchanged with the incoming vapors. They are passed through a mild steel cooler where about 50 per cent of the acetone or 80 per cent of the methyl ethyl ketone condenses. The uncondensed vapors are washed out of the hydrogen by passage up a ring-packed tower countercurrent to a flow of water. This tower is 12 in. in diameter and 20 ft in height, being split into sections by three short multitubular indirect coolers of the same diameter as the column. The flow of water is such as to give a final ketone concentration of 20 per cent in the water. The issuing gas contains about 0.5 per cent of ketone vapor and is hydrogen of over 99 per cent purity, the main impurity being propylene.

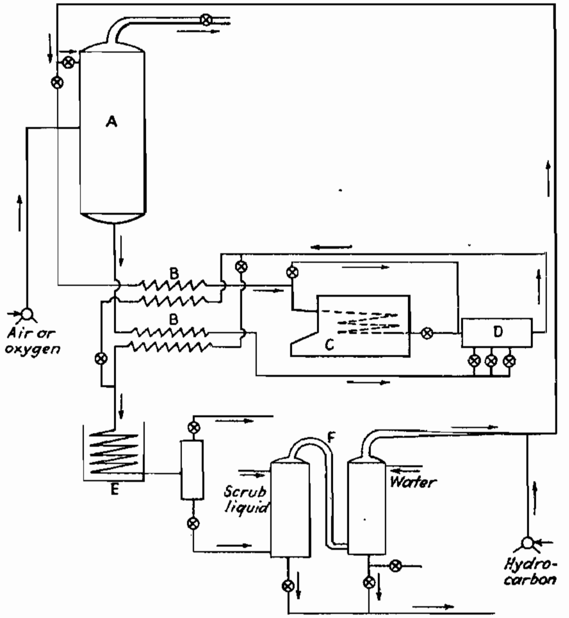
The anhydrous and wet ketones are collected separately and redistilled. The 2 per cent of alcohol undecomposed and distilled from the ketones is returned to the feed to the catalyst chamber. The zinc oxide catalyst has a life of 6 months and is then discarded.

Oxidation of Low-molecular-weight Paraffin Hydrocarbons

To obtain useful and desirable intermediate oxygen-containing products of oxidation from the lower aliphatic hydrocarbons, it is necessary that only relatively small proportions of oxygen be made to react with the hydrocarbon molecule. However, this limited reaction is difficult of practical attainment; and with the normally gaseous straight-chain aliphatic hydrocarbons, almost regardless of molecular weight, appreciable yields of only formaldehyde have been reported to result from the oxidation in the presence of solid catalysts at atmospheric pressure. Alcohols have been obtained under certain special conditions to be discussed later, and ketones have been reported to result from the oxidation of branched-chain hydrocarbons. The higher-molecular-weight aliphatic hydrocarbons, oxidizing more readily under less stringent conditions, may be converted to relatively long-chain acids, etc.

Numerous materials have been reported and patented as catalysts for the oxidation of the gaseous paraffin hydrocarbons. The majority of these, consisting mainly of metals or metal oxides, are far too active and too nonspecific in action to permit the recovery of more than small amounts of intermediate oxidation product. With such relatively mild catalysts as copper oxide and glass surfaces, some high yields of formaldehyde have been obtained from methane and ethane under experimental conditions. Under conditions where less than 10 per cent of the entering hydrocarbon is oxidized, conversions of over 50 per cent of reacting hydrocarbon to formaldehyde have been reported. The use of elevated pressures, as shown in Fig. 9-6, for the oxidation of methane and ethane has been found to enhance yields of useful products.

Oxidation of natural gas with very low oxygen concentrations under slight pressure and in the presence of a catalyst, such as copper–copper oxide, has been shown capable of producing a useful mixture of oxygenated products, i.e., formaldehyde, acetaldehyde, and methanol. Such a process, representing a by-product of the major industry of transporting natural gas, is capable of yielding formaldehyde in competition with the usual method of forming it from methanol by oxidation.[1]



A Oxygen saturator
B Preheater (heat exchangers)
C Furnace
D High-pressure reactor
E Cooler and gas separator
F Scrubbing system

FIG. 9-6. Schematic layout for pressure oxidation of aliphatic hydrocarbons.

Direct oxidation of methane (natural gas) with tonnage oxygen of about 95 per cent purity is assuming increasing importance in connection with the production of hydrogen-carbon monoxide synthesis gas, raw material for the American modified Fischer-Tropsch synthesis of liquid fuels and chemicals.[2]

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[1] BROOKS, *J. Inst. Petroleum Technol.*, **24**, 744 (1928); BURRELL, *Natl. Petroleum News*, **22** (22), 80 (1930); WIRGES and PALM (Cities Service Oil Co.), *Oil Gas J.*, **48**, 90–192, 114 (May 12, 1949); SHERWOOD, *Petroleum Processing*, **4** (7), 794–800 (1949).

[2] *Chem. Eng.*, **54**, 129 (1947); KEITH, *Chem. Inds.*, **59**, 58 (1946); RUTHERFORD, *Ind. Chemist*, **19**, 178 (1943).

One plant located in Texas, when completed, will operate at a rate of 40 million cu ft of tonnage oxygen per day.[1]

The oxygen partial combustion of natural gas has now become well established industrially as a means for producing synthesis gas for ammonia and methanol manufacture and in the modified Fischer-Tropsch process. Advantages of the partial-combustion process relative to steam or CO_2 reforming of natural gas is the lower product costs made possible by the availability of low-cost tonnage oxygen. In such partial-oxidation process, equilibrium between CH_4, H_2, CO, CO_2, and H_2O depends on the temperature level, higher temperatures favoring H_2O and CO.[2]

Modification of conditions of operation of the oxygen partial combustion of natural gas for synthesis gas has reached the commercial scale for acetylene production.[3] The Sachse process developed in Germany and engineered for use in the United States is based on the formation of acetylene at temperatures of 1500–1600°C by the reaction

$$2CH_4 \rightarrow C_2H_2 + 3H_2 - 91 \text{ kcal}$$

Heat for the reaction is obtained by burning a portion of the natural gas with oxygen. For the production of 1 ton of 99.5 per cent acetylene, 5.6 tons of 95 per cent oxygen and 193,000 cu ft of natural gas are required.

Oxygen and natural gas, separately preheated in fuel-fired heaters, are thoroughly premixed prior to ignition by a jet burner.. The burner gas is quenched by water spray to 90°C and further cooled by water washing in a column. Carbon soot is partly removed at each of these stages. Final carbon removal is by filtration through a moving bed of wet coke. Burner gas composition is shown in Table 9-1.

The filtered gas is fed to an absorber where C_2H_2, higher acetylenes, and some CO_2 are absorbed in a solvent. The rich solvent is then stripped to produce commercially pure C_2H_2.

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[1] Alden and Clark, paper before Western Petroleum Refiners' Association, Apr. 5, 1948; *Petroleum Processing*, **3**, 425–430 (May, 1948); Bland, *Natl. Petroleum News*, **40**, 22 (Feb. 18, 1948); *Chem. Eng. News*, **26**, 610–615, 682 (1948); Keith, *Chem. Inds.*, **60**, 58 (1946); Kemp, *Natl. Petroleum News*, **40**, 49 (Feb. 11, 1948); Murphree, *Oil Gas J.*, **45**, 66 (Apr. 8, 1948); Schroeder, *Chem. Inds.*, **62**, 574–577, 682 (1948); Storch, *Chem. Eng. Progr.*, **44**, 469–480 (1948); Sullivan, *ibid.*, **43** (12), 13 (1947); Weil and Lane, "Synthetic Petroleum from the Synthine Process," Chemical Publishing Company, Inc., New York, 1938.

[2] Reidel, *Oil Gas J.*, 52, 66–68, (Oct. 26, 1953); **52**, 66 (Nov. 9, 1953); 52, 52 (Nov. 23, 1953); *Chem. Eng. Progr.*, **50** (3), 46 (1954); *Chem. Eng.*, **61** (4), 126 (1954); Kelly and Cain, 124th Meeting American Chemical Society, Chicago, Sept. 6–11, 1953; Sherwood, *Petroleum Processing*, **8**, 1633–1638 (1952).

[3] *U.S. Bur. Mines, Inform. Circ.* 7375, August, 1946; Thurston, Carpenter, and Derbenwick, Manufacture of Acrylonitrile from Natural Gas, Fourth World Petroleum Congress, Rome, 1955. Sec. *IV*/C; Bartholome, Acetylene by Partial Oxidation of Methane, *ibid.*; Strelzoff, *Petroleum Refiner*, **35** (3), 167–170 (1956); *Oil Gas J.*, Sept. **5**, 1955, pp. 110–113.

TABLE 9-1. GAS COMPOSITION

(Dry Basis, Per Cent Volume)

	Burner gas	Tail gas
C_2H_2	8.0	0.1
C_2H_4	0.3	0.3
CH_4	4.4	4.8
CO	25.9	28.2
CO_2	3.9	4.3
H_2	54.8	59.8
O_2	0.3	0.3
Higher acetylenes	0.4	0
$N_2 + A$	4.0	2.2

The tail gas from the acetylene scrubber may be used for synthesis of ammonia or methanol or for hydrogenation processes.

The aliphatic hydrocarbons become progressively more easily oxidized as the number of carbon atoms in the free straight chain is increased and as the pressure is increased.[1] Table 9-2 shows the temperature at which oxidation is first detectable at a series of pressures. Reaction temperature in noncatalytic vapor-phase oxidations has a striking effect on the product character, the higher ranges above 300–400°C tending to result in dehydrogenation and cracking reactions in the case of *n*-butane rather than the desirable oxygenation. With less than 10 per cent oxygen mixed with *n*-butane and temperatures in the range of 450–550°C, reaction is primarily dehydrogenation.[2]

TABLE 9-2. TEMPERATURE-PRESSURE RELATIONS: OXIDATION OF PARAFFINS

Hydrocarbon	Oxidation initiation temperature, °C			
	1 atm	50 atm	100 atm	150 atm
Methane	420	350	330	320
Ethane	285	276	260	—
Propane	270	255	245	232
n-Butane	—	248	220	210

An example of the controlled noncatalytic oxidation of low-molecular-weight paraffin hydrocarbons to form commercially practicable yields of oxidation products is given by a process devised by Bludworth. In the oxidation of butane or other low-molecular-weight paraffin hydrocarbon, he

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[1] MITCHELL, *Petroleum Refiner*, **35** (7), 179–182 (1956).

[2] APPLEBY et al., *J. Am. Chem. Soc.*, **75**, 1809–1814 (1953).

uses a large excess of a diluent such as steam, a short reaction time, a limited proportion of air to hydrocarbon, and a water quench.[1]

TABLE 9-3. NONCATALYTIC OXIDATION OF PARAFFINS

Products	Yields based on 100 parts butane	
	A, parts	*B*, parts
Acetaldehyde	19.6	23.0
Acetone	7.0	10.0
Methanol	19.0	3.0
Propanol	1.0	3.0
Butanol	0.5	3.0
Organic acids	11.4	7.0
Formaldehyde	15.2	15.0
Total	73.7	64.0

Examples taken from the patents show that, under the given conditions, yields of products listed in Table 9-3 may be obtained:

A. Ratio by weight of 1 part of butane, 5 parts of air, and 34 parts of steam; preferred pressure range, 20–30 atm; temperature, 399°C; time of reaction, 1.15 sec; and quench to 149°C.

B. Ratio by weight of 1 part of butane, 5 parts of air, and 18.5 parts of steam (plus recycled unreacted hydrocarbon gases); preferred pressure range, 3.5–20 atm; temperature, 288°C; time of reaction, 0.3 sec. Any type of low-molecular-weight hydrocarbon is suitable for the process, such as butane, pentane, casing-head gasoline, and the C_3–C_6 fraction of refinery gas.

A single plant operating in Texas, based on the noncatalytic controlled oxidation of propane-butane hydrocarbons, is reported to consume over 50 million gal annually of these light hydrocarbons together with large volumes of natural gas in the production of over 300 million lb of chemicals per year.[2] Chemical products include formaldehyde purified to resin grade by means of ion-exchange resins, acetic acid, methanol, propanol, isobutanol, butanol, acetaldehyde, acetone, methyl ethyl ketone, mixtures of C_4–C_7 ketones, mixtures of C_4–C_7 alcohols, and propylene and butylene oxides. Catalytic liquid-phase oxidation of propane and butane is much more specific, and major yields of acetic acid are obtained.

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[1] BLUDWORTH, U.S. 2,128,908; 2,128,909 (1938); 2,369,710 (1944); POWERS, World Petroleum Congress, Rome, June 6–15, 1955; MEYER, *Oil Gas J.*, **54**, 82–86, (June 20, 1955); SHERWOOD, *Petroleum Engr.*, **27**, C14–C18 (December, 1955); **28**, C33–C42 (January, 1956); *Chem. Age*, Dec. 24, 1955, pp. 1363–1369.

[2] BLUDWORTH, *Oil Gas J.*, **45**, 76 (Apr. 12, 1947); *Petroleum Refiner*, **27**, 110 (April, 1948); POWERS, *Oil Gas J.*, **54**, 74–76 (Aug. 29, 1955).

Oxidation of Low-molecular-weight Olefin Hydrocarbons

Ethylene. The catalytic oxidation of ethylene to ethylene oxide based on the invention of Lefort has been practiced commercially on a large scale.[1] Ethylene oxide has become an important organic chemical, being used in the manufacture of ethylene glycol, ethanolamines, β-phenylethyl alcohol, plastics, plasticizers, resins, insecticides, surface-active agents, solvents, explosives, etc.

Although many materials have been tested and patented as catalysts for the direct oxidation of ethylene to ethylene oxide, silver supported on some form of inert material seems to be the best so far developed.[2] The Lefort patent discloses catalysts of silver alone; silver activated with small amounts of iron, copper, or gold; mixtures of silver, antimony, and bismuth; and mixtures of silver and bismuth. The introduction of water or hydrogen along with the ethylene-oxygen (air) mixture is claimed to reduce the amount of oxidation leading to wasteful formation of CO_2. Operating temperatures in the range of 150–400°C and pressures above atmospheric are mentioned in the pertinent literature.

Various catalyst improvements have been suggested. Addition of 0.5–5.0 per cent sodium oxalate is claimed to activate the silver.[3] Activation by the addition of platinum and palladium has been claimed,[4] and the addition of small amounts of barium peroxide and lithium bromide to alundum-carrier-based silver catalysts is said to improve effectiveness.[5] A superior catalyst is claimed to result from supporting the silver on a silica carrier having a certain specific amount of α-alumina in its composition.[6] With this latter catalyst, mixtures containing 3–5 per cent ethylene in air gave conversions up to 50 per cent at temperatures of 266–268°C and space velocities of 660–690 reciprocal hours. Experimental results with catalysts of silver deposited on alumina and silicon carbide have been reported to show conversions of ethylene to ethylene oxide of 40–70 per cent, depending on conditions.[7] Partial poisoning of the silver crystal face by sulfur or chlorine atoms increases the ratio of ethylene oxide: carbon dioxide by forcing separation of the oxygen atoms on the silver surface.[8]

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[1] Lefort, U.S. 1,998,878 (1935); reissue 20,370 (1937); reissue 22,241 (1942); *F.I.A.T. Final Rept.* 875 (Field Information Agency Technical).

[2] CAMBRON and ALEXANDER, *Can. J. Chem.*, **34**, 665–671 (1956).

[3] Cambron and McKim, U.S. 2,426,761 (1947); Evans, U.S. 2,404,438 (1946).

[4] METZGLER, Ammonia Laboratory, I.G. Farbenindustrie, Oppau, 1938, Reports; *F.I.A.T.*, Film 18, frames 5818–5834, 5835–5842, 5909–5920, 6437–6488; Metzger and Andrussow, U.S. 2,178,454 (1939).

[5] Brengle and Stewart, U.S. 2,709,173 (1955).

[6] Heider and Stehman, U.S. 2,458,266 (1949).

[7] ARIES, paper before regional meeting, American Institute of Chemical Engineers, Tulsa, Okla., May 9–11. 1949; U.S. 2,477,435 (1949).

[8] KUMMER, *J. Phys. Chem.*, **60**, 666–670 (1956).

Improvements in the direct-oxidation route to ethylene oxide, contributing to reduced costs, have resulted in increased manufacturing capacity which now surpasses the chlorohydrin process capacity. By the direct-oxidation route, catalysts costs have been reported to be in the range 0.38–0.40 cents per pound ethylene oxide.[1] Fixed-bed catalyst plants have been stated to attain yields of 55–65 per cent in commercial practice. Investment costs for large-scale direct-oxidation ethylene oxide plants have been reported to be 10–11 cents per annual pound of capacity.[2]

One of the problems in commercial plant design for direct oxidation of ethylene to ethylene oxide is the removal of reaction heat at reaction temperature. A form of reactor similar to that used for phthalic anhydride manufacture is characteristic, with catalyst enclosed in long narrow tubes, many of which are mounted together with suitable headers to form a reactor assembly. Heat is removed and the temperature controlled by means of a suitable fluid, such as oil, circulating around the outside of the catalyst tubes and then to an outside heat exchanger for removal of heat.

The fluid-catalyst technique for ethylene oxidation with powdered supported silver catalysts has been patented.[3] Considerable difficulty has been experienced in fluidizing finely divided silver catalysts for ethylene oxidation. Characteristically the catalyst does not remain "fluid" and either sinters into porous masses or degenerates by action of the silver collecting on reactor walls or in conglomerates. It is claimed that dilution of such supported silver catalysts with graphite overcomes the difficulty.[4] Catalysts consisting of silver deposited on magnesium aluminate spinel are claimed to be successful in fluid-bed processing.[5]

Pilot-plant demonstrations with a special catalyst in a completely captive fluid catalyst bed without regeneration have shown economic optimum yields of 60 per cent with ethylene at 4.5 cents per pound. At higher ethylene cost, yields can be boosted to 70 per cent.[6]

One of the improvements on the Lefort process has been based on the introduction of an "anticatalyst" to repress the amount of complete oxidation of ethylene to CO_2.[7] The more important of these are volatile halogen-containing compounds, of which ethylene dichloride is an example. When added in the ratio of 0.02 part by weight per part of ethylene to the reaction

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[1] *Chem. Week*, May 23, 1954, pp. 46–54; *Petroleum Refiner*, **32** (9), 154–158 (1953).

[2] Landau, *Petroleum Engr.*, **27**, C71–C75 (1955).

[3] Becker and Arveson, U.S. 2,376,987 (1945); Becker, U.S. 2,430,443 (1947).

[4] Sears, U.S. 2,615,899; 2,615,900 (1952).

[5] Calingaert, U.S. 2,713,586 (1955).

[6] CORRIGAN, *Petroleum Refiner*, **32** (2), 87–90 (1953); JACKNIN, *Virginia Polytech. Inst.*, **13** (4), 527–528 (1953).

[7] Law and Chitwood, U.S. 2,279,469; 2,279,470 (1942); Berl, U.S. 2,270,780 (1942); McNamee and Blair, U.S. 2,238,474 (1941); NATIONAL RESEARCH COUNCIL OF CANADA, *Chem. Ind.*, **56** (2), 242 (1944).

mixture, ethylene dichloride is described as acting so as to direct the reaction of ethylene 60 per cent to ethylene oxide and 40 per cent to CO_2 and water at 290–300°C over a barium oxide–promoted silver catalyst.

In practice, account must be taken of the lower and upper limits of flammability of ethylene in air or oxygen mixtures. These limits have been reported as follows:[1]

Ethylene in air	3% (lower)–29% (upper) ethylene
Ethylene in oxygen	2.9% (lower)–79.9% (upper) ethylene
Ethylene oxide in air	3% (lower)–80% (upper) ethylene oxide

Under experimental conditions, the advantages of oxygen over air have been shown to be (1) a fourfold increase in space-time yield of product and (2) a sixfold increase in ethylene oxide concentration in the product stream.[2]

Propylene. The comparatively recent development of commercial means for the direct oxidation of propylene to acrolein promises to open up new areas of chemical synthesis which may in time rival those of ethylene oxide. The methods and conditions employed in the direct oxidation of ethylene to ethylene oxide have been found not suitable for propylene oxidation. Oxidation with air of olefins of three or more carbon atoms in the presence of a cuprous oxide catalyst under specific conditions has been found to result in formation of vinyl type of aldehydes or ketones.[3]

Conditions for the direct oxidation of propylene to acrolein include use of a catalyst of cuprous oxide deposited on granular silicon carbide, catalyst temperature of 375°C, feed stream composition by volume of 20 per cent propylene, 20 per cent air, and 60 per cent steam, and contact time of 1 sec.[4] Recovery and primary purification of the acrolein from the reaction product are effected by quench scrubbing the reactor effluent with water and with liquid propylene. The composition of the carbonylic compounds in the product is, approximately, acrolein, 90 per cent by weight; acetaldehyde, 6 per cent; propionaldehyde, 2 per cent; and acetone, 2 per cent.[5] At reaction temperatures of about 300°C and conversions of about 50 per cent, a selectivity to acrolein of about 40 per cent is reported for 10 per cent propylene-in-air mixtures.[6]

In this direct propylene-oxidation process, catalyst life is maintained at high levels by periodically interrupting or lowering the flow of oxygen without changing other conditions.[7] Removal of carbon monoxide from the

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[1] Coward and Jones, *U.S. Bur. Mines Bull.* 503, 1952.

[2] Wan, *Ind. Eng. Chem.*, 45 (1), 234–238 (1953).

[3] *Chem. Eng.*, **56** (8), 74, (11), 67 (1949); 57 (4), 183 (1950); Meyer, *Chem. Eng. News*, **28**, 1908 (1950).

[4] Detling and Skei, U.S. 2,614,125 (1952).

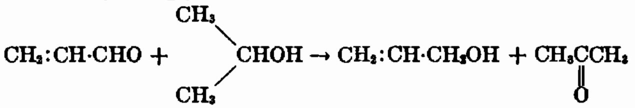
[5] Cole, Dunn, and Pierotti, U.S. 2,606,932; 2,606,933 (1952).

[6] Connolly and Cottle, U.S. 2,627,527 (1953).

[7] Detling and Skei, U.S. 2,608,585 (1952).

recycle propylene stream also serves to maintain catalyst activity.[1] Presence of elementary selenium in the reaction zone of the copper catalyst serves to maintain catalyst activity at a high level.[2]

A new process for the synthesis of glycerine is based on this direct oxidation process for acrolein. Reaction of acrolein with isopropanol gives allyl alcohol and acetone as products. Hydroxylation of allyl alcohol by reaction with hydrogen peroxide, obtained from liquid-phase oxidation of isopropanol, is made to yield glycerine as a product.[3]



$$CH_2{:}CH{\cdot}CHO + \underset{CH_3}{\overset{CH_3}{>}}CHOH \rightarrow CH_2{:}CH{\cdot}CH_2OH + CH_3\underset{\underset{O}{\|}}{C}CH_3$$

$$CH_2{:}CH{\cdot}CH_2OH + H_2O_2 \rightarrow CH_2OHCHOHCH_2OH$$

Higher Olefins. Vapor-phase oxidation of olefins in the presence of vanadium pentoxide catalysts results in substantial yields of maleic anhydride which increase with increase in molecular weight of the olefin. Thus, from pentene-2, trimethylethylene, technical amylene, methyl pentene, heptene, and octene, approximate relative conversions of 10, 25, 27, and 30 per cent, respectively, were obtained from 5, 6, 7, and 8 C-atom olefins.[4] Optimum temperatures of about 425°C were found for amylene oxidation. Catalysts used for 250 hr showed no reduction in activity.

The effect of halogenation of paraffin hydrocarbons is comparable with that of unsaturation with respect to catalytic oxidation to maleic anhydride or fumaric acid.[5] Thus, in the presence of vanadium oxides supported on Alfrax pellets or pelleted aluminum turnings, such halogenated hydrocarbons as *n*-butyl chloride, *n*-butyl bromide, 1,2-dichlorobutane, mixed amyl chlorides, dichlorpentane, polychlorpentanes, *n*-hexyl chloride, and chlorinated kerosene yield varying amounts of maleic anhydride (fumaric acid). With commercial dichloropentane at 425–450°C and a space velocity of 50 reciprocal hours, a conversion of 0.35 mole fumaric acid and 1.88 moles HCl per mole of dichlorpentane was obtained. From 2-chlorobutene-2 at 375°C over a tin vanadate–molybdenum catalyst, Finch and Evans obtained a 7.9 mole per cent yield of fumaric acid.

Oxidation of Liquid Petroleum Hydrocarbons. The James process (Fig. 9-7) has been directed principally to the vapor-phase catalytic oxidation of kerosene, although heavier fractions have been processed by the

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[1] Detling and Guinn, U.S. 2,620,358 (1952).

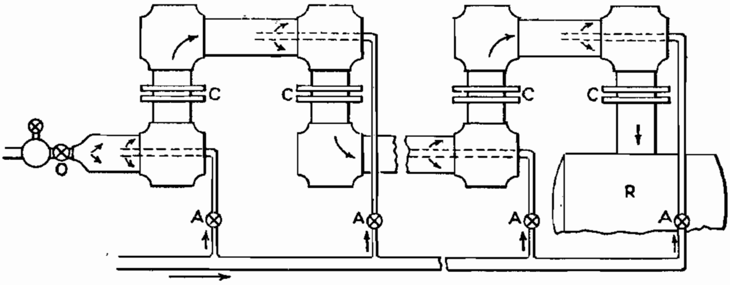
[2] Goodings and Hadley, U.S. 2,593,437 (1952); Hadley and Woodcock, U.S. 2,716,665 (1955).

[3] *Chem. Week*, Mar. 24, 1956, pp. 44–46.

[4] Faith and Dendurent, *Refiner*, **18** (10), 61–64 (1939).

[5] Faith, *Ind. Eng. Chem.*, **37**, 438 (1945); Finch and Evans, U.S. 2,358,775 (1944); Faith, U.S. 2,365,631 (1944).

method.[1] The apparatus consists of a device for vaporizing the hydrocarbon, a reactor containing the catalysts and provided with inlets for oxygen or air, and finally a cooling and collection system. The oil vapors pass through a succession of thin catalyst screens, and fresh air in controlled quantities is added to the vapor stream before the first and each succeeding catalyst screen. In this way, air is admitted at each point only sufficient to maintain the catalyst screens at the operating temperature of 350–400°C for kerosene.



A Air-control valves
C Catalyst screens
O Oil-control valve
R Product receiver

FIG. 9-7. Type of apparatus used for oxidation of mineral oils by James process.

The oxides of certain metals of high atomic weight and low atomic volume, such as molybdenum and uranium, have been found to act as useful catalysts in the process. Salts such as diuranyl vanadate have also been found to give good results. The catalyst is arranged in the form of multiple screens which may all be alike or contain different oxides. Temperature control is obtained by regulation of the rate at which oil vapors pass through the apparatus, of the proportion of air or oxygen admitted between catalyst screens, and in the loss of heat from the surface of the tubular chambers. Vapor-phase catalysts such as tetraethyllead and nitric acid give product mixtures similar to these screen catalysts.[2]

The products from the oxidation of such mixtures of hydrocarbons as are contained in kerosene or gas oil are very complex—so much so as to defy accurate analysis. They contain aldehydes, alcohols, ketones, acids, ethers, and esters. In the oxidation of kerosene, the oxidized oil may be as high as 40 per cent of the total and consist of 30–40 per cent of mixed aldehydes, 40–45 per cent of mixed alcohols, 5 per cent of free acids, 10 per cent of esters, and some ethers. About 85 per cent recovery is claimed with kero-

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[1] JAMES, *Trans. Am. Inst. Chem. Engrs.*, **14**, 189–199 (1921); **14**, 201–210 (1922); *Chem. Met. Eng.*, **26**; 209–212 (1922); BITLER and JAMES, *Trans. Am. Inst. Chem. Engrs.*, **20**, 95–100 (1927).

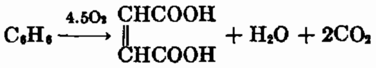
[2] PARKS and STORY, *Oil Gas J.*, **39**, 54, 56, 58, 61 (1940).

sene. With heavy oils, recovery is said to reach 92 per cent. By oxidizing naphtha, kerosene, and wax distillate, lacquer solvents comprising mixtures of esters, alcohols, and ethers may be obtained. The acids—generally aldehydic or aldehydic-hydroxy in type—are difficult to free of complex aldehydes, which impart objectionable odors and resinous polymerization products to soaps formed by saponification of the acid fraction with hot alkali. Methods involving the intermediate formation of calcium soaps have been proposed to avoid the inclusion of aldehydic bodies in the alkali soaps. Sulfonation of the oxidized product leads to the formation of emulsifying agents and "activators" for emulsified insecticides.

VI. VAPOR-PHASE OXIDATION OF AROMATIC HYDROCARBONS

Benzene. Benzene presents a very stable configuration toward both thermal dissociation and oxidation. The primary effect of exposure of benzene to elevated temperatures is the dissociation of a hydrogen atom accompanied by the joining of the residues to form diphenyl, a more stable substance which may be recovered in good yield. Vapor-phase oxidation to phenol is possible and has been attained with comparatively low yields and conversions. However, phenol does not present any great stability toward oxidation, and its commercial production by this method has not proved practical. Continued oxidation results in the formation of quinol and quinone, both of which have been identified in the vapor-phase oxidation products of benzene.[1] High yields have not been obtained, however, owing, no doubt, to the comparative instability of the ring at this stage of oxidation. Continued oxidation results in rupture of the ring and leads to the formation of maleic acid, which may be obtained in good yields. The complete combustion of benzene thus probably involves the formation of quinone and maleic acid as the main points of stability before complete combustion products are reached. No phenyl derivatives occur as products in the rapid autoignition of benzene-air mixtures at about 527°C and 20 atm pressure, indicating that once the ring is destroyed subsequent reactions are very rapid under these conditions.[2]

The commercial production of maleic acid by oxidation of benzene has, in a large measure, been due to the early work of Weiss and Downs on this



$$C_6H_6 \xrightarrow{4.5O_2} \begin{matrix} CHCOOH \\ \| \\ CHCOOH \end{matrix} + H_2O + 2CO_2$$

particular reaction and of Gibbs and his associates at the Bureau of Chemistry in Washington on aromatic oxidations in general.[3]

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[1] Norrish and Taylor, *Proc. Roy. Soc.* (*London*), A234, 160–177 (1956).

[2] Beckers and Levedahl, *Ind. Eng. Chem.*, **48**, 411–412 (1956).

[3] Weiss and Downs, *Ind. Eng. Chem.*, **12**, 228 (1920); *J. Am. Chem. Soc.*, **45**, 1003, 2341 (1923); *J. Soc. Chem. Ind.*, **45T**, 193 (1926); Weiss, Downs, and Burns, *Ind. Eng. Chem.*, **15**, 965 (1923); Weiss, Downs, and Corson, *ibid.*, **15**, 628 (1923).

The stability of benzene and the fact that nine atoms of oxygen is required for the oxidation of a molecule of benzene to maleic anhydride necessitate the use of high air:hydrocarbon ratios in the oxidation. Thus, the theoretical requirement would be about 106 cu ft of dry air at room temperature per pound of benzene oxidized to maleic anhydride. In practice, higher ratios than this are used, and yields of 60–75 lb of maleic acid per 100 lb of benzene reacted are obtained. This represents an efficiency of conversion of benzene to maleic acid of about 40–50 per cent.

The heat theoretically liberated in the oxidation of benzene to maleic acid is about 10,500 Btu per lb of benzene reacting, and the heat liberated in the complete combustion of benzene is approximately 18,000 Btu per lb. In practice, where 40 per cent or more of the benzene may undergo complete combustion during reaction, the heat liberated would be 13,500 Btu or more per pound of benzene reacted. It is imperative that this reaction heat be removed from the catalyst zone and that the catalyst temperature be maintained at the proper operating level. Special means have been provided for this in commercial operation.

A variety of catalysts have been patented for this oxidation, and the oxides of metals of the fifth and sixth groups of the periodic system have been particularly stressed. Of these, vanadium pentoxide has been shown to be one of the best when used as a single-component catalyst supported on an inert carrier such as aluminum turnings or diatomaceous earth. Vanadium pentoxide becomes active in promoting the oxidation at a temperature of about 300°C and reaches its maximum usefulness in the range of 400–500°C.

Toluene. The oxidation of hydrocarbons having an aromatic nucleus and one or more side chains may be effected in the side chain without marked rupture of the ring itself, since each component behaves more or less as it would if it alone constituted the major part of the molecule. Thus, the ring component exhibits the characteristic stability of the aromatic compounds, and the aliphatic substituent shows the relatively greater ease of oxidation of the aliphatic hydrocarbons. Under specific conditions, oxidation of such substituted aromatic hydrocarbons may be controlled to give satisfactory yields of the side-chain products; viz., toluene may be oxidized to benzaldehyde or benzoic acid; *o*-xylene, to phthalic anhydride; ethylbenzene, to benzoic acid; etc.

Considerable benzoic acid is manufactured by the decarboxylation of phthalic acid, a process that yields a chlorine-free product. The development of this decarboxylation process has served to restrict the investigation of air-oxidation methods.

The products of toluene oxidation, chiefly benzaldehyde, benzoic acid, maleic acid, and anthraquinone, are obtained in proportions that depend upon catalyst, temperature, oxygen ratio, and time of contact. High temperatures, mild catalysts, and short times of contact promote the formation of benzaldehyde. High oxygen ratios and long times of contact are, in general, conducive to acid formation. At temperatures of 280–300°C, reaction begins in the presence of vanadium oxide catalysts, but reaction is slow; long times of contact are required, and benzoic acid tends to be the major product. At temperatures of 400–450°C, reaction becomes more rapid over the vanadium oxide catalysts, and benzaldehyde, representing about 50 per cent of the toluene oxidized, becomes the principal product. Molybdenum oxide is a milder catalyst, and a temperature of 450–530°C is necessary for good per-pass yields and high conversion to benzaldehyde. In the temperature range of 420–450°C and in the presence of vanadium oxide catalysts, as much as 5 per cent of the reacted toluene may appear in the product as anthraquinone. At temperatures above 500°C in the presence of molybdenum oxide catalysts, considerable proportions of the reacted toluene may appear in the product as a complex high-boiling oil. The results of oxidations with tin vanadate as a catalyst are given in Table 9-4.

TABLE 9-4. VAPOR-PHASE OXIDATION OF TOLUENE*

Catalyst of Tin Vandate. Toluene Carbureter Temperature, 40°C; Catalyst Temperature, 290°C.

Space velocity of		Vol. of air/ vol. of toluene vapor‡	Yield benzoic acid, %	Space-time yields of acid§
Primary air†	Secondary air			
200	500	40.8	53.3	0.020
200	700	52.5	41.0	0.0112
200	1,000	70.0	36.3	0.0135
300	2,000	88.6	32.9	0.0137
300	3,000	128.6	23.8	0.0105

* MAXTED, *J. Soc. Chem. Ind.*, **47**, 101–105T (1928).

† Primary air is the air admitted directly with the hydrocarbon; secondary air is subsequently admitted to this primary mixture.

‡ Calculated on basis of saturation of air by toluene vapor in carbureter.

§ Space-time yield = g of product/(hr) (cc of catalyst space).

Oxidation of toluene with large excess of air over an alumina- (Alfrax-) supported vanadium oxide catalyst has been claimed to be an effective method for benzoic acid production.[1] Thus, the use of air:toluene weight ratios of 39–49:1, temperatures on the order of 410–430°C, and contact times of 0.25–0.75 sec are claimed to result in yields of benzoic acid of about 34 per cent with corresponding maleic acid yields of 7–11 per cent based on toluene consumed in the process.

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[1] Parks and Yula, U.S. 2,289,036 (1942).

Styrene from Ethylbenzene. Styrene is prepared by dehydrogenating ethylbenzene over a zinc oxide catalyst at approximately 600°C.[1] The main reaction is

$$C_6H_5C_2H_5 \rightarrow C_6H_5CH:CH_2 + H_2$$

In addition to this main reaction, a number of side reactions lead to the formation of unwanted products. The side reactions are of two main classes: (1) the cracking of ethylbenzene to give benzene, toluene, methane, ethane, etc.; and (2) the cracking of such hydrocarbons to carbon, followed by reaction of this carbon with the steam used as diluent, with the consequent formation of carbon oxides. Lastly, very small quantities of materials such as stilbene and diphenyl have been detected in the products.

For economic operations, the production of by-products must be kept to a minimum. Conditions which favor thermal cracking are high temperature and contact with ferrous metal, while the water-gas reaction is promoted by carbon formation which results when the reactants entering the converter are not sufficiently diluted. The normal diluent is steam, which should be present in a ratio of not less than 0.8 part by weight to 1 part ethylbenzene; in practice, a ratio of about 1.2–1.5: 1 is used. There is no objection to the use of a higher steam ratio other than unnecessary consumption of heat.

The dehydrogenation reaction is endothermic, and a considerable amount of heat has to be added to the converter in order to maintain the reaction temperature. This is supplied by flue gases, and the converter has been designed with the object of achieving as high a rate of heat transfer as possible between flue gases and reactants. The flue-gas temperature is normally 100–200°C higher than that of the reactants so that there may be a serious risk of thermal cracking of material passing close to the converter-tube surfaces if the heat exchange is insufficient. With the object of reducing such cracking as far as possible, the converter and its associated equipment operating at high temperatures are lined with a copper-manganese alloy which gives no cracking up to 600°C. The essential factor is the copper, the small percentage of manganese being added to produce an alloy of sufficient strength at 600°C.

The most important single factor controlling successful dehydrogenation is the type of catalyst employed. A catalyst consisting principally of zinc oxide with the addition of certain promoters such as alumina and chromates has been found to be most satisfactory. This catalyst gives a conversion of about 40 per cent per pass, with an over-all conversion efficiency of about 92 per cent, and has a life of about nine months. It can be employed for conversions up to 60 per cent per pass, but the over-all efficiency then drops noticeably, as a higher operating temperature is required.

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[1] *B.I.O.S. Final Rept.* 1781, Item 22.

General Description of Process. Ethylbenzene and steam are fed continuously into an evaporator (Fig. 9-8). The mixed vapors, after preheating in heat exchangers, are led into a converter, where dehydrogenation of ethylbenzene to styrene occurs in the presence of a zinc oxide–based catalyst. The gases leaving the converter are partially cooled in the heat exchangers referred to above and then further cooled in a condenser system.

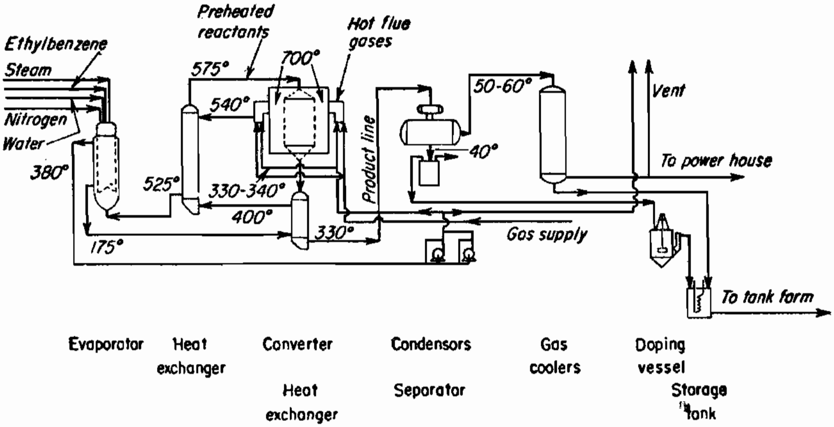

FIG. 9-8. Flow diagram: dehydrogenation of ethylbenzene to styrene.

After condensation, the hydrocarbon products are separated from water, inoculated with a stabilizer, and finally separated by fractional distillation in a series of columns, where benzene and toluene are first removed; then unreacted ethylbenzene is separated and returned to the reaction, and finally styrene is separated.

The normal ratio of feed materials to a converter is 500 liters ethylbenzene to 625 kg steam.

The corresponding approximate composition of the products on the hydrocarbon stream is

	Per Cent
Styrene	40
Ethylbenzene	59
Benzene, etc.	1

The temperature of reaction is normally 580–600°C and is maintained by flue gases surrounding the converter tubes. Apart from the composition and form of the catalyst, temperature is one of the most important variables controlling the reaction; the other important variable is the rate of passage of the reactants. The catalyst is used in the form of small pellets, efficiency of conversion increasing as the size of pellet is decreased, a practical limit being pellets of 6–7.5 mm, below which size the pressure drop in the converter becomes uneconomical.

The yields of styrene based on ethylbenzene consumed are about 90 per cent of theory.

Xylenes. The proportions of the isomers present in coal-tar xylenes are about 15 per cent ortho, 15 per cent para, and 70 per cent meta. The proportions of the isomers from the petroleum processing may vary somewhat (depending upon the source of the crude), but they approximate 25–30 per cent ortho, 20± per cent para, 40–50 per cent meta, plus some ethylbenzene.

Ortho-xylene is readily separated from the isomeric mixture by fractional distillation and was the first of the isomers to achieve commercial importance as a raw material for oxidation to a dicarboxylic acid, phthalic anhydride. Methods have been perfected by the petroleum industry for separation of the para and meta isomers. Para-xylene is important as the raw material for terephthalic acid, and meta-xylene has recently entered the large commercial scale as raw material for oxidation to isophthalic acid.[1]

Only two oxidation agents have been used in the past for conversion of xylene isomers to phthalic acids—air and nitric acid. No single process has been found completely satisfactory for use with all three isomers, and at present a different process is used for each.

Ortho-xylene may be oxidized directly by air in vapor phase over vanadium pentoxide catalysts under conditions resembling those used in oxidation of naphthalene to phthalic anhydride. The stability of the cyclic anhydride structure of phthalic anhydride at the temperatures required and in the presence of oxidizing conditions is, of course, the distinctive feature. Since the oxidation of *o*-xylene to phthalic anhydride requires the theoretical interaction of only six atoms of oxygen relative to the nine required by naphthalene, the amount of heat generated per unit of product is less, and the volume of diluent gases in the product stream may be lower. Because of decreased formation of quinones and color bodies, product purification should be easier. Very little is available by way of information relative to commercial operating conditions.[2] Some laboratory results of early work showed a maximum conversion to total acids of 18.2 per cent when commercial xylene was oxidized in vapor phase over unfused vanadium oxide catalyst.[3] Recent work with *o*-xylene showed a conversion of 42.7 per cent to phthalic anhydride over unfused vanadium oxide catalyst and conversions up to 61.7 per cent to phthalic anhydride plus 9.6 per cent to maleic

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[1] *Oil Gas J.*, **54**, 232–239 (July 25, 1955).

[2] *Chem. Inds.*, July, 1946, pp. 68–69; *Chem. Met. Eng.*, **53**, 116 (1946).

[3] Parks and Allard, *Ind. Eng. Chem.*, **31**, 1162 (1939).

anhydride over fused vanadium oxide catalysts at temperatures near 460°C.[1]

Catalytic vapor-phase oxidation of *m*-xylene results in formation of maleic anhydride in yields comparable to those obtained from benzene, e.g., about 40–50 per cent of theoretical. Relative to benzene, *m*-xylene requires more oxidation to convert it to maleic anhydride and, under the present circumstances, is a relatively more expensive raw material.

Naphthalene. In point of volume and importance to the dye and synthetic organic chemical industries, the oxidation of naphthalene to phthalic anhydride is without peer among the various processes involving aromatic-hydrocarbon oxidation. Production has increased from about 23 million lb in 1935 to 254 million lb in 1954. In 1956 there were eight commercial producers of phthalic anhydride in the United States having a combined annual production capacity of about 350 million lb which will be increased to meet greater requirements and will include 50 million lb projected operating capacity for isophthalic acid.[2]

The stability of the naphthalene structure is such that, at temperatures up to 400–500°C, a catalyst is necessary for commercial rates of oxidation with air as the oxidizing agent. Theoretically, nine atoms of oxygen is required per molecule of naphthalene for oxidation to phthalic anhydride. This means that 64.5 cu ft of dry air measured at room temperature is theoretically required for the oxidation of 1 lb of naphthalene to phthalic anhydride. In practice, considerable excess air is used, up to three times that theoretically required. Thus, 20–60 moles of air must be used per mole of naphthalene oxidized.

The heat of oxidation theoretically amounts to 5460 Btu per lb of naphthalene oxidized. Owing to the fact that some complete combustion also occurs, the heat actually liberated amounts more nearly to 10,000 Btu per lb of naphthalene oxidized. Specially designed catalyst chambers must be used to remove this heat without disturbing the temperature equilibrium of the catalyst mass.

Catalysts similar to those mentioned for benzene oxidation are applicable to the naphthalene reaction. The early work and published results have shown that vanadium and molybdenum oxides are effective and quite active catalysts. With supported vanadium pentoxide catalysts, commercial yields of phthalic anhydride on the order of 80–85 per cent of the weight of the naphthalene are obtained. Such catalysts have a long life—6 months or more of continuous use—and have yielded up to 20,000 times their weight of phthalic anhydride.[3] Fused or supported vanadium pentox-

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[1] GULATI and BHATTACHARYYA, *Chemistry & Industry*, **1954**, 1425–1426.

[2] *Chem. Week*, Sept. 3, 1955, pp. 71–74, for information on United States production, exports, imports, and uses. SHERWOOD, *Chem. Age*, May 19, 1956, p. 1131.

[3] DOWNS, *J. Soc. Chem. Ind.*, **45**, 188T (1926).

ide catalysts become active for the oxidation at temperatures of 270–280°C and induce reaction at commercial rates at temperatures of near 400°C.

Considerable interest has centered around the F.I.A.T. and B.I.O.S. reports of the catalysts used in Germany for phthalic anhydride manufacture.[1] The life of the vanadium pentoxide catalyst used for the manufacture of phthalic anhydride at the Ludwigshafen works was over ten years. The Germans were reported to have obtained yields of 1 lb of phthalic anhydride per pound of naphthalene equal to over 86 per cent with product purities in the range 97–98 per cent. These German results compare with previously reported results in this country of 80 per cent yields and catalyst life of less than one year.

The catalyst was prepared from vanadium pentoxide by first converting it to the sulfate, using sulfuric acid and sulfur dioxide, mixing this into a paste with a carrier base consisting mainly of finely precipitated silica, and molding into pellets in a press between stainless-steel platens. The pellets were 5 mm in diameter. After preliminary drying for 1–2 hr at 50°C, the pellets were baked for 12 hr at 400–500°C in a calcining furnace. They were then screened to remove dust. The catalyst in pellet form contains approximately 10 per cent vanadium pentoxide, 20–30 per cent potassium sulfate, and the remainder silica. The converter consisted of 2,946 tubes of 25 mm inside diameter, 30 mm outside diameter and 3,288 mm length. The catalyst was supported inside the tubes on grids of stainless-steel wire mesh. The cooling medium surrounding the tubes was an equimolecular mixture of sodium and potassium nitrates, melting at 141°C. This, in turn, was cooled by blowing air through another set of tubes passing through the bath.

American manufacture of this new catalyst is from silica gel prepared from potassium silicate and sulfuric acid and impregnated after drying with vanadyl sulfate to contain 10 per cent vanadium pentoxide. One phthalic anhydride plant is reported to be using this new catalyst in a fluidized-bed reactor. Although contact times are longer, the yields are higher than with the usual vanadium pentoxide catalyst on alundum or the like, and with increasing naphthalene costs the improved yields tend to offset the decreased throughput. Catalyst requirements are about 25 lb of catalyst in the bed per pound of naphthalene feed per hour.[2]

It has been claimed that mixtures of the metal oxides form better catalysts than one oxide alone. For instance, a mixture of 85 per cent vanadium pentoxide with 15 per cent molybdenum oxide is claimed to be better than the vanadium oxide alone; and a mixture of 65 per cent vanadium

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[1] Hunter, Manufacture of Phthalic Anhydride and Phthalates, P.B. 47718, *B.I.O.S. Final Rept.* 1124, Item 22; Nash, Catalysts for Manufacture of Phthalic Anhydride and Aniline, P.B. 81279, *F.I.A.T. Final Rept.* 649; Young, P.B. 63699, *B.I.O.S. Final Rept.* 1482, Item 22; Scott et al., *B.I.O.S. Final Rept.* 1597, Item 22.

[2] Hathaway and Myrick, *Chem. Inds.*, **64**, 581 (1949).

pentoxide, 30 per cent molybdenum oxide, and 5 per cent either manganese or calcium oxide, still better.[1] Porous, granular bright orange-yellow intimate mixtures of the trioxides of tungsten and molybdenum in molecular ratios between 10:1 and 1:10 have been described as effective oxidation catalysts.[2] To avoid loss in activity through attrition in fluid-bed reactors, homogeneous mixtures of catalyst and supporting gel are recommended rather than coated or impregnated catalysts.[3]

For the recovery of phthalic anhydride from the hot dilute mixture of gases and vapors issuing from the catalytic converter, the normal technique is to effect condensation of the phthalic anhydride in large, roomlike cooling chambers (indicated in Fig. 9-11) where the product deposits in the form of a bulky mass of long needlelike crystals.

To reduce the space required for this recovery, to improve the density and control the purity, and to reduce the amount of manual labor required, it has been proposed to accomplish recovery by use of a sequence of steps: (1) cool the vaporous mixture by passage through a water-cooled tubular cooler condenser, (2) remove the bulk of the condensed material by means of a scraper-screw conveyer in the cold end of this cooler, and (3) recover dust from the cold gases by means of a bag filter.[4] Fractional condensation of phthalic anhydride from gas-vapor mixtures containing maleic anhydride may be accomplished by maintaining the mixture in the temperature range of 80–90°C to 132°C by indirect heat exchange with a fluid confined in tubular conduits.[5]

VII. KINETICS AND THERMOCHEMISTRY

Kinetics. Oxidation reactions, such as those enumerated in Sec. I, are accompanied by the formation of water, carbon oxides, or both, or by the introduction of elemental oxygen in the organic molecule, or by the stepdown of an oxidizing compound from an unstable state of high oxidation to a more stable state of lower oxidation. These reactions are exothermic and accompanied by a free-energy decrease. Equilibrium, therefore, is favorable, and in practically all cases no means need be provided to force the completion of the reaction. Indeed, in the majority of cases, steps must be taken to limit the extent of the reaction and prevent complete loss of product through continued oxidation.

However favorable equilibrium may be, a useful process does not result until a favorable rate of reaction is obtained. The steps that have been

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[1] Craver, U.S. 1,489,741 (1924); see Wohl, U.S. 1,971,888 (1934), for other catalyst compositions.

[2] Arnold, U.S. 2,439,880 (1948).

[3] Fugate and Tribit, U.S. 2,698,330 (1954).

[4] Riegler, U.S. 2,067,019 (1937).

[5] Pietzsch, U.S. 2,455,314 (1948).

taken to provide these favorable reaction rates and favorable methods of control in the case of organic oxidations have led to the great variety of oxidation processes now in use. The diversity of substances that may be subjected to oxidation processes in order to obtain more useful substances has made necessary a diversity of methods.

The conditions imposed in these processes are such that two definite techniques are used: vapor-phase and liquid-phase methods. Oxidations are conducted in the liquid phase in cases where high-molecular-weight, complex, and more or less thermally unstable substances are dealt with and where the oxidizing agent is relatively nonvolatile. Temperatures are low or moderate, and the extent of oxidation may be readily controlled by (1) limiting the duration of operation, (2) controlling the temperature, and (3) limiting the amount of oxidizing agent. Oxidation may occur through the action of an oxidizing agent that becomes reduced during the operation or through the action of molecular oxygen in the presence of a catalyst. Vapor-phase oxidation reactions can be effectively applied only to readily volatile substances that are of sufficient thermal stability to resist dissociation at elevated temperatures. A further limitation exists in that the desired product must also be thermally stable and comparatively resistant to continued oxidation. Solid- or vapor-phase catalysts may be employed with air or oxygen to produce the desired oxidation. The temperatures, as already implied, are usually high. Control is effected by limiting the time of contact, temperature, proportion of oxygen, or type of catalyst or by combinations of these factors.

Although the use of commercially pure oxygen is required only rarely for organic oxidations by molecular oxygen, the advantages resulting from the absence of the diluent nitrogen of air in product recovery may warrant the additional cost of oxygen. Substantial developments have occurred in the mechanical method of producing oxygen by the rectification of liquid air, permitting production of gaseous oxygen at low cost. In 1956, over 30 billion cu ft of high-purity oxygen was produced, about 75 per cent of which was used in steel production and metal fabrication.

Developments have since been directed toward large-volume low-cost production of oxygen of somewhat lower purity than that required for welding and cutting of metals.[1] The costs of tonnage oxygen will vary with the size of plant, operating conditions, power costs, and design characteristics. For what may be called average conditions—power at 5 mils per

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[1] *Chem. Eng.*, **53**, 125 (1946); **54**, 123–131 (1947); Downs and Rushton, *Chem. Eng. Progr.*, 1, 12 (1947); Lobo, *ibid.*, 1, 21 (1947); Rushton and Stevenson, *Trans. Chem. Eng. Progr.*, **43**, 61–67 (1947); Clark, *O.P.B. Rept.* 41229, *B.I.O.S. Final Rept.* 591; Lobo, *Tech. Data, O.P.B. Rept.* 8900, 1948; Van Dyke, *Chem. Eng. Progr.* **44**, 20, 38, 42 (1948); *Steel*, **123** (12), 103–104, 136–146 (1948); Cadogan and Kinney, *Ind. Eng. Chem.*, **48** (7), 7A–10A (1956).

kwhr, steam at 40 cents per 1,000 lb, labor at $1.40 per hour, fixed charges at 10 per cent of plant cost per year, maintenance and supplies at 1.5 per cent of plant cost per year, and continuous operation—the cost of tonnage oxygen in equipment of several of the equipment companies in this field has been reported as follows:[1]

95% Oxygen, tons per day	*Approximate cost per ton, $*
50	8.70–9.70
100	6.60–7.40
250	4.94–5.50
500	4.20–4.46

Mechanism of Reaction. Much of the effort expended on oxidation mechanism has been directed at combustion studies in more or less homogeneous systems. These studies have received increased attention recently because of the tremendous military and commercial importance of jet propulsion, particularly of aircraft.

The very considerable research work of Bone and his associates led to his support of the hydroxylation mechanism for homogeneous oxidation of hydrocarbons with molecular oxygen.[2] According to this mechanism, reaction between methane and oxygen takes place in steps: methanol, formaldehyde, formic acid, and carbon dioxide, in the order named. That methanol has not been found among the products of methane oxidation under conditions where its presence could logically be expected does not necessarily preclude the possibility that it was the initial product.[3] This is due to the thermal instability of methanol under the conditions and its tendency to decompose to hydrogen, carbon monoxide, and formaldehyde.

By conducting the oxidation of the low-molecular-weight paraffin hydrocarbons under high pressures (see Fig. 9-6) it has been possible to obtain alcohols, increased yields of aldehydes, and acids as oxidation products.[4] Conditions claimed for the pressure processes include (1) pressures of 50–250 atm, (2) temperatures from 200–600°C, (3) low oxygen : hydrocarbon ratios ranging from 5–15 moles per cent, (4) short time of contact, and (5) the presence of a variety of catalysts. The more extreme conditions have been found necessary for the lower members of the paraffin series. Although the low proportions of oxygen may account for part of the effects that have been

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[1] SHERWOOD, *Chem. Eng.*, **56** (12), 97–100 (1949).

[2] BONE, *Trans. Chem. Soc.*, **61**, 871 (1892); **71**, 26, 46 (1897); **78**, 1042 (1900); **81**, 535 (1902); **85**, 693, 1637 (1904); **87**, 910, 1232 (1905); **89**, 652, 660, 939, 1614 (1909); **93**, 1198 (1908); *J. Chem. Soc.*, **83**, 1074 (1903); BONE and DRUGMAN, *J. Chem. Soc.*, **89**, 660–671 (1906); BONE et al., *Trans. Roy. Soc. (London)*, **215A**, 288–308 (1915); BONE, *Nature*, **122**, 203–204 (1928).

[3] FROLICH, HARRINGTON, and WAITT, *J. Am. Chem. Soc.*, **50**, 3216 (1928).

[4] NEWITT and HAFFNER, *Proc. Roy. Soc. (London)*, **A134**, 591–604 (1932).

observed from pressure oxidation, the major results must be attributed to the effect of the elevated pressure.

Although considerable controversy has existed regarding the exact mechanism of hydrocarbon oxidation, one observation stands out from the mass of data that have accumulated, and this is that aldehydes appear early in the process and are prominent in the products. It is generally recognized that aldehydes are not the primary products, and it has been proposed that the most probable primary product is peroxidic in type.

The *peroxide theory* has developed largely from the efforts to solve problems associated with the knocking phenomenon of internal-combustion engines. Evidence supporting the peroxidation theory comes from the presence of very active forms of oxygen during oxidation reactions, the tendency for chain-reaction mechanisms to be evident, and the inhibition of the oxidation by certain substances and by container walls. Under some conditions, it has been possible to recover peroxidic products from oxidation reactions. Thus, the aqueous condensate from reaction of a 90 per cent propane–10 per cent oxygen mixture for 5 sec at 470°C contains 13.2 g active peroxide per liter, of which 30 per cent is organic peroxide and 70 per cent is H_2O_2.[1] Even so, the peroxidation theory of mechanism has been variously criticized.[2]

Other Mechanisms. On the surface of an active oxidation catalyst such as vanadium pentoxide, copper–copper oxide, or silver–silver oxide, other mechanisms are presumed to operate. In oxidations of gaseous hydrocarbons over vanadium oxide, definite changes in color, corresponding to different oxide forms, from blue green to orange have been observed. The phenomenon has been associated with alternative oxidation and reduction of the vanadium oxide.[3] Still another example is to be found in the oxidation of air-methanol mixtures to formaldehyde over copper–copper oxide where the color changes are pronounced, depending on the proportions of oxygen present.[4]

In the catalytic oxidation of aliphatic hydrocarbons at atmospheric pressure, the oxidation reactions are probably stepwise, each successive step occurring with greater ease. The type of reaction for the successive steps is the same, and when a carbon compound containing oxygen is oxidized further, it is the hydrogen atoms joined to the carbon atoms already in combination with oxygen that are attacked.[5] Thus, the point of first attack continues to be the point for successive attacks. This has been clearly shown for the case of the oxidation of the isomeric octanes, where

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[1] Lacomble, U.S. 2,376,257 (1945); Kooijman, U.S. 2,461,988 (1949).

[2] Marek and Hahn, "Catalytic Oxidation of Organic Compounds," pp. 305–311, Reinhold Publishing Corporation, New York, 1932.

[3] Weiss, Downs, and Burns, *J. Ind. Eng. Chem.*, **15**, 965 (1923).

[4] Pease and Taylor, *J. Am. Chem. Soc.*, **43**, 2279 (1921); **44**, 1637 (1922).

[5] Ewell has shown that the chlorination of paraffins follows a similar pattern.

the methyl group at the end of the longest free straight chain is first attacked and the oxidation continues along the chain to a point where a resistance to further oxidation is encountered. At such a point—represented by formation of a ketone structure at the point where the chain branch ends in the case of the isooctanes—oxidation may be partly arrested and the product recovered before decomposition or oxidation can destroy it. However, a considerable portion of the hydrocarbon will have been destroyed when this point is reached; a large amount of heat will consequently have been liberated; and only a low yield of any single ketone will have been obtained from such a mixture of isomeric hydrocarbons.

Based on the experience of the I. G. Farbenindustrie with the liquid-phase catalyzed air oxidation of paraffin wax, a tentative scheme was proposed by Krauch[1] for the oxidation mechanism. By this scheme, oxygen attacked the paraffin molecule toward the middle and not on the ends. This proposal was supported by the finding that a portion of the acids formed contains about half the number of carbon atoms as the original paraffin molecule and that the small amounts of carbon oxides and low-molecular-weight oxidation products preclude oxidation from one end of the large molecules to form the acids in the product.

However, the fact that the acid product from oxidation of paraffin wax averaging 24C atoms per molecule consists of a variety of acids of varying chain length makes it seem more probable that the oxygen attack is distributed and that rupture may occur at various points in the molecules.[2]

The aromatic hydrocarbons are characterized by offering several points of resistance to further oxidation or decomposition during the course of the interaction with oxygen, making possible the isolation of intermediate oxidation products. For instance, in the case of naphthalene oxidation, the interaction of 3 atoms of oxygen results in the formation of α-naphthoquinone, a point of resistance since appreciable quantities of this compound may be obtained under the proper conditions. The interaction of a total of 9 oxygen atoms results in the formation of phthalic anhydride. Another resistance point occurs after the reaction of 18 oxygen atoms when maleic anhydride is formed. Thus, it is possible to obtain commercial yields of phthalic anhydride from naphthalene, maleic anhydride from benzene, anthraquinone from anthracene, etc. Because of the thermal stability and resistance to oxidation of the aromatic hydrocarbons and the intermediate reaction products, it is necessary to employ excess oxygen, operate at elevated temperatures, and make use of active catalysts. These factors make it possible to conduct the oxidation so as to obtain commercial yields at practically complete reaction of raw material with only a single pass over the catalyst.

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[1] **Krauch**, *Proc. 2d Intern. Conf. Bituminous Coal*, **I**, 43 (1928).

[2] **Burwell**, *Ind. Eng. Chem.*, **26**, 204–207 (1934).

Oxidation of hydrocarbons containing an aromatic nucleus and one or more aliphatic side chains may be effected in the side chain. The side chains behave, in general, like aliphatic hydrocarbons and, as such, are more susceptible to attack by oxygen than the ring. Indeed, it is possible to effect oxidation of the side chains of alkylated aromatic hydrocarbons without ring rupture by the use of air or oxygen under pressure in a noncatalytic liquid-phase reaction.[1] At atmospheric pressure, the principal point of resistance in such oxidized compounds is the aromatic acid formed after oxidation has reached and affected the last carbon atom attached to the nucleus. Unless low concentrations of oxygen are used or mild conditions imposed, this resistance point is the first one to be effective. Thus, ethyl benzene is oxidized to benzoic acid just as toluene is.[2] The ring structure is so stable toward oxidation or dissociation that, regardless of the length of side chains, carboxylic acids result before ring rupture occurs. Under special conditions, such as elevated pressures (50 atm) and mild temperatures (210°C), it has been shown that hydroxylated derivatives such as benzyl alcohol and products from oxidation of the aromatic nucleus such as dihydroxy toluene may be recovered.[3]

Noncatalytic oxidation of the aromatic hydrocarbons is slow at temperatures below 500°C. Benzene is not vigorously oxidized in glass apparatus until temperatures near 700°C are reached. Under similar conditions, toluene is noticeably oxidized at 650°C, and xylene at 575°C.[4] Even with an active catalyst such as vanadium pentoxide, a temperature of 400–450°C is required for the commercial oxidation of naphthalene to phthalic anhydride by air. Furthermore, quantities of air from one to three times that theoretically necessary for the conversion must be used. This means that 20–60 moles of air must be used per mole of naphthalene in the reaction mixture.

Thermodynamics. In oxidation reactions, especially those based on elemental oxygen, the important thermochemical aspect is the heat evolved. Equilibrium is favorable, and the problems are largely the removal of heat at the desired reaction temperature level and the limitation of the oxidation to the desired product by avoidance of complete combustion.

Hence, there is little need to consider free-energy changes and to calculate equilibriums. Catalysts are generally used in an effort to obtain the oxidation reaction at as low a temperature as possible and to direct the reaction to the desired products. Where any one or more of several products may result from the oxidation, the predominant ones are determined generally by reaction mechanism rather than equilibrium phenomena.

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[1] Forrest and Frolich, U.S. 1,902,550; 1,936,427 (1933).

[2] Maxted, *J. Soc. Chem. Ind.*, **47**, 101–105T (1928).

[3] Newitt and Szego, *J. Soc. Chem. Ind.*, **52**, 645 (1933); Bone, *ibid.*, **53**, 963 (1934).

[4] Mardles, *Trans. Faraday Soc.*, **27**, 681 (1931).

TABLE 9-5. THERMOCHEMICAL DATA: HYDROCARBONS AND OXYGENATED DERIVATIVES*

Organic compound	Mol. wt	Heat of formation,† $\Delta H^\circ_{298} = -Q_f$, kg-cal/mole	Heat of combustion, constant pressure (I.C.T.),‡ kg-cal/mole	Free energy of formation, ΔF°_{298} kg-cal/mole
H_2	2.016	0.000		
H_2O (*g*)	18.016	−57.798	....	−54.635
H_2O_2 (*g*)	34.016	−31.83		
C (*c*) diamond	12.00	0.000		
CO (*g*)	28.00	−26.42	−67.61	−32.81
CO_2 (*g*)	44.00	−94.05	....	−94.26
CH_4 (*g*) methane	16.042	−17.89	−212.95	−12.14
C_2H_2 (*g*) acetylene	26.036	+54.194	−311.1	+50.00
C_2H_4 (*g*) ethylene	28.052	+12.496	−336.6	+16.282
C_2H_6 (*g*) ethane	30.068	−20.236	−373.05	−7.860
C_3H_6 (*g*) propylene	42.078	+4.879	−490.2	+14.99
C_3H_8 (*g*) propane	44.094	−24.82	−526.3	−5.614
C_4H_8 (*g*) 1-butene	56.104	+0.280	....	+17.217
C_4H_{10} (*g*) *n*-butane	58.120	−29.812	....	−3.754
C_6H_6 (*g*) benzene	78.108	+19.820	−787.2	+30.989
C_7H_8 (*g*) toluene	92.134	+11.950	−936	+29.228
$C_6H_4(CH_3)_2$ (*l*) *o*-xylene	106.160	+4.540	−1,093	+29.177
$C_{10}H_8$ (*s*) naphthalene	128.164	....	−1,231.8	
HCHO (*g*) formaldehyde	30.016	−27.7	−134	−26.2
CH_3CHO (*g*) acetaldehyde	44.032	−39.76	−280.5	−31.96
CH_3COCH_3 acetone	58.048	....	−427	
CH_3OH (*g*) methanol	32.042	−48.10	−182.75	−38.70
C_2H_5OH (*g*) ethanol	46.068	−56.24	−337.06	−40.30
C_3H_7OH (*l*) isopropanol	60.094	....	−474.8	
C_6H_5OH phenol	94.108	....	−732	
C_2H_4O (*g*) ethylene oxide	44.052	−12.19	....	−2.79
$C_2H_6O_2$ (*l*) ethylene glycol	62.068	−108.58	−281.9	−77.12
HCOOH (*g*) formic acid	46.026	−86.67	−62.8	−80.24
CH_3COOH (*l*) acetic acid	60.052	−116.4	−208.3	−93.8
$C_2H_2(CO)_2O$ (*s*) maleic anhyd.	98.056	....	−333.9	
$(CHCOOH)_2$ (*s*) maleic acid	116.076	....	−326.1	
$C_6H_4(CO_2)_2O$ (*s*) phthalic anhyd.	148.112	....	−781.5	

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* BICHOWSKY and ROSSINI, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936; "International Critical Tables," McGraw-Hill Book Company, Inc., New York; ROSSINI et al., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, 1947–1949.

† The heat evolved in the reaction of forming the given substance from its elements in their standard states (298°K and 1 atm) at constant pressure.

‡ International Critical Tables.

Tables 9-5 and 9-6 present thermochemical data on some hydrocarbons and products of oxidation reactions.

TABLE 9-6. HEATS OF REACTION: OXIDATION OF METHANE, ETHANE, and ETHYLENE

Oxidation by elemental O_2	*Heat of reaction,** $\Delta H = -Q$, *kg-cal/mole*
CH_4 to H_2CO (*g*) + H_2O (*g*)	−67.608
to CH_3OH (*g*)	−30.21
to $CO + 2H_2$	−8.53
to $C + 2H_2O$ (*g*)	−97.706
to $CO_2 + 2H_2O$ (*g*)	−191.756
C_2H_6 to CH_3CHO (*g*) + H_2O (*g*)	−77.322
to CH_3COOH (*l*)	−96.164
to C_2H_5OH (*g*)	−36.004
to $2CO_2 + 3H_2O$ (*g*)	−341.258
to $C_2H_4 + H_2O$ (*g*)	−25.066
C_2H_4 to C_2H_4O	−24.686
to CH_3CHO	−52.256
to $2CO_2 + 2H_2O$ (*g*)	−323.932

* The heat evolved when the given reaction takes place at constant pressure.

To determine the heat of any reaction involving the disappearance of a substance or substances and the appearance of other or the same substances in different states: add the heats of formation of the products of the reaction and subtract therefrom the sum of the heats of formation of the reactants. The value thus obtained represents the heat evolved when the given process occurs at constant pressure of 1 atm and a temperature of 18°C.

VIII. APPARATUS FOR OXIDATIONS

Liquid-phase Reactions. Liquid-phase reactions in which oxidation is secured by the use of oxidizing compounds need no special apparatus in the sense that elaborate means must be provided for temperature control and heat removal. There is usually provided a kettle form of apparatus, closed to prevent the loss of volatile materials and fitted with a reflux condenser to return vaporized materials to the reaction zone, provided with suitable means for adding reactants rapidly or slowly as may be required and for removing the product and provided with adequate jackets or coils through which heating or cooling means may be circulated as required. Examples of such apparatus are scattered throughout this book, and no specific examples are required here.

In the case of liquid-phase reactions in which oxidation is secured by means of atmospheric oxygen, for example, the oxidation of liquid hydrocarbons to fatty acids, special means must be provided to secure adequate mixing and contact of the two immiscible phases of gaseous oxidizing agent and the liquid being oxidized. Although temperature must be controlled and heat removed, the requirements are not severe, since the temperatures are generally low and the rate of heat generation is controllable by regulation of the rate of air admission. All these factors are important, and the apparatus must provide for them.

Figures 9-1 to 9-3 show how, in general, this may be accomplished. Heat may be removed and temperature controlled by circulation of either the liquid being oxidized or a special cooling fluid through the reaction zone and then through an external heat exchanger. Mixing may be obtained by the use of special distributor inlets for the air, designed to spread the air throughout the liquid and constructed of materials capable of withstanding temperatures that may be considerably higher at these inlet ports than in the main body of the liquid. With materials that are sensitive to overoxidation and under conditions where good contact must be used partly to offset the retarding effect of necessarily low temperatures, thorough mixing may be provided by the use of mechanical stirring or frothing of the liquid.

Problem of Heat Transfer in Vapor-phase Reactions

By their very nature, the vapor-phase oxidation processes result in the concentration of reaction heat in the catalyst zone, from which it must be removed in large quantities at high-temperature levels. Removal of heat is essential to prevent destruction of apparatus, catalyst, or raw material, and maintenance of temperature at the proper level is necessary to ensure the correct rate and degree of oxidation. With laboratory-scale apparatus, removal of this heat is relatively easy; in some instances, it is even necessary to provide an external supply of heat in order to maintain the operating temperature at the proper level. With plant-scale operation and with reactions involving deep-seated oxidation, removal of heat constitutes a major problem. With limited oxidation, however, it may become necessary to supply heat even to oxidations conducted on a plant scale.

In the case of vapor-phase oxidation of aliphatic substances such as methanol and the lower-molecular-weight aliphatic hydrocarbons, the ratio of reacting oxygen is generally lower than in the case of the aromatic hydrocarbons for the formation of the desired products, and for this reason heat removal is simpler. Furthermore, in the case of the hydrocarbons, the proportion of oxygen in the reaction mixture is generally low, resulting in low per-pass conversions and, in some instances, necessitating preliminary heating of the reactants to reaction temperature. Figure 9-4 shows a schematic layout for the oxidation of methanol to formaldehyde. Figures 9-6 and 9-7 show apparatus for the oxidation of hydrocarbons.

Rather elaborate means have been perfected for the oxidation of the aromatic hydrocarbons to useful compounds. Such apparatus must be designed to permit the maintenance of constant elevated temperatures, to permit the removal of large quantities of heat at these elevated temperatures, and to provide adequate catalyst surface to promote the reactions. One form of converter adapted to accomplish these ends consists of numerous small catalyst tubes immersed in a liquid bath.[1] The liquid bath may be used to remove heat from the reaction as latent heat of evaporation of the liquid; it may be subjected to forced circulation in contact with the catalyst tubes and cooled in an external heat exchanger; or it may be used as a means of getting reaction heat to an outer retaining shell from which the heat is dissipated to the atmosphere.

Figure 9-9 is a diagrammatic section of a single-tube reactor and shows the principles involved in the removal of reaction heat as heat of evaporation and the dissipation of this heat to cooling water. The entering air-hydrocarbon (naphthalene) mixture first comes in heat-transferring contact with the heated vapors of the boiling liquid and is thus preheated before coming in direct contact with the catalyst. Cooling of the first section of the catalyst is thus avoided to a certain extent, and the catalyst mass is made more effective in promoting the reaction. Reaction heat, liberated at the catalyst surface, passes from the catalyst mass through the tube wall and to the surrounding liquid, where it is removed at constant temperature by the evaporization of the liquid. The evolved vapors from the bath may be condensed in a separate condenser provided with cooling water and the condensed material returned to the bath. Continuous operation is thus obtained. In practice, it is customary to use a large number of such tubular catalyst chambers in parallel, connected at the top and bottom by common headers. Such a converter is largely automatic in operation and does not depend upon atmospheric conditions for satisfactory operation. As shown in Fig. 9-10, a suitable air- and water-cooled condensing system returns the mercury to the liquid reservoir and removes the heat of reaction thereby.

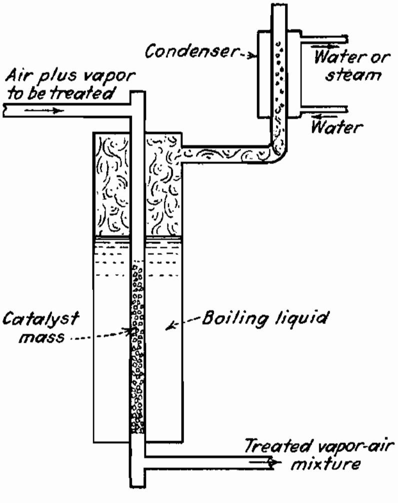

FIG. 9-9. Section of single-tube reactor with boiling-liquid heat removal and temperature control.

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[1] DOWNS, *J. Soc. Chem. Ind.*, **45**, 188–193T (1926); U.S. 1,374,020; 1,374,021 (1921); 1,604,739 (1926); Canon and Andrews, U.S. 1,614,185 (1927); reissue 16,824 (1927).

The mercury (liquid and vapor) is thus the means for removing the heat of a reaction at a constant temperature of about 425°C and for dissipating it to cooling water at a temperature of about 100°C. Heat is thus effectively removed without affecting the temperature of the catalyst adversely.

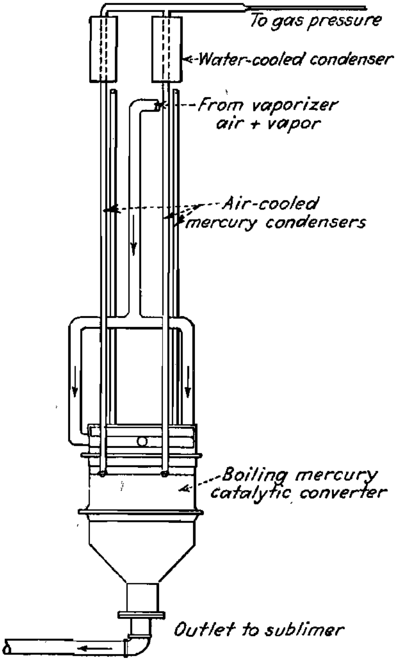
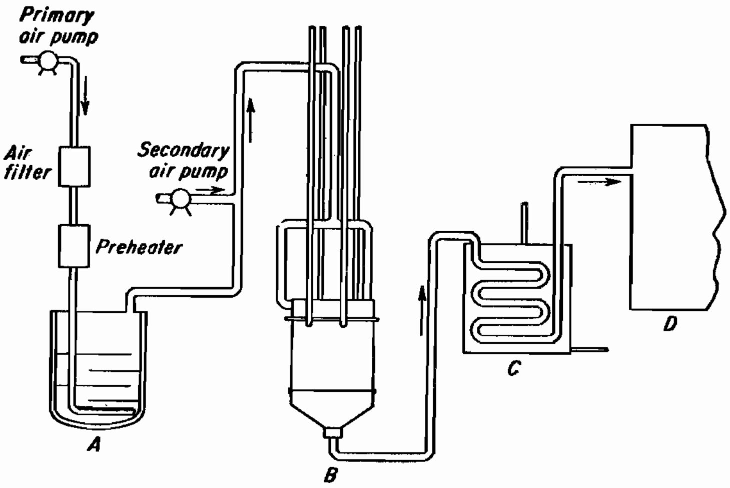


FIG. 9-10. Multiple-tube converter using two-phase mercury system.

By varying the pressure on the two-phase mercury system, it is possible to control the temperature of the liquid bath and of the catalyst mass. This may be accomplished by the use of nitrogen pressure. Also, the boiling point of the mercury can be altered by introducing alloying metals such as cadmium.

The capacity of such a converter is 1,500–1,800 lb (816.5 kg) or even more of phthalic anhydride per 24 hr, depending upon catalyst activity, rate of feed, etc. Production at this rate means the generation of large quantities of heat in the converter. Although the heat of oxidation of naphthalene to phthalic anhydride is about 6000 Btu per lb (3330 cal per kg) of naphthalene, the occurrence of a certain amount of complete combustion during the oxidation reaction brings the heat evolution up to approximately 10,000 Btu per lb (5550 cal per kg) of naphthalene fed to the converter. About 21,000,000 Btu (5,300,000 cal) is generated per day and removed by the boiling mercury and as sensible heat in the hot exit products during operation on the above basis. Figure 9-11 shows a general layout of equipment for naphthalene oxidation.

Mercury has both advantages and disadvantages for use as the heat-removing fluid. Its boiling point of 357°C at atmospheric pressure may be easily raised to 400–450°C by the application of nitrogen pressure. It is fluid at room temperature and introduces no hazard of equipment damage due to solidification through accidental cooling because of shutdown of equipment. Latent heat of evaporation at 357°C is 117 Btu per lb (65 cal per kg). Mercury vapor is toxic; the liquid is heavy; and leaks in the pressure system are difficult to prevent. These last factors, together with cost, operate as disadvantages. Some of these objectionable features have been



A Vaporizer for naphthalene
B Converter for oxidation reaction
C Cooler
D Condenser for phthalic anhydride

FIG. 9-11. Schematic layout for oxidation of naphthalene to phthalic anhydride.

overcome in practice. Proper construction and design have reduced mercury loss by leakage to about 1 per cent per year. Mercury has a low coefficient of thermal conductivity and does not wet the steel-tube walls. However, the violent motion given to the mercury by its own boiling tends to counteract these effects. Other materials, fluid at operating temperatures, have been proposed as superior to mercury in some respects. Among them sulfur, diphenyl, diphenyl oxide, and mercury amalgams may be mentioned here.

Instead of removing reaction heat by evaporation, the liquid surrounding a batch of catalyst tubes may serve simply as a means of heat transfer. Thus, Fig. 9-12 shows a method of removing heat from the surface of a retaining shell by releasing it to the atmosphere. Either forced or natural circulation of the fluid may be used to convey the heat from the catalyst tubes to the point of disposal. Fluids of low vapor pressures are preferable in such methods, and fused salts such as potassium–sodium nitrate mixtures may be used.

The fluid catalyst or jiggling process, developed in recent years for catalytic cracking of petroleum in gasoline production, has been adapted for the oxidation of naphthalene to phthalic anhydride.[1] A plant designed for 3 million lb of phthalic anhydride annually and subsequently expanded to 6 million lb has been claimed to give 92 lb of phthalic anhydride per 100

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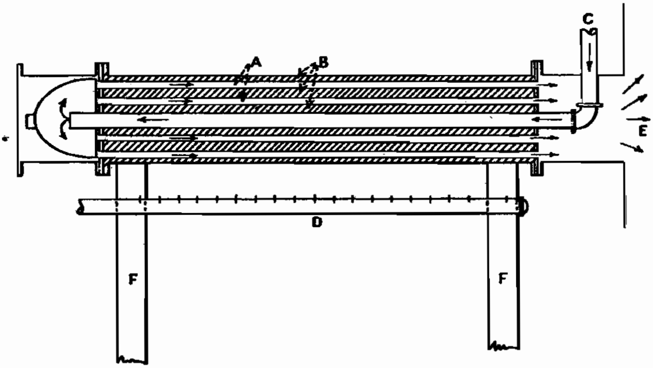
[1] LEE, *Chem. Met. Eng.*, **52** (7), 100–101 (1945).



A Tubes containing catalyst
B Heat-conducting medium
C Inlet for air and vapors
D Gas burners for starting
E Condenser
F Supports

FIG. 9-12. Catalytic multiple-tube converter for oxidation reaction with heat removal from surface of shell to atmosphere.

lb of 169–170°F melting point naphthalene. Air from reciprocating compressors is passed through preheaters and into the 5 ft diameter by 30 ft tall reactor containing the powdered catalyst. Melted naphthalene is sprayed into the reactor at the rate of 400 lb per hr, vaporizes, and mixes with the air therein. Some of the powdered catalyst passes out with the product stream and is removed by cyclones and filters. Phthalic anhydride is recovered in condensers. The tail gases are scrubbed and passed to the air. Advantages claimed are higher purity of product, lower air ratio, less explosion hazard, less labor, outdoor equipment, and lower operating temperatures. A 35-million lb per year plant has now been built in England to use this fluid-bed catalyst.

CHAPTER 10

HYDROGENATION

BY MERRELL R. FENSKE AND JENNINGS H. JONES

I. Introduction

Definition and Scope. The unit process hydrogenation (as contrasted with the general term reduction) specifically refers to the chemical reaction of a substance with molecular hydrogen in the presence of a catalyst. The process includes reactions in which hydrogen simply adds to a molecule (hydrogenation), reactions in which molecules are cleaved by hydrogen (hydrogenolysis or destructive hydrogenation), and also reactions such as isomerization, cyclization, and the like which occur in the presence of molecular hydrogen and catalysts. Accordingly, the information presented in this chapter will be limited almost exclusively to such reactions. A complete review of the chemical literature on hydrogenation and hydrogenolysis processes appears annually.[1]

Other reactions which involve molecular hydrogen and catalysts are reductive amination (hydroammonolysis), hydroformylation (Oxo and Oxoyl reactions), and the synthesis of ammonia. These processes, however, will not be considered in this chapter. The first two of the processes use a third reactant (ammonia and carbon monoxide, respectively) and are discussed in detail in separate chapters. The third process, the synthesis of ammonia, is considered to be beyond the scope of this chapter.

Hydrogenation, in the exact usage of the designation, is synonymous with reduction, which is the term usually applied to a reaction in which oxygen or some other element (most commonly nitrogen, sulfur, carbon, or halogen) is withdrawn from or hydrogen is added to a molecule. Such a reaction may be performed in a variety of methods; however, if catalytic hydrogenation will yield the desired reduction product, it is generally the simplest and most useful procedure in that the yields are usually high, the products clean, and it is not necessary to use large volumes of solvents or solutions in the processing step. The latter factor becomes important when it is desired to use the process commercially, since catalytic reductions are applicable to preparations of any size.

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[1] ARNOLD, *Ind. Eng. Chem.*, **48**, 1629 (1956).

Examples of important methods of reduction other than catalytic hydrogenation are: (1) by metals in acid or basic solution, (2) by alkali metals in alcoholic solution, (3) by electrolysis, (4) by alkali metals and hydrazine, (5) by complex metal hydrides,[1] and (6) by hydrogen transfer.[2]

Of the above methods the one most frequently confused with catalytic hydrogenation is hydrogen transfer, which involves the saturation of ethylenic double bonds by the direct exchange of hydrogen generally from one substance to another with essentially no participation of free molecular hydrogen. The process is recognized as being separate and distinct from hydrogenation or dehydrogenation and apparently proceeds by an ionic mechanism taking place over an acid catalyst. Typical catalysts are coprecipitated silica-alumina catalysts containing 60–90 per cent silica when in the most active form. Such catalysts are not efficient for normal hydrogenation reactions. Hydrogen-transfer reactions are important in the petroleum industry, especially in exchanging hydrogen from naphthenes to olefins to prepare aromatics and isoparaffins. The reaction is especially promising when low-cost olefin concentrates or cracked fractions can be used as the hydrogen acceptor; thus, an olefin-containing gasoline produced by catalytic cracking upon recycling over a silica-alumina catalyst yields a gasoline lower in olefin content but higher in aromatics and isoparaffins.

Alcohols also undergo a similar hydrogen-exchange reaction with ethylene as the acceptor to give aldehydes or ketones in yields of 40–75 per cent.[3] The reaction takes place at atmospheric pressure, at a temperature of about 280°C, while using a copper-zinc-nickel-barium chromate as the catalyst.

In the well-known Oppenauer oxidation reaction, alcohol groups can be converted to the corresponding carbonyls by using a hydrogen acceptor such as acetone or cyclohexanone. Aluminum *t*-butoxide or aluminum isopropoxide is the catalyst.[4]

Survey of Hydrogenation. Catalytic hydrogenation is used extensively both in the laboratory and in industrial processes. In the laboratory it is used in chemical syntheses, as a basis for many analytical procedures, and as a research tool in the identification and determination of the structure of organic compounds. In industry, large quantities of hydrogen are consumed in the manufacture of ammonia, methanol, liquid fuels, oxygenated

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[1] Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, 1956.

[2] Thomas, *J. Am. Chem. Soc.*, **66**, 1586 (1944); Blue and Engle, *Ind. Eng. Chem.*, **43**, 494 (1951); Reeve and Adkins, *J. Am. Chem. Soc.*, **62**, 2874 (1940); Kelly and Lee, *Ind. Eng. Chem.*, **47**, 757 (1955); Natta, Pino, and Ercoli, *J. Am. Chem. Soc.*, **74**, 4496 (1952); Haldeman and Emmett, *ibid.*, **78**, 2922 (1956); Voge, Good, and Greenfelder, *Ind. Eng. Chem.*, **38**, 1033 (1946).

[3] Reeve and Adkins, *loc. cit.*

[4] Djerassi, "Organic Reactions," vol. 6, p. 207, John Wiley & Sons, Inc., New York, 1951.

compounds, hydrogenated vegetable oils, and a variety of organic chemicals. Further; increasing quantities of hydrogen are being used for petroleum processing, and in the future additional quantities may be demanded for coal hydrogenation to produce fuels and chemicals.

The foundation for the present industry was laid in 1897 when Sabatier and Senderens illustrated the catalytic effect of nickel in vapor-phase hydrogenation reactions. The earliest technical application of hydrogenation was in the reduction of the double bonds between two carbon atoms for the purpose of converting liquid fats into solid fats, or as it is often called, fat hardening. This industry is now very large.

The commercialization of hydrogenation developed over the years with the work of Haber in ammonia synthesis, Bergius in coal and heavy-oil hydrogenation, and Fischer and Tropsch in fuel synthesis.

Coal Hydrogenation. The destructive hydrogenation of coal to produce gasoline has been undertaken at various times in countries where the existence of petroleum had not, at the time, been proved. After the initial work of Bergius, brown coal was first hydrogenated commercially in Germany in 1927—followed by the first plant processing bituminous coal in Great Britain in 1935. Bituminous coals, having a lower hydrogen content than brown coals, are more difficult to hydrogenate. By 1945, a dozen such plants were operating in Germany and producing aviation-gasoline components at the rate of 2 million tons per year. Of these dozen plants, about half processed either brown or bituminous coal while the remainder operated using tars obtained from the carbonization of coal, pitch, or petroleum residues. The latter feedstocks were easier to process than coal since they contained a larger proportion of hydrogen and were liquid in form.

Coal is no longer being hydrogenated in Europe either because of the location of newly discovered petroleum sources (as in Germany where the hydrogenation equipment has been integrated with the conventional refinery installations) or because the relative prices of coal and oil have changed so that coal hydrogenation is no longer economical (as in Great Britain). In the latter country, a part of the coal hydrogenation equipment is now being used for other purposes such as the Oxo process, catalytic hydration of olefins, and the synthesis of phenol; the remainder of the equipment is being used for the destructive hydrogenation of creosote or tar oils to produce gasoline.

Coal hydrogenation to produce motor fuels is not as yet economical, even after allowing credit for various by-product chemicals such as phenol, cresols, xylenols, toluene, xylenes, naphthalene, and liquified hydrocarbon gases. The immediate future of coal hydrogenation probably depends on the recent developments such as those of Union Carbide Chemicals Company toward the production of high yields of chemicals, although a large proportion of these consists of complex structures that are not well-known.

Petroleum Hydrogenation. In this country a destructive hydrogenation plant processing various petroleum feedstocks was in operation at Baton Rouge, La., previous to World War II. However, in the years prior to 1950 hydrogenation played only a minor role in petroleum technology, largely because of the preventive cost of hydrogen. The outstanding exception was the hydrogenation of high-octane olefinic fractions for the production of aviation naphthas during World War II. However, with the advent of the catalytic reforming processes by which heavy naphthas are upgraded in octane value, large quantities of by-product hydrogen became available to the petroleum industry, and this hydrogen is now being used for improving a wide range of products. At the end of 1956 about 70,000 tons per year of hydrogen was consumed for this purpose. The reforming capacity of refineries in this country at this time exceeded 924,000 bbl per day and yielded over 1,600 tons per day (580,000 tons per year) of by-product hydrogen having a purity ranging from 75–95 per cent—depending on the severity of the operation and the nature of the feedstock. At present a large portion of this hydrogen is being diverted to ammonia synthesis.

Mild hydrogenation is being used extensively in petroleum processing, especially in product finishing of naphtha, kerosene, diesel fuel, heating oil, and distillate lubricating oils. This mild hydrogen treatment serves primarily to replace other less efficient methods for removing sulfur compounds, improving color and odor, and increasing the storage stability of the products.

The synthetic-ammonia process represents at present the largest single demand for hydrogen, followed by petroleum processing (a poor second), fat hydrogenation, and synthetic methanol. At the end of 1956 there were more than 63 synthetic-ammonia plants in this country with a capacity of about 4.8 million tons of ammonia per year. This quantity of ammonia is equivalent to a yearly demand of about 850,000 tons of hydrogen.

Fat Hydrogenation. Fat hydrogenation, the addition of hydrogen to fatty acids—particularly edible oils such as cottonseed and soybean—although accounting for less than one per cent by weight of the oil, is an important outlet for hydrogen. This use probably is third in importance to ammonia and a close second to petroleum processing. In 1956 in the United States the output of hydrogenated fats amounted to about 1.5 million tons. This amount consisted largely of oleomargarine and shortening.

The fats resulting from the hardening of whale oil, fish oil, and the vegetable oils such as linseed, soybean, and cottonseed oil, by the addition of hydrogen under pressure, are of two types—edible and nonedible. The edible fats are used as lard, butter substitutes, and shortening compositions in the baking industry and for the manufacture of creams and coatings for confections. The soap industry is the largest consumer of nonedible hardened oils. Other minor uses for the nonedible products are in leather dressings, electrical insulations, candlemaking, paint manufacture, and pharmaceutical ointments.

Another development of importance to the soap industry is the manufacture of sulfuric acid esters of long-chain aliphatic alcohols such as lauryl, cetyl, and stearyl alcohols. Instead of making the sodium salt of palmitic or stearic acid, as in ordinary soap manufacture, these acids are first reduced to the corresponding alcohols by hydrogenation at high pressure, and the alcohols are then esterified with sulfuric acid. These detergents, which are used in the form of the sodium salt, have some very interesting properties; thus, they are equally soluble in hard or soft water. They are well suited for hard waters, and their emulsifying and wetting powers are better than ordinary soaps. Whereas ordinary soaps in acid media are decomposed into fatty acids that are difficultly removed, particularly from fine fabrics, the sodium palmityl and stearyl sulfates are soluble in acid, neutral, or alkaline media without decomposition into insoluble compounds. Fatty acids either may interfere with dyeing operations or later may become rancid and give off disagreeable odors. The sulfuric acid esters do not become rancid and, because of their high solubility, are easily and completely washed out of fabrics. These detergents, although more expensive than the ordinary soap, find many applications in washing fine fabrics and fibers, in toilet preparations, and wherever their advantages more than offset their higher price.

Other Hydrogenations. Synthetic methanol also consumes much hydrogen. In 1956 the rate of synthesis amounted to about 800,000 tons of methanol per year; the hydrogen requirement was about 100,000 tons.

The hydrogenation and hydrogenolysis of carbohydrates have been the subject of considerable research in recent years. Glucose, sucrose, molasses, starch, and other saccharides have been treated with hydrogen at temperatures ranging from 100–250°C and pressures from 80–300 atm, using nickel, iron, and copper catalysts, to prepare propylene glycol and glycerol in good yields.[1] Lesser quantities of hexyl alcohol, ethylene glycol, ethanol, and methanol are also formed. By a two-stage hydrogenation of hexose, some 1,530 tons of glycerogen (a glycerol substitute) containing 40 per cent glycerol, 40 per cent propylene glycol, and 20 per cent hexyl alcohol was produced in Germany during World War II.[2]

In the manufacture of organic chemicals there are many examples in which hydrogen is required to the extent of 1 to 5 per cent by weight of the product, but none of the outlets is large. The most important use of

[1] Natta, Rigamonti, and Beati, *Ber. deut. chem. Ges.*, **76B**, 641–656 (1943); Stengel, U.S. 2,325,206 (1943); *Chem. Abstracts*, **38**, 375 (1944); Yosikawa and Hanai, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **17**, 1262–1277 (1938); *Chem. Abstracts*, **34**, 2796 (1940).

[2] *O.P.B. Declassified Rept.* 183 (Office of Publications Board, U.S. Department of Commerce). Reported by Leaper, *Mfg. Chemist*, **19**, 114 (1948).

hydrogenation in the chemical industry probably is in the aldol process for producing alcohols having chains of four to eight carbons. However, the importance of aldol processes is decreasing in favor of the Oxo process which uses less hydrogen. Other organic chemicals being hydrogenated are glycolic acid (as its ester) to make ethylene glycol, adiponitrile to hexamethylenediamine (used in the synthesis of nylon), dextrose to sorbitol (used in the manufacture of vitamin C—ascorbic acid), phenol to cyclohexanol (Hexalin) and cyclohexanone (used in the synthesis of adipic acid), and naphthalene to tetralin (which results when four atoms of hydrogen is added) and decalin (which results when ten atoms of hydrogen is added).

Hydrogen is also used in the conversion of benzene to cyclohexane and of acetylene derivatives to butanediol. In the food industry, hydrogen is used to remove acids from fatty oils. In the future, hydrogen may be of importance in processing shale oils and in the manufacture of powdered metals. The latter industry consumed more than 1,500 tons of hydrogen in 1956 for this purpose.

Catalytic hydrogenation has been applied to materials of widely varying molecular weights and structures. Thus, materials such as wood, rubber, vitamins, proteins, steroids, elastomers, cotton linters, and nylon are typical of the variety of compounds subjected to the reaction. Further, nitric oxide on hydrogenation over a platinum-carbon catalyst yields hydroxylamine—such a process has commercial possibilities.

Large quantities of catalysts are consumed in hydrogenation processes. In the fat hydrogenation industry, for example, 300–600 tons of nickel is consumed per year in this manner. In petroleum processing in 1956, about 125 tons of chromium (as the oxide) was used in hydrogenation catalysts and an additional 490 tons was used in reforming processes. Also, in the same year about 350 tons of molybdenum was used in catalysts for hydrogenation and reforming.

In the future, catalytic hydrogenation probably will continue to increase steadily in importance, size, and the variety of processes. New outlets for large volumes of hydrogen will be needed to take advantage of the increasingly large volume generated in catalytic reformers. The conversion of petroleum residues and shale oils to lighter fractions may become economically attractive. The possible commercialization of coal-hydrogenation processes for producing chemicals is another example. Homogeneous catalysis—in which the catalyst is in the same phase as the reactants—also, undoubtedly, will receive much attention.

II. HYDROGEN: PRODUCTION AND PROPERTIES

In the development and operation of processes involving reduction by means of hydrogenation, the problem of the hydrogen supply is important. In the small-scale or research phase of the problem, hydrogen is readily available in cylinders and is usually of sufficient purity, so that at this stage of the development work no thought need be given to the hydrogen supply. However, as soon as semiplant or commercial operation of the process begins, not only the problems of hydrogen production but also those of purification, handling, storage, and compression appear. Sometimes, these seem to outweigh all the earlier problems concerned with getting the desired reaction to proceed. The most important methods available for hydrogen production are discussed below.

Hydrogen from Hydrocarbons. Hydrogen is available from hydrocarbons by four processes: (1) thermal decomposition, (2) steam reforming, (3) partial oxidation, and (4) as a by-product from catalytic reforming.

Thermal Decomposition. The first of these reactions involves the complete decomposition, or cracking, of natural gas into carbon and hydrogen. At present, gases high in methane are cracked to produce carbon black by the thermatomic-carbon process. The hydrogen is a by-product and is used principally for fuel.

Steam Reforming. The second of the above processes is one of the best methods available to petroleum hydrogenation or synthesis plants for the production of hydrogen from natural gas, from waste refinery gas, or from the gaseous products resulting from hydrogenation. These gases are composed principally of methane, and the reaction with steam is

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

This is a catalytic reaction and occurs at about 1000°C (1800°F) in special furnaces. The catalyst is an aluminum oxide base in the form of small pellets or cubes. The reaction is highly endothermic, and so the catalyst is contained in tubes consisting of a high-chromium, high-nickel alloy steel capable of withstanding these high temperatures. The waste heat in the flue gas from the furnaces is utilized by means of waste-heat boilers to produce about half the steam required in the process. If a carbon monoxide–hydrogen mixture is needed, as in producing methanol or synthetic hydrocarbons, the reaction between light hydrocarbons and steam is commonly used. Extensive work has been done on reacting natural gas with steam for this purpose.[1] More steam is added to the carbon monoxide–hydrogen mixture, and the water-gas catalytic reaction is then made to take place over an iron-base catalyst at 450–500°C (840–930°F). The gases leaving this converter contain about 79 per cent hydrogen, 20 per cent carbon dioxide, and 1 per cent unconverted hydrocarbons and miscellaneous gases. They are cooled and scrubbed to remove the carbon dioxide, just as in the water-gas catalytic process.

The reaction of hydrocarbons and steam is thus a continuous process,

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[1] Clark, Kallenberger, Browne, and Phillips, *Chem. Eng. Progr.*, **45** (11), 651 (1949).

capable of making available the large quantities of combined hydrogen existing in natural and refinery gases principally as methane, ethane, and some unsaturated hydrocarbons. This reaction is used in many hydrogenation plants in this country.

A flow diagram for the production of hydrogen from natural gas, refinery gas, propane, or butane is presented in Fig. 10-1.[1]

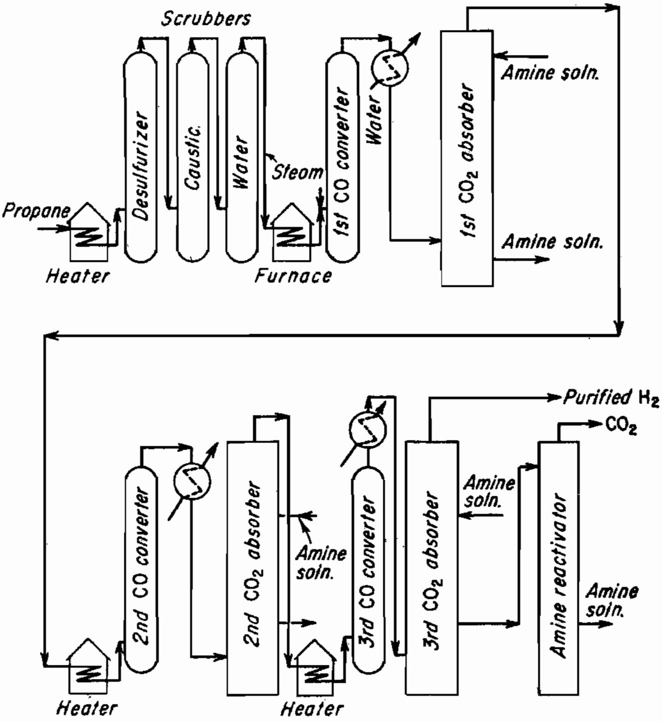

FIG. 10-1. Production of hydrogen from propane by steam reforming.

Partial Oxidation or Oxygen Reforming. The third of the above processes available for producing hydrogen from hydrocarbons is that of partial oxidation.[2] This relatively new process developed by The Texas Company is economically competitive with or superior to steam reforming because of the development in recent years of low-cost oxygen. About ten syn-

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[1] The Girdler Corp., Louisville, Ky.; REED, *Trans. Am. Inst. Chem. Engrs.*, **41** (4), 453 (1945); **42** (2), 379 (1946).

[2] EASTMAN, *Ind. Eng. Chem.*, **48**, 1118 (1956); MUNGEN and KRATZER, *ibid.*, **43**, 2780 (1951).

thesis-gas plants using this process either have been built or are being built. The process operates by a noncatalytic flame reaction of oxygen with natural gas or fuel oil to produce hydrogen and carbon monoxide mixtures.

A specially designed burner permitting mixing to be done in the reaction zone is used, and the reactor is designed with cylindrical carbon-steel pressure shells lined with successive layers of special refractories built to withstand pressures of 200–300 psig and temperatures above 1100°C. (Temperatures as high as 3300°C develop if conditions are not properly controlled; although under normal operating conditions the refractories are subject only to temperatures allowable for firebrick.) The "cold gas efficiency" or the heating value of the hydrogen and carbon monoxide expressed as a percentage of the fuel used is in the range of 80–85 per cent. A volume of about 250–270 cu ft of pure oxygen is required per 1,000 cu ft of hydrogen plus carbon monoxide formed. The reaction appears to proceed in two steps. In the first step a rapid consumption of oxygen occurs and only a portion of the hydrocarbon (such as methane) is converted, producing large amounts of water and/or carbon dioxide. In the second step, which is rate controlling, the remaining hydrocarbon undergoes reaction with water or carbon dioxide. The over-all reaction is strongly exothermic, although some of the reaction heat liberated in the first step is absorbed by the endothermic reforming reactions. The carbon monoxide in the gas thus produced can be converted to more hydrogen, using the water-gas shift reaction by which the carbon monoxide is changed to carbon dioxide and more hydrogen. The process has the advantage of utilizing fully the high pressure at which the hydrocarbon feed gas is available and thus of making hydrogen under pressure from simple raw materials.

The oxygen-reforming process was first developed for use with natural gas as a fuel but also has been applied to light oils and heavy bunker-type fuel oils. The flexibility of the process with respect to fuels is particularly attractive since it is possible to establish plants needing hydrogen at locations where neither natural gas nor coal is economically available but to which fuel oils can be easily transported.

The typical compositions of gaseous products obtained by partial oxidation and subsequent steam reforming of a variety of feedstocks is shown in Table 10-1.

With the partial-oxidation process an oxygen plant is necessary, and because nitrogen is a by-product it is possible to use low-temperature purification techniques for stripping hydrogen from the reformed gas after the latter goes through a shift reaction.

Variations of the second and third processes also are possible.[1] Thus,

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[1] PFEIFFER and SANDLER, *Proc. Am. Petroleum Inst.*, **35** (III), 294 (1955).

TABLE 10-1. COMPOSITIONS OF HYDROGEN-CONTAINING GASES FROM THE PARTIAL OXIDATION OF VARIOUS FEEDSTOCKS

Constituents	Composition, mole %, of gas from		
	Natural gas	Fuel gas	Coal gas
CO	38.0	48.0	54.4
CO_2	2.2	3.7	5.7
H_2	59.5	47.5	38.9
N_2	0.2	0.2	0.8
CH_4	0.1	0.3	0.1
H_2S	...	0.4	0.2

either 95 per cent oxygen or enriched air may be used in a combination partial oxidation–reforming procedure. Such combination processes are similar to partial oxidation except that the hydrocarbon feed is reacted in the presence of both steam and oxygen over a nickel catalyst at about 940°C. The lower temperature allows the use of smaller preheating surfaces and imposes less severe conditions on all combustion equipment than are encountered in partial oxidation with oxygen alone. The main advantage of the process, however, is that the requirement for 95 per cent oxygen is lower than in simple partial oxidation. The process also may be carried out using just enough air enriched with 95 per cent oxygen to produce the correct 3:1 hydrogen:nitrogen ratio in the gas (after reforming and converting the carbon monoxide) for ammonia synthesis.

Another variation of the partial-oxidation process is one in which a heavy-oil fraction is cracked in the presence of an inert solid and a hydrogen-rich gas under conditions which result in the saturation of olefins and diolefins. During the process some coke and residual material deposits on the inert solid. The latter then flows by gravity to a combustion zone where the coke is burned off the solid in the presence of oxygen and steam to produce the hydrogen-rich gas used in the cracking cycle.[1]

By-product Hydrogen from Catalytic Reforming. The fourth process for preparing hydrogen from hydrocarbons—catalytic reforming—yields as a by-product an off-gas containing 77–95 per cent hydrogen. Vast quantities of hydrogen are now available from such processes, and at the end of 1956 the production of hydrogen amounted to about 1,600 tons per day. Most refiners are unprepared to utilize this high hydrogen-content off-gas, and in a majority of catalytic-reformer installations the gas is simply burned for fuel. Much of the gas, however, is rapidly being diverted for use in ammonia synthesis, and in the future large portions

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[1] *Petroleum Engr.*, **27** (8), C-25 (1955).

of this hydrogen will be used in the desulfurization of petroleum feedstocks and in hydrogenating olefinic feeds prior to catalytic reforming.

Hydrogen from Water Gas and Steam. The water-gas catalytic, or Bosch, process is one of the most important for producing industrial hydrogen today. Water gas is readily made in standard water-gas generators from very cheap raw materials, viz., coal or coke, steam, and air. An average analysis of water gas is

	Per cent
Hydrogen	49.2
Carbon monoxide	41.3
Carbon dioxide	4.2
Oxygen	0.2
Methane	0.8
Nitrogen	4.3

The carbon monoxide in the gas is made to react with steam in the presence of an iron oxide catalyst, and additional hydrogen along with carbon dioxide is obtained.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The result of this reaction is that the water gas is converted essentially into a gas composed of carbon dioxide and hydrogen. The carbon dioxide is easily removed by scrubbing with water under pressure or by absorbents such as triethanolamine, leaving a gas composed essentially of hydrogen. If necessary, it is purified further to remove the small amounts of the other gases. For example, small amounts of carbon monoxide are removed by scrubbing with ammoniacal solutions of copper salts.

The water-gas catalytic process is usually carried out at about 450–500°C (840–930°F) and generally at substantially atmospheric pressure. The reaction is exothermic, so once it is started it is self-supporting. Although there are many catalysts that may be used, they generally consist of oxides of iron promoted by chromium oxide, cobalt oxide, and alumina. The reaction is reversible, so that if the temperature is too high, the conversion is not complete. It can be forced to greater conversion, however, by using an excess of steam, which is usually the practice. The steam is easily condensed and so removed from the gases as they are cooled.

These gases, containing 60–80 per cent hydrogen, 20–40 per cent carbon dioxide, less than 1 per cent carbon monoxide, and smaller amounts of other gases, are then usually stored in gasholders. They are taken as needed from the holders to the compressors, for the hydrogen is practically always used at elevated pressure. At some intermediate stage in the compression, where the pressure may be 250–1,000 psig, the mixture of gases is led from the compressors to the scrubbing towers where the carbon dioxide is removed, after which the gas goes back to the compressors to be compressed to the final working pressure.

Hydrogen by Electrolysis of Water. Cheap electrical power is the principal factor determining the production of hydrogen by the electrolysis of water. The purity of this hydrogen is an asset. This method of hydrogen production is perhaps the best available for small plants where the operations are not large enough to warrant the large-scale water-gas catalytic method of production. Such plants generally use hydrogen in various syntheses or in the preparation of organic chemicals. Even though the cost of producing hydrogen by electrolysis is more than by other methods, it is a convenient and workable method for plant work on a small scale.

Solutions of potassium or sodium hydroxide are commonly employed in the electrolytic cells. The solution must be circulated through the cells to avoid metal concentration at the cathode and dilution at the anode. High current efficiencies of 96–100 per cent are obtained in modern units. At 100 per cent efficiency the production of 1,000 cu ft of hydrogen and 500 cu ft of oxygen would require 78.8 kwhr of direct current. The minimum voltage required is 1.7 volts; the theoretical is 1.23 volts. The difference is known as "overvoltage." The actual operating voltage required is about 2–2.3 volts; so at 100 per cent efficiency the power consumption amounts to about 130–145 kwhr per 1,000 cu ft of hydrogen.

Hydrogen also is a by-product from the manufacture by electrolytic methods of chlorine, sodium hydroxide, chlorates, and perchlorates.

Hydrogen from Steam and Iron. The principal reactions for the production of hydrogen from steam and iron are

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 \tag{1}$$

$$\left.\begin{array}{l} Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O \\ Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2 \end{array}\right\} \tag{2}$$

The reaction is intermittent, the iron being oxidized to produce the hydrogen and then regenerated as indicated by reactions (2) by passing water gas over it. This method has been used for some time and is adapted to small- or moderate-scale operations. However, it is gradually being supplanted by other methods of hydrogen production. The production of hydrogen from steam and iron has been extensively used in the past in connection with hardening or hydrogenation of vegetable oils. Because of the relative simplicity of such installations, the bulk of the hydrogen for barrage balloons over England during World War II was made by the steam-iron process.

Hydrogen from Methanol and Steam. The steam-methanol process which proceeds by the following equation

$$CH_3OH + H_2O \xrightarrow{260°C} 3H_2 + CO_2$$

was used in small portable hydrogen manufacturing plants by the armed forces during World War II as a method for producing hydrogen and carbon dioxide. A volume totaling 1,000 cu ft of hydrogen and about 40 lb of carbon dioxide can be produced from 5 gal of methanol. Some of the portable plants had capacities of 4,000 cu ft of hydrogen per hour; the burning of about 4 gal of fuel oil per hour was required to furnish heat for the reaction and equipment.

Hydrogen from Ammonia. The dissociation of ammonia is a potentially important process for producing hydrogen where relatively small quantities are desired for special applications. It is claimed that a single 150-lb cylinder of liquid ammonia can replace more than 30 cylinders of gaseous hydrogen since each pound of liquid ammonia yields 34 cu ft of hydrogen and 11 cu ft of nitrogen. The dissociation takes place at 900–1000°C over a nickel catalyst at 1–20 atm pressure.

Miscellaneous Processes. Hydrogen also may be obtained from calcium hydride, from sodium hydride, as a by-product from fermentation processes (butyl alcohol process), from coke-oven gas, and by the partial oxidation of powdered coal by a process similar to that described for hydrocarbons.

Hydrogen Separation by Liquefaction.[1] This is a physical process of purification based on the difference in boiling points of the components of the gas when liquefied. It developed through the work of Claude, Patart, and the Linde Company in Europe, where the only source of hydrogen during the past thirty years was coke-oven or water gas. The technique was developed in order to strip hydrogen from the coke-oven gas and to return the hydrocarbon gases as a fuel richer in Btu value than the original feed gas. Coke-oven gas, because of its nitrogen content, is usually worked up for ammonia synthesis, whereas water gas is more suitable for the production of hydrogen alone. Coke-oven gas may contain about 50 per cent hydrogen and some 15–20 per cent nitrogen, together with 20–30 per cent methane, unsaturated hydrocarbons, and carbon monoxide. The process with certain refinements is now used in this country in purifying hydrogen from catalytic reformers. The gas is first compressed to about 300 psig and passed through a prepurification step for complete removal of impurities such as carbon dioxide and hydrogen sulfide. The purified gas then is dried to a moisture content of about 1 ppm and chilled to about 35°C, where the bulk of the propane and all the heavier hydrocarbons are condensed. The gas flows next to a second exchanger operated at about -120°C, in which the C_2 hydrocarbons and the remaining propane are condensed. This system sometimes includes a reflux type of condenser for the removal of acetylene which forms an azeotrope with ethylene. In a third exchanger the bulk of the methane and the remaining C_2-hydrocarbons are condensed as well as some nitrogen and carbon monoxide (if the latter two are present).

[1] Hugill and Kerry, *Proc. Am. Petroleum Inst.*, **35** (III), 324 (1955).

If no carbon monoxide is present in the gas, the design of the methane exchanger system demands a close study to prevent the formation of solid methane. Solid methane is difficult to sublime and remove from such a system and can plug valves and block exchanger tubes. The gas next enters the final column and is scrubbed with liquid nitrogen entering at the top. The purified hydrogen leaving at the top consists of a mixture of hydrogen (90 per cent) and nitrogen (10 per cent). This pure stream is then returned through the entire exchanger system, and additional high-purity nitrogen is added if it is desired to synthesize ammonia.

The refrigeration necessary to run the plant is supplied by a cascade system consisting of liquid ammonia, a closed ethylene refrigeration cycle, and a high-pressure nitrogen cycle.

Cost of Hydrogen. For any plant the total cost of hydrogen will depend on (1) the location and proximity to cheap fuel and power, (2) the size of the plant, (3) the purity of the hydrogen required, (4) the pressure at which it is employed, and (5) the type process by which it is made. Comparative data on the cost of producing hydrogen by a variety of processes are presented in Table 10-2. For this estimate[1] the following costs were assumed: natural gas, $0.30 per million Btu; fuel oil, $2.50 per bbl; propane, $0.11 per gal; methanol, $0.30 per gal; refinery off-gas, $0.50 per thousand cubic feet of H_2; ammonia, $90.00 per ton; coke $18.50 per ton; steam at 125 psig, $0.50 per thousand lb; cooling water, $0.02 per thousand gallons; electricity, $0.01 per kwhr and $0.005 per kwhr as noted; labor, $50,000 per year per man per 24-hr day (including supervision); depreciation, 10 per cent of investment per year; repairs and replacement, 5 per cent of investment per year; taxes, insurance, etc., 2.5 per cent of investment per year. In addition, the investment cost of the plant for processing refinery off-gas includes the cost ($150,000–$200,000) of a hydrogen pipeline 4 miles in length.

The data of Table 10-2 indicate that purification of reformer off-gas offers a cheap process for obtaining hydrogen, assuming that hydrogen may be purchased from the refinery for $0.50 per 1,000 cu ft. Other estimates[2] on the recovery of hydrogen from such off-gas indicate that 99.9 mole per cent hydrogen at 300 psig can be delivered at a cost of $0.08–$0.10 per 1,000 cu ft by liquefaction processes in a plant having a capacity of 10 million standard cubic feet per day. For a plant of 1 million standard cubic feet per day capacity, the processing cost would amount to about $0.38 per 1,000 cu ft. These latter estimates do not include the cost of refinery off-gas.

Plant operating costs for the production of hydrogen by electrolysis and by propane reforming are compared in Table 10-3 for various sizes of

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[1] FAIRCLOUGH, *Petroleum Refiner*, **35** (9), 333 (1956).

[2] PALAZZO, SCHREINER, and SKAPERDAS, Division of Petroleum Chemistry, *ACS Preprint* 1 (4), 123 (September, 1956), BAKER, *Chem. Eng. Progr.*, **51**, 399 (1955).

TABLE 10-2. PRODUCTION AND PLANT INVESTMENT COSTS FOR MANUFACTURING HYDROGEN BY VARIOUS PROCESSES

Capacity standard cu ft/day	Propane reforming	Natural gas reforming	Partial oxidation of natural gas	Partial oxidation of fuel oil	Purification of reformer off-gas	Steam-iron	Electrolysis of water	Steam-methanol	Dissociation of ammonia
Production Cost, Dollars/Thousand Cu Ft									
100,000	4.30	3.30	....	....	....	3.30	4.15	4.60	3.30
500,000	2.35	2.05	....	....	....	2.50	2.80	2.80	2.60
1,000,000	1.90	1.70	1.60	1.80	1.00	2.20	2.60	2.50	2.50
5,000,000	1.30	0.95	0.85	1.05	0.80	1.75	....	2.00	1.80
10,000,000	....	0.85	0.70	0.85	0.70				
15,000,000	....	0.80	0.65	0.80	0.65				
Plant Investment Cost, Thousands of Dollars									
100,000	390	350	.....	.....	.....	320	300	200	150
500,000	1,150	960	.....	.....	.....	950	900	400	450
1,000,000	1,600	1,200	1,300	2,000	500	1,500	1,500	450	550
5,000,000	4,400	3,900	4,200	5,700	1,400	5,200	.....	1,000	2,000
10,000,000	7,200	6,500	7,000	7,800	2,000				
15,000,000	.....	8,800	8,800	9,500	2,200				

TABLE 10-3. COST OF HYDROGEN MANUFACTURE BY ELECTROLYSIS AND BY REFORMING

	Electrolysis			Propane reforming		
	Capacity, standard cu ft/day					
	100,000	500,000	1,000,000	100,000	500,000	1,000,000
Hydrogen Plant Operating Costs, Dollars/Thousand Standard Cu Ft						
Raw material	0	0	0	0.30	0.30	0.30
Labor	0	0	0	0.55	0.11	0.06
Power	1.82	1.82	1.82	0.90	0.90	0.90
Variable, other	0.54	0.32	0.22	0.67	0.35	0.23
Depreciation	0.93	0.88	0.86	1.21	0.61	0.41
Fixed, other	0.45	0.43	0.41	0.68	0.31	0.21
Total	3.74	3.46	3.31	4.31	2.58	2.11
Hydrogen Plant Investment Costs, Millions of Dollars						
Investment costs	0.2	1.2	2.3	0.3	0.85	1.1

plants.[1] The results indicate that for plant capacities below 100,000 standard cu ft per day, the electrolytic process may be cheaper. For plants of 300,000 standard cu ft per day capacity, propane reforming should be cheaper.

Compressing hydrogen to 3,000 psig would cost about $0.20 per 1,000 cu ft, if power were available at $0.01 per kwhr. On this basis, the energy cost would be just about one-half the total cost; fixed charges, labor, maintenance, and repairs account for the other half.

It is reported[2] that to produce about 5 million cu ft of hydrogen per hour from coal there are needed about 19,000 kwhr of electrical energy, 302,000 lb per hr of steam, about 900,000 cu ft per hr of fuel gas, and 42 tons per hr of moisture- and ash-free coal.

Along with the cost of hydrogen, it is necessary to know the amount consumed in the various processes. For the case of relatively pure or definite chemical compounds, the required amount of hydrogen is readily calculated. In the fat-hardening industry, about 34 cu ft of hydrogen is consumed per ton of oil per unit drop in iodine value. Fo hardening the common oils such as castor, cottonseed, linseed, olive, palm, rapeseed, soybean, sunflower seed, and whale oils, the hydrogen consumption amounts to 0.8–2 cu ft per lb. For hydrogenating coal to liquid fuels, about 0.1 lb of hydrogen is used per pound of coal hydrogenated.

In the petroleum industry about 7.5 cu ft of hydrogen per barrel is needed to saturate the olefins in a naphtha when the concentration is 1 per cent. About 3.5 cu ft is required per barrel for the hydrogenolysis of nitrogen compounds (assuming pyridine) when the nitrogen content is 0.01 per cent. Similarly, for naphthas containing 0.01 per cent sulfur, the volume of hydrogen required for hydrodesulfurization varies from 0.3 cu ft per bbl for mercaptans to 1.2 cu ft per bbl for thiophenes. Naphthas containing 0.01 per cent oxygen require 0.3–1.2 cu ft of hydrogen per barrel for hydrogenolysis.

Thus, in hydrogenating common chemicals, the cost of hydrogen would probably not be more than 1 cent per lb of material hydrogenated; in the fat-hardening industry, it would be only a few mills per pound of hardened oil. In the petroleum, tar, and coal hydrogenation processes, the cost of hydrogen is from a fraction of a cent to 2 cents per gal of finished product. These figures are merely the cost of the hydrogen compressed to the pressure needed and do not include the operating costs, fixed charges, catalyst costs, and the like.

Properties of Hydrogen. Apart from the more commonly known physical and chemical properties of hydrogen are a few that are of primary im-

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[1] West, "Chemical Engineering in Practice," p. 39, Reinhold Publishing Corporation, New York, 1954.

[2] Skinner, Dressler, Chaffee, Miller, and Hirst, *Ind. Eng. Chem.*, 41, 87 (1949).

portance in the handling and use of hydrogen and hydrogenation equipment. Because it is the lightest gas, it will diffuse or leak where other heavier gases will not, particularly at high pressure. It is usually more difficult to have gastight connections and fittings when working with hydrogen than with other gases such as air or steam. Particular attention should be given to all fittings, valves, and connections that are to be used on hydrogen. A leak not only means a loss of hydrogen but is, in addition, a decided hazard because of the inflammability and very wide explosive limits that hydrogen possesses. These limits are much wider than for most gases, as Table 10-4 shows.

TABLE 10-4. EXPLOSIVE LIMITS OF GASES*
(Per Cent by Volume in Air)

Gas or vapor	Percentage of gas	Gas or vapor	Percentage of gas
Hydrogen	4.15–75.0	Ethylene	3.2–34.0
Carbon monoxide	12.5 –75.0	Propylene	2.2– 9.7
Methane	4.9 –15.4	Acetylene	1.5–80.5
Ethane	2.5 –15.0	Benzene	1.4– 8.0
Propane	2.2 – 7.3	Toluene	1.3– 6.8

* YEAW, *Ind. Eng. Chem.*, **21**, 1030 (1929); JONES, *Chem. Rev.*, **22**, 1 (1938).

These data show that a relatively small leakage of hydrogen or any carelessness in allowing air to mix with hydrogen might be dangerous. Adding 4.15 per cent or more of hydrogen to air or 25 per cent or more air to hydrogen results in explosive mixtures. Too much care cannot be exercised in designing and operating equipment in which hydrogen is used. All apparatus and lines should be carefully purged by an inert gas such as nitrogen, carbon dioxide, or flue gases not containing oxygen, before hydrogen is admitted.

Hydrogen at elevated temperatures and pressures in contact with ordinary carbon steels is particularly corrosive. The tensile strength of these carbon steels is due to a particular iron structure and to their carbon content. With iron alone, hydrogen forms a hard, brittle hydride; with carbon steels, in addition to the embrittling action, it causes trouble by attacking and removing carbon, reducing oxides, and producing blisters, cracks, and fissures. With embrittlement and the removal of carbon, the tensile strength of the steel is greatly reduced, so that continued use of the apparatus may be dangerous. Special alloy steels are entirely resistant to this hydrogen attack. The attack of hydrogen and hydrogen sulfide on steels has been studied extensively.[1]

[1] COX, *Chem. Met. Eng.*, **40**, 407 (1933); BERTHELOT, *Chem. Abstracts*, **33**, 2088 (1939); PUCHNER, *ibid.*, **37**, 6621 (1943).

In 1951, hydrogen blistering became a serious operating problem in gas-compression and fractionation units associated with catalytic cracking plants—presumably as a result of certain changes in the feedstock. Much damage resulted, and more frequent shutdowns and replacement of equipment were necessitated. Apparently molecular hydrogen plays no part in the attack on steel; the harmful hydrogen is the dissociated hydrogen present on the corroding surface of the steel and originates from the hydrogen ions in the water. After penetration, the atomic hydrogen converts to molecular hydrogen at internal discontinuities in the steel, accompanied by a great increase in volume and pressure which rips and tears the steel along the relatively weak junctions of the discontinuities.[1] In certain instances, pressures in the voids reach values as high as 5,000 psig where external pressures are less than 100 psig.

Alloy steels are more resistive than carbon steels. Chrome-vanadium, chrome-vanadium-aluminum, chrome-nickel-vanadium-aluminum steels; stainless steels (18 per cent chromium and 8 per cent nickel, or 24 per cent chromium and 20 per cent nickel); and BTG metal (12 per cent chromium, 60 per cent nickel, 2.5 per cent tungsten) have been found to be completely resistant. BTG metal is the special alloy developed for the Claude ammonia synthesis, where operating pressures extend to 15,000 psig and temperatures to 560°C.

Chromium has been found particularly efficient in preventing penetration and the attack of hydrogen. Chrome-vanadium steels are used frequently for high-pressure hydrogenation reactors. These steels average about 0.30 per cent carbon, 2 per cent chromium, and 0.02 per cent vanadium.

Protective liners such as concrete, neoprene-type rubber, or plastics also may be used to prevent hydrogen attack. Other procedures which are helpful are removal of cyanides, removal of sulfur compounds from feedstocks, and the injection of polysulfides which form a film over the interior of the vessel.[2]

A compressibility chart for hydrogen is available.[3]

Ortho- and Para-hydrogen. The hydrogen atom consists of one proton (the nucleus) and one electron. Both have two possible directions of spin. However, since only atoms with antiparallel electron spins can combine when two such atoms are joined to make molecular hydrogen, the nuclear spins may be either parallel or antiparallel. These two forms have been designated "ortho" and "para," respectively. At normal conditions a ratio of ortho:para of about 3:1 exists. At low temperature the equilibrium is on the side of para-hydrogen.

The ortho-para conversion is slow but can be accelerated by catalysts

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[1] NEUMAIER and SCHILLMOLLER, *Proc. Am. Petroleum Inst.*, **35** (III), 92 (1955).

[2] KING, *Petroleum Refiner*, **35** (1), 124 (1956).

[3] MASLAN and LITTMAN, *Ind. Eng. Chem.*, **45**, 1566 (1953).

such as chromium oxide.[1] In certain cases when prolonged storage of liquid hydrogen is necessary, it becomes desirable to make the conversion of the ortho to para a part of the liquefaction process. Otherwise, the heat of conversion would give rise to an evaporation loss during storage as the liquid hydrogen approaches equilibrium conditions of high para concentration.

Heavy Hydrogen (Deuterium). This is an isotope of hydrogen which is present in normal hydrogen to the extent of about 1 part in 6,000 parts in rain water and about 1 part in 30,000 parts in electrolytic hydrogen. Deuterium differs from hydrogen in that its nucleus contains a neutron as well as a proton, making the atom heavier. It is found mainly as deuterium oxide (heavy water) which may be separated from normal water by such methods as electrolysis, fractional desorption from an absorbent such as charcoal, fractional diffusion, fractional distillation, and by the catalytic exchange of deuterium between hydrogen gas and water. The latter two methods were used on a production basis by the atomic-energy program during the war.

Analysis of Hydrogen. Hydrogen can be determined by a variety of methods. In a standard Orsat apparatus, analysis may be made to within an accuracy of about ±0.2 per cent by passing the hydrogen-containing gas over hot copper oxide. If greater accuracy is needed, the hydrogen can be concentrated by passing several liters of gas through silica gel cooled to the temperature of liquid nitrogen. At this low temperature all impurities are absorbed while the major portion of the hydrogen passes through. The impurities may be desorbed by warming. Analysis also may be made gravimetrically by passing the gas sample through a combustion train and absorbing the products.[2]

The mass spectrometer is an excellent method for analyzing for hydrogen either in simple or complex mixtures. The majority of instruments used for analyzing for hydrogen are based on the thermal conductivity of the mixture in which hydrogen is present. The thermal conductivity is determined by the rate at which the flowing gas removes heat from an electrically heated wire. Hydrogen also may be determined by measuring the absolute pressure inside a thin-walled palladium or platinum container after evacuation and contact with the test gas. This method is based on the porosity of the metals to hydrogen molecules in comparison with the larger molecules of other gases.[3] Another method used for hydrogen analysis is that of β-particle absorptivity.[4] Hydrogen has a higher β-ray absorbing power per unit mass than any other element, and this difference

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[1] ROGERS, *Ind. Eng. Chem.*, **45**, 1574 (1953).

[2] BARTHAUER, HAGGERTY, and FRIEDRICH, *Anal. Chem.*, **25**, 256 (1953).

[3] THOMAS, *Ind. Eng. Chem.*, **46** (9), 79A (1954).

[4] SMITH and OTVOS, *Anal. Chem.*, **26**, 359 (1954).

in absorptivity can be used for measuring the ratio of hydrogen to carbon in liquid mixtures. This method is possible since the hydrogen molecule or atom is unique in that the total number of electrons equals its atomic weight.

III. CATALYTIC HYDROGENATION AND HYDROGENOLYSIS: TYPE REACTIONS

This section contains a variety of examples of catalytic reduction reactions presented in the two separate parts: hydrogenation and hydrogenolysis. In many cases differentiation is not clear-cut and there is overlapping of the two parts; further, it should be noted that hydrogenolysis, in many examples, can supersede hydrogenation simply by changing the reaction conditions.

Hydrogenation Reactions

Acetylenes. Such compounds readily add 2 moles of hydrogen under catalytic conditions to give the corresponding saturated derivatives. Under proper conditions the reduction can be stopped at the intermediate olefin stage, as is shown by the equation $R{-}C{\equiv}C{-}R' + H_2 \rightarrow RCH{=}CHR' + H_2 \rightarrow RCH_2CH_2R'$, where R and R′ are aliphatic, aromatic, or certain other groups.

The selective reaction as illustrated by the first step of the above equation is utilized commercially in the purification of ethylene by removing traces of acetylene impurities. For example, the gaseous product resulting from the pyrolysis of ethane, propane, butane, or light naphthas contains 26–33 per cent of ethylene and 0.18–0.45 per cent (2,300–5,000 ppm) of acetylene. This proportion of acetylene must be removed from the ethylene before polymerization to polyethylene, for instance. Otherwise the quality of the final product is lowered. Selective hydrogenation of the acetylene to ethylene is accomplished by passing the mixture, which also contains 10–35 per cent of hydrogen, over a catalyst at a temperature ranging from 200–315°C and at pressures of 45–155 psig. In this manner the acetylene content may be reduced to about 10 ppm. At the same time, essentially none of the ethylene undergoes reduction. Catalysts claimed to be useful for this selective hydrogenation are molybdenum sulfide, iron, nickel, copper, palladium, aluminum, zinc, cadmium, and magnesium.[1]

In Germany during World War II, acetylene (from calcium carbide) was selectively hydrogenated to ethylene (5,000 tons per month capacity), using a palladium catalyst on silica gel.[2] The catalyst required periodic

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[1] SCHUTT and ZDONIK, *Oil Gas J.*, **54** (60), 92 (1956); FLEMING et al., *Petroleum Refiner*, **32** (9), 138 (1953).

[2] O'BOYLE, *Ind. Eng. Chem.*, **42**, 1705 (1950).

regeneration to remove deposits of tar and polymers. The reaction was carried out at a temperature of about 250°C and at atmospheric pressure.

Raney iron[1] and palladium on strontium carbonate[2] also have been used as catalysts in reducing certain acetylenes to olefins.

Other compounds in which the acetylenic group has been reduced to the olefin are listed in Table 10-5.

TABLE 10-5. HYDROGENATION OF A VARIETY OF COMPOUNDS CONTAINING AN ACETYLENE GROUP

Compound	Catalyst	Temperature, °C	Pressure, psig	Product	Yield, %	Ref.*
Propargyl alcohol	Nickel	....	......	Allyl alcohol		
3-Butyn-1-ol	Palladium on calcium carbonate	25	30	3-Butene-1-ol	65	1
2-Butyn-1,4-diol	Iron	50–100	2,500	2-Butene-1,4-diol	..	3
5-Octynoic acid	Raney nickel	25	0	5-Octenoic acid	..	
A Triene-mono-yne	Raney nickel	25	50	A Tetraene	..	4
1-Hexyne	Raney nickel	25	50	1-Hexene	27	2
1-Heptyne	Raney nickel	25	50	1-Heptene	77	2
5-Undecyne	Raney nickel	25	50	5-Undecene	86	2

* (1) ROBERTS and MAZUR, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (2) CAMPBELL and O'CONNOR, *J. Am. Chem. Soc.*, **61**, 2897 (1939); (3) O'BOYLE, *Ind. Eng. Chem.*, **42**, 1705 (1950); (4) OROSHNIK, KARMAS and MEBANE, *J. Am. Chem. Soc.*, **74**, 295 (1952).

Olefins. Compounds of this class readily undergo catalytic hydrogenation, usually in the presence of a nickel or nickel-containing catalyst and sometimes with platinum or palladium catalysts. In general, the hydrogen pressures need not be high, except when the hydrogenation is slow; then increased pressure usually speeds the reaction. Many of the lower-molecular-weight olefins such as ethylene, propylene, butenes, pentenes, and hexenes are readily hydrogenated in the vapor phase by passing the olefin and hydrogen over a nickel-containing catalyst at atmospheric pressure and 100–200°C. Care must be taken to keep the temperature as low as possible and still permit reaction; otherwise, at higher temperatures side reactions involving cleavages of the hydrocarbon occur.

Higher-molecular-weight olefins are generally hydrogenated in the liquid phase unless their volatility is sufficient at the temperature of hydrogenation (150–200°C), in which case the reaction may be conducted in the vapor phase.

Polybutadiene may be hydrogenated over nickel catalyst at 260°C to hydrorubbers (Hydropol) of various degrees of unsaturation.[3] These rubbers have outstanding properties as thermoplastics, especially as to low-temperature properties, oil resistance, and tensile strength.

Most olefinic substances hydrogenate at temperatures below 150–200°C,

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[1] THOMPSON and WYATT, *J. Am. Chem. Soc.*, **62**, 2555 (1940).

[2] STORK, WAGLE, and MUKHARJI, *J. Am. Chem. Soc.*, **75**, 3197 (1953).

[3] JONES, MOBERLY, and REYNOLDS, *Ind. Eng. Chem.*, **45**, 1117 (1953).

if active catalysts and hydrogen pressures of the order of 100–200 atm are employed. Ethylene has been noted to undergo catalytic hydrogenation at temperatures as low as −89°C. The *cis* forms of olefins usually hydrogenate more rapidly than the *trans* forms.

Olefinic bonds also undergo hydrogenation in the presence of copper–chromium oxide catalyst but usually require a temperature above 150–200°C. The latter catalyst is useful if it is desired to reduce certain other groups in the molecule at the same time. Zinc chromium oxide is even less active for hydrogenating an ethylenic linkage.

Table 10-6 illustrates the conditions applicable for the hydrogenation of a variety of olefinic compounds. It is to be noted that the hydrogenation of olefinic groups in alcohols, carbonyls, etc., differs from that in hydrocarbons in that the conditions of hydrogenation must be milder and better controlled in order to reduce the ethylenic linkage and not the carbonyl or other group. The reduction of unsaturated alcohols, aldehydes, or ketones generally proceeds smoothly either by passing the vapor along with excess hydrogen over a catalyst in the vapor phase or by hydrogenation in the liquid phase using hydrogen pressures of 3–100 atm or more.

TABLE 10-6. HYDROGENATION OF A VARIETY OF COMPOUNDS CONTAINING AN OLEFINIC LINKAGE

Compound	Catalyst	Temperature, °C	Pressure, psig	Product	Ref.*
Allyl alcohol	Nickel	130–170	15	Propyl alcohol	1
Mesityl oxide	Platinum	25	15–30	2-Methyl-4 pentanone	2
Dibenzalacetone	Platinum	25–80	30–50	Dibenzylacetone	3
Cinnamic alcohol	Platinum	25	15–50	Cyclohexylpropanol	4
Benzalacetophenone	Platinum	25	50	Benzylacetophenone	5
Furan	Palladium	25	50–100	Tetrahydrofuran	6
Dihydropyran	Raney nickel	25	40	Tetrahydropyran	7
1,2-Diphenyl-1-butene	Copper chromium oxide	120–140	1,500	1,2-Diphenylbutane	8
Vinyl cyclobutene	Raney nickel	100	1,000	Ethyl cyclobutane	9
2-Cyclopropyl propene	Copper chromium oxide–barium promoted	100	1,500	2-Cyclopropyl propane	10
Diisobutene(s)	Nickel	100–300	50–100	2,2,4-Trimethylpentane	
Oleic acid	Nickel	250	100	Stearic acid	11
Cinnamic acid	Copper chromium oxide	175	1,500	Phenylpropionic acid	12
Cinnamic acid	Nickel	300	1,500	Cyclohexylpropionic acid	13
Crotonic acid	Platinum	25	0	Butyric acid	14
A β, β-Diaryl acrylic acid	Palladium barium sulfate	25	50	A β, β-Diaryl propionic acid	15

* (1) SABATIER, *Compt. rend.*, **144**, 879 (1907); (2) SKITA, *Ber deut. chem. Ges.*, **48**, 1494 (1915); (3) PAAL, *Ber. deut. chem. Ges.*, **45**, 2226 (1912); (4) WASER, *Helv. Chim. Acta*, **8**, 123 (1925); (5) ADAMS, KERN, and SHRINER, "Organic Syntheses," 2d ed., coll. vol. I, p. 101, John Wiley & Sons, Inc., New York, 1941; (6) STARR and HIXON, "Organic Syntheses," coll. vol. II, p. 566, 1943; (7) ANDRUS and JOHNSON, "Organic Syntheses," vol. 23, p. 90, 1943; (8) SERIJAN and WISE, *J. Am. Chem. Soc.*, **74**, 365 (1952); (9) DERFER, GREENLEE, and BOORD, *J. Am. Chem. Soc.*, **71**, 175 (1949); (10) SLABEY and WISE, *J. Am. Chem. Soc.*, **74**, 3887 (1952); (11) LUSH, *J. Soc. Chem. Ind.*, **42**, 219T (1923); **43**, 53T (1924); **44**, 129T (1925); **46**, 454T (1927); (12) ADKINS and CONNOR, *J. Am. Chem. Soc.*, **53**, 1903 (1931); (13) IPATIEF, *J. Russ. Phys. Chem. Soc.*, **41**, 1414 (1909); (14) BÖESEKEN, WEIDE, and MOM, *Rec. trav. chim.*, **35**, 269 (1915); (15) BERGMANN et al., *J. Am. Chem. Soc.*, **70**, 1612 (1948).

Diolefins. Compounds containing such linkages undergo catalytic hydrogenation to give the corresponding saturated hydrocarbons. If the conditions of hydrogenation are mild and the amount of hydrogen is limited to 1 mole per mole of diolefin, then olefins may be isolated. However, under such conditions a mixture of olefins results. Thus, isoprene on treatment with 1 mole of hydrogen yields a mixture consisting of 3-methyl-1-butene, 12 per cent; 2-methyl-1-butene, 13 per cent; 2-methyl-2-butene, 15 per cent; isoprene, 30 per cent; and isopentane, 30 per cent.

Butadiene in 95 per cent ethyl alcohol when hydrogenated to its point of disappearance (also the maximum concentration of butene) gives the results shown in Table 10-7 for a variety of catalysts.[1]

As the data of Table 10-7 indicate, butadiene can be selectively reduced to butene in good yield with the proper choice of conditions. Further, the composition of the butene fraction varies with the conditions and catalyst, as shown in Table 10-8.

TABLE 10-7. COMPOSITION OF PRODUCT AT THE POINT OF DISAPPEARANCE OF BUTADIENE

(Hydrogen Pressure 1–2 Atm)

Hydrogenation catalyst	Temp, °C	% Hydrogenation	Composition, %		
			Butadiene	Butene	Butane
Platinum	−12	70	0	61	39
Palladium	−12	54	0	94	6
Palladium on barium sulfate	−8	80	0	40	60
Raney nickel	−8	83	0	34	66

TABLE 10-8. COMPOSITION OF BUTENES OBTAINED FROM PARTIAL HYDROGENATION OF BUTADIENE IN 95 PER CENT ETHYL ALCOHOL

Hydrogenation catalyst	Temp, °C	% Hydrogenation	Composition, %		
			1-Butene	*trans*-2-Butene	*cis*-2-Butene
Platinum	−12	68	72.1	18.4	9.5
Palladium	−12	50	48.5	40.1	11.4
Palladium on barium sulfate	28	55–75	5.0	67.5	25.7
Palladium on barium sulfate	−8	78	6.0	75.0	19.0
Nickel	28	55–75	21.5	61.0	17.5

1-Phenyl-1,3-butadiene on hydrogenation over a palladium catalyst can be interrupted at the intermediate 1-phenyl-1-butene stage. Similarly,

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[1] YOUNG et al., *J. Am. Chem. Soc.*, **69**, 2046 (1947).

penta-2,4-dienoic acid can be partially hydrogenated to penta-2-enoic acid.[1]

Nickel sulfide and tungsten nickel sulfide also are useful catalysts for selectively hydrogenating conjugated diolefins in mixtures with monoolefins.[2]

On hydrogenation under mild conditions, 1,3- and 1,4-cyclohexadiene yield cyclohexane as the sole product.[3] To date, the hydrogenation has not been stopped at the cyclohexene stage. The 1,3 isomer is reduced more rapidly than the 1,4 isomer.

Aromatics. Such compounds generally require temperatures above 180°C for complete hydrogenation over nickel catalysts. Since olefins rapidly hydrogenate at a much lower temperature, such a difference in reactivity is the basis of an analytical procedure for differentiating between olefinic and aromatic bonds.[4]

The catalytic reduction of aromatics may be carried out either in the vapor phase at atmospheric pressure or in the liquid phase at hydrogen pressures of 100–200 atm. In the latter case, the reaction usually can be accomplished within a few hours for aromatics such as benzene, toluene, *o*-xylene, 1,2,4-trimethylbenzene, *n*-propylbenzene, *p*-cymene, and hydrindene. In the case of naphthalene or substituted naphthalenes, the product may be the tetra- or decahydronaphthalene derivative. With more substituent groups or with chains longer than butyl or amyl, secondary decomposition products resulting from cracking or the breaking of carbon-carbon linkages in the chain appear and the use of lower temperatures, higher hydrogen pressures, and/or more active catalysts becomes necessary.

While nickel is the most widely used catalyst for hydrogenating aromatic nuclei, other catalysts such as platinum oxide and rhodium also are useful. Platinum oxide is effective at room temperature and at hydrogen pressures of only 2–3 atm; however, in many cases the reaction is slow and requires 2–50 hr for completion. Glacial acetic acid is useful as a solvent. Certain commercial platinum and rhodium catalysts may be more efficient at the mild conditions. Copper chromium oxide is not generally useful as a catalyst for reducing an aromatic ring and thus is valuable for selectively reducing nonaromatic groups present in the same molecule. The naphthalene nucleus is reduced to a tetralin over copper chromium oxide at 150–200°C.[5]

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[1] Farmer et al., *J. Chem. Soc.*, **1932**, 430; **1934**, 304, 1929.

[2] Anderson et al., *Ind. Eng. Chem.*, **40**, 2295 (1948); Casagrande et al., *ibid.*, **47**, 744 (1955).

[3] Smith and Meriwether, *J. Am. Chem. Soc.*, **71**, 413 (1949).

[4] Miron, *Anal. Chem.*, **27**, 1947 (1955).

[5] Adkins and Burgoyne, *J. Am. Chem. Soc.*, **71**, 3528 (1949).

Catalytic reduction of the aromatic ring in phenolic compounds is activated by the addition of alkali to the reaction mixture when nickel is used as a catalyst. The presence of the base lowers the reaction temperature.[1]

Examples of the catalytic reduction of a variety of compounds containing an aromatic ring are presented in Table 10-9.

Carbonyls (Aldehydes and Ketones). Compounds of this class are easily reduced by catalytic hydrogenation in the presence of mild catalysts to the corresponding primary or secondary alcohols according to the equation: $RCOR' + H_2 \rightarrow RCHOHR'$, where R is an aliphatic or aromatic group and R′ may be the same or a hydrogen atom. If more severe conditions are employed, or if the carbonyl group is conjugated, then the reaction proceeds beyond the alcohol stage to give a hydrocarbon.[2] For the case in which the carbonyl group is conjugated, reduction to the hydrocarbon occurs at normal temperature and pressure over a palladium-charcoal catalyst.

In general, aldehydes are reduced more rapidly than ketones, although there are numerous examples in which both aldehydes and ketones undergo reduction at room temperature and at only a few atmospheres of hydrogen pressure in the presence of platinum or palladium catalysts. Ruthenium and nickel catalysts also are useful for such reductions. Copper chromium oxide generally requires a higher temperature (100–200°C) and high hydrogen pressures (50–150 atm) when used with aldehydes or ketones.

Unsaturated aldehydes and ketones can be selectively hydrogenated to the corresponding saturated carbonyl; however, it is difficult to reduce the ethylenic group without also attacking the carbonyl group, although such a reduction may be achieved for certain compounds such as mesityl oxide (2-methyl-pentene-2-one-4) using a platinum catalyst at room temperature.

Crotonaldehyde on hydrogenation over nickel catalyst at atmospheric pressure and 25°C in the presence of chloroform gives butyraldehyde as the major product; in the absence of chloroform, butyl alcohol is formed.

Catalytic hydrogenation is not widely used in reducing carbonyl groups to the methylene group since other points in the molecule may be reduced simultaneously; for such reductions the Wolff-Kishner reaction is more advantageous.

Many carbonyl compounds undergo catalytic hydrogenation simply on refluxing in the presence of an excess of Raney nickel[3] from which absorbed

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[1] UNGNADE et al., *J. Am. Chem. Soc.*, **66**, 118 (1944); **72**, 2112 (1950); STORK, *ibid.*, **69**, 576 (1947).

[2] MILLER, HARTUNG, ROCK, and CROSSLEY, *J. Am. Chem. Soc.*, **60**, 7 (1938); JU, SHEN, and WOOD, *J. Inst. Petroleum*, **26**, 514 (1940).

[3] MOZINGO, SPENCER, and FOLKERS, *J. Am. Chem. Soc.*, **66**, 1859 (1944).

Table 10-9. Hydrogenation of Compounds Containing Aromatic Nuclei

Compound	Catalyst	Temperature, °C	Pressure, psig	Product	Ref.*
t-Amylbenzene	Nickel	200	1,800	*t*-Amylcyclohexane	1
Naphthalene	Copper chromium oxide	200	2,000–3,000	Tetralin	2
Phenanthrene	Copper chromium oxide	150	3,000–4,000	9,10-Dihydrophenanthrene	3*a*
Phenanthrene	Raney nickel	100	3,000–4,000	*sym*-Octahydrophenanthrene	3*b*
Phenanthrene	Raney nickel	250	3,000–4,000	Perhydrophenanthrene	3*b*
Diphenylmethane	Platinum	25	50	Phenylcyclohexylmethane	4
1,6-Diphenylhexane	Nickel	190	1,700	1,6-Dicyclohexylhexane	15
Phenol	Nickel	150	1,500	Cyclohexanol	
p-Cresol	Raney nickel	120	1,500–4,000	*trans*-4-Methylcyclohexanol	5
t-Amylphenol	Nickel	200	1,800	*t*-Amylcyclohexanol	1
Hydroquinone	Nickel	150	1,800	1,4-Cyclohexanediol	6
2,6-Xylenol	Raney nickel	190	1,850	2,6-Dimethylcyclohexanol	7
β-Naphthol	Palladium charcoal	180	1,800	β-Tetralone	8
β-Naphthol	Copper chromium oxide	200	2,000–3,000	1,2,3,4-Tetrahydronaphthol	2
Resorcinol	Raney nickel	50	1,000–1,500	Dihydroresorcinol	12
2,6-Diethyl-4-methyl phenol	Nickel + NaOH	235	1,500–4,000	2,6-Diethyl-4-methylcyclohexanol	5
2-Acetyl phenol	Nickel	70–180	1,500–4,000	2-Ethylcyclohexanol	5
6-Hydroxy-1-naphthoic acid	Raney nickel	75	2,500	1,2,3,4-Tetrahydro derivative	10
6-Hydroxy-1-naphthoic acid	Raney nickel	150	2,500	Decahydro derivative	10
Benzilic acid	Platinum	25	50	Phenylcyclohexyl glycolic acid	11
γ-(4-Hydroxyphenyl)-butyric acid	Raney nickel	25	2,500	Hexahydro derivative	9
Aniline	Raney nickel	200	1,500	Cyclohexylamine and dicyclohexylamine	13
Isoquinoline	Copper chromium oxide	200	3,000	1,2,3,4-Tetrahydroisoquinoline	14

* (1) Inatome, Greenlee, Derfer, and Boord, *J. Am. Chem. Soc.*, **74**, 292 (1952); (2) Adkins and Reid, *J. Am. Chem. Soc.*, **63**, 742 (1941); Adkins, Rossow, and Carnahan, *ibid.*, **70**, 4247 (1948); (3*a*) Durland and Adkins, *J. Am. Chem. Soc.*, **60**, 1501 (1938); (3*b*) Phillips, "Organic Syntheses," vol. 34, p. 31, John Wiley & Sons, Inc., New York, 1954; (4) Smith, Alderman, Shacklett, and Welch, *J. Am. Chem. Soc.*, **71**, 3772 (1949); (5) Ungnade and McLaren, *J. Am. Chem. Soc.*, **66**, 118 (1944); (6) Olberg, Pines, and Ipatieff, *J. Am. Chem. Soc.*, **66**, 1096 (1944); (7) Carlin and Landerl, *J. Am. Chem. Soc.*, **67**, 928 (1945); (8) Stork and Foreman, *J. Am. Chem. Soc.*, **68**, 2172 (1946); (9) Fieser et al., *J. Am. Chem. Soc.*, **70**, 3196 (1948); (10) Dauben, Hiskey, and Markhart, *J. Am. Chem. Soc.*, **73**, 1393 (1951); (11) Smith et al., *J. Am. Chem. Soc.*, **74**, 4534 (1952); (12) Thompson, "Organic Syntheses," vol. 27, p. 21, 1947; (13) Winans, *Ind. Eng. Chem.*, **32**, 1215 (1940); (14) Leonard and Leubner, *J. Am. Chem. Soc.*, **71**, 3408 (1949); (15) Serijan and Wise, *J. Am. Chem. Soc.*, **73**, 5191, 4766 (1951); Lamneck and Wise, *ibid.*, **76**, 3475 (1954).

hydrogen is available. Cobalt polysulfide[1] also is a useful catalyst for the hydrogenation of certain carbonyls.

Examples of the conditions required for the catalytic reduction of typical carbonyls are given in Table 10-10.

Carbon monoxide may be considered the simplest compound containing the carbonyl group, and its hydrogenation leads to the syntheses of alcohols, ketones, acids, and hydrocarbons, the latter containing as many as several hundred carbon atoms.[2] Such a reaction is possible because carbon monoxide on partial reduction can yield compounds or molecular fragments, e.g., —$(CH_2)_n$—, which are capable of undergoing extensive condensation on the same catalysts that effect the initial hydrogenation. Thus, from the simple substances carbon monoxide (and, in some cases, carbon dioxide) and hydrogen, practically unlimited syntheses are possible; the greatest problem associated with these reactions is the separation of individual compounds. Details on processes for the hydrogenation of carbon monoxide appear in a separate section (p. 617) and in Chap. 11.

Acid Chlorides. Compounds in this class undergo selective hydrogenation in the presence of a palladium on barium sulfate catalyst to yield the corresponding aldehyde. A "poison" or "regulator" such as thioquinanthrene is necessary to prevent further reduction of the aldehyde. This procedure is known as the Rosenmund reaction.[3]

Esters and Acids. Such chemicals react with hydrogen in the presence of catalysts according to the general equation: $RCOOR' + 2H_2 \rightleftharpoons RCH_2OH + R'OH$, where R is usually an aliphatic group and R′ is the same or a hydrogen atom. The reaction is reversible, with the temperature and pressure determining the relative equilibrium proportions. For the case of *n*-octyl caprylate the concentration of ester at equilibrium at 260°C is about 80 per cent at 140 psig, 10 per cent at 1,200 psig, and 1 per cent at 4,000 psig of hydrogen. The higher the temperature, the higher is the concentration of ester at equilibrium. If the ester is one such as ethyl laurate, then, because of the equilibrium type of reaction, three new esters, i.e., dodecyl laurate, dodecyl acetate, and ethyl acetate, may be found in the product. An even greater number of esters may result from the hydrogenation of a dibasic acid ester such as diethyl adipate.

The general reaction indicated above proceeds either by hydrogenation or by hydrogenolysis, depending on the choice of mechanism—the exact nature is not known at present.

Copper chromium oxide is unexcelled as a catalyst for hydrogenating

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[1] FARLOW et al., *J. Am. Chem. Soc.*, **70**, 1392 (1948).

[2] FISCHER, TROPSCH, and NEDDEN, *Ber. deut. chem. Ges.*, **60B**, 1330 (1927); PICHLER, *Brennstoff-Chem.*, **19**, 226 (1938).

[3] MOSETTIG, "Organic Reactions," vol. 4, p. 362, 1948; HERSHBERG and CASON, "Organic Syntheses," vol. 21, p. 84, John Wiley & Sons, Inc., New York, 1941.

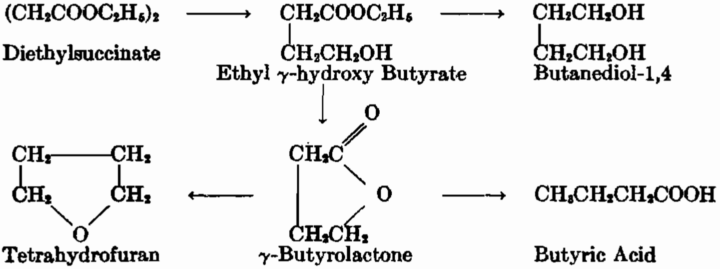
TABLE 10-10. HYDROGENATION OF ALDEHYDES AND KETONES

Compound	Catalyst	Temperature, °C	Pressure, psig	Product	Ref.*
Acetaldehyde	Nickel	25	1,600	Ethyl alcohol	1
Heptaldehyde	Platinum oxide	25	50	Heptyl alcohol	2
Benzaldehyde	Nickel	25	1,600	Benzyl alcohol	1
Aldol	Nickel	125	2,000–3,000	Butanediol-1,3	3*a*
Aldol	Copper chromium oxide	100	4,000	Butanediol-1,3	3*b*
β-Methyl-glutaraldehyde	Raney nickel	125	1,625	3-Methyl-pentanediol-1,5	4
Acetone	Nickel	23	30–50	Isopropyl alcohol	5
Acetone	Copper chromium oxide	150	1,500–2,000	Isopropyl alcohol	6
Methylisobutyl ketone	Nickel	150	1,700	Methylisobutyl carbinol	7
Acetophenone	Nickel	175	1,700	Methylphenyl carbinol and ethylcyclohexane	7
Benzophenone	Platinum black	25	15–30	Benzohydrol	8
Benzalacetophenone	Platinum oxide	25	50	Benzylacetophenone	9
Pinacolone	Copper chromium oxide	150	1,700	2,2-dimethyl-butanol-3	6
Furfural	Copper chromium oxide	150	1,700	Furfuryl alcohol	6
Acetoacetic ester	Copper chromium oxide	150	1,700	Ethyl β-hydroxybutyrate	6
Methylcyclopropyl ketone	Raney nickel	100	1,200	Methylcyclopropyl carbinol and 2-pentanol	10
Methylcyclopropyl ketone	Copper chromium oxide (Ba)	100	1,500–2,000	Methylcyclopropyl carbinol	10
Hexanedione-2,4†	Raney nickel	100	1,500	Hexan-2-ol-4-one	11
1-Furyl-1-butene-3-one	Copper chromium oxide	125	1,700	1-Furyl-3-butanol	12

* (1) COVERT and ADKINS, *J. Am. Chem. Soc.*, **54,** 4117 (1932); (2) CAROTHERS and ADAMS, *J. Am. Chem. Soc.*, **46,** 1682 (1924); (3*a*) ADKINS and CONNOR, *J. Am. Chem. Soc.*, **54,** 4678 (1932); (3*b*) HANCOCK, *Ind. Eng. Chem.*, **44,** 1003 (1952); **45,** 629 (1953); (4) LONGLEY and EMERSON, "Organic Syntheses," vol. 34, p. 71, John Wiley & Sons, Inc., New York, 1954; (5) COVERT and ADKINS, *J. Am. Chem. Soc.*, **54,** 4117 (1932); (6) ADKINS and CONNOR, *J. Am. Chem. Soc.*, **53,** 1093 (1931); (7) COVERT, CONNOR, and ADKINS, *J. Am. Chem. Soc.*, **54,** 1658 (1932); (8) VAVON, *Ann. chim. (Paris)*, **9** (1), 144 (1914); (9) ADAMS, KERN, and SHRINER, "Organic Syntheses," 2d ed., coll. vol. I, p. 101, 1941. (10) SLABEY and WISE, *J. Am. Chem. Soc.*, **71,** 3252 (1949); (11) STUTSMAN and ADKINS, *J. Am. Chem. Soc.*, **61,** 3303 (1939); (12) ALEXANDER et al., *J. Am. Chem. Soc.*, **72,** 5506 (1950).

† Hydrogen limited to 1 mole per mole of diketone.

esters and is most frequently used at pressures of 2,000–6,000 psig and temperatures of 175–250°C. Zinc chromium oxide and active Raney nickel (W-6) are also effective catalysts in certain instances. Solvents are not usually needed as a reaction medium, but dioxane, methanol, or ethanol is sometimes used to serve as a solvent for any water produced. In general, alcohols and glycols may be prepared in yields greater than 90 per cent on hydrogenating esters of monobasic and higher dibasic acids. Esters of dibasic acids with more than two carbon atoms separating the carbalkoxy groups give glycols in yields above 95 per cent; the yield from a succinate may be lower because of the occurrence of some hydrogenolysis, leading to the conversion of a portion of the glycol to an alcohol. Thus, for the case of diethyl succinate, hydrogenation over copper chromium oxide at 250°C and 300 atm of hydrogen gives, in addition to the glycol (74 per cent), butyrolactone, butyric acid, and tetrahydrofuran.[1]



Examples of the catalytic reduction of acids and esters are presented in Table 10-11.

Heterocyclic Compounds. Such materials undergo catalytic hydrogenation to yield the corresponding saturated derivatives. Thus, pyrrole is slowly converted to pyrrolidine at 200°C over either a nickel or copper–chromium oxide catalyst; pyridine and pyridine derivatives[2] behave similarly. Compounds such as furan and dihydropyran reduce rapidly and behave more like olefins in reactivity. Similarly, thiophene is converted to the tetrahydro derivative.

Hydrogenolysis Reactions

The term *hydrogenolysis* is a more exact expression than destructive hydrogenation and refers particularly to cleavages in a molecule associated with the addition of hydrogen. Hydrogenolysis is analogous to the reactions commonly termed hydrolysis, alcoholysis, and ammonolysis which involve cleavage of a bond induced by the action of water, alcohol, or am-

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[1] ADKINS, "Organic Reactions," vol. 8, p. 1, 1954.

[2] ADKINS, KUICK, FARLOW, and WOJCIK, *J. Am. Chem. Soc.*, **56**, 2425 (1934).

TABLE 10-11. HYDROGENATION OF ACIDS AND ESTERS

Compound	Catalyst	Temperature, °C	Pressure, psig	Product	Ref.*
Acetic acid	Zinc manganese chromium oxides	400	200	Ethyl, propyl, and butyl alcohols	1
Stearic acid	Zinc copper chromium oxide	325	280	Stearyl alcohol	2
γ-Ketocapric acid	Raney nickel	135	1,000	γ-Caprilactone	3
Phenyl propionate	Copper chromium oxide	250	2,200	Propyl alcohol and cyclohexanol	4
n-Hexyl caproate	Copper chromium oxide	225	2,700	1-Hexanol	4
Diethyl ethylmalonate	Copper chromium oxide	150	5,000	2-Ethyl-1,3-propanediol	4
Diethyl adipate	Copper chromium oxide	255	3,000	1,6-Hexanediol	4
Ethyl benzoate	Copper chromium oxide	125	4,500	Benzyl alcohol	4
Ethyl α-phenylbutyrate	Copper chromium oxide	250	2,500	2-Phenyl-1-butanol	4
Ethyl lactate	Copper chromium oxide	125	5,000	1,2-Propanediol	4
Ethyl lactate	Raney nickel (W-6)	100	5,000	1,2-Propanediol	4
Dimethyl tartrate	Copper chromium oxide	165	5,000	1,2,3,4-Butanetetrol	4
γ-Valerolactone	Copper chromium oxide	250	4,000	1,4-Pentanediol	4

* (1) FROLICH and CRYDER, *Ind. Eng. Chem.*, **22**, 1057 (1930); CRYDER, D.Sc. Thesis, Massachusetts Institute of Technology, 1930; (2) SCHRAUTH, SCHENK, and STICKDORN, *Ber. deut. chem. Ges.* **64B**, 1314 (1931); (3) PATRICK and ERICKSON, "Organic Syntheses," vol. 34, p. 53, John Wiley & Sons, Inc., New York, 1954; (4) ADKINS, "Organic Reactions," vol. 8, p. 1, John Wiley & Sons, Inc., New York, 1954.

monia, respectively. Some typical cleavages taking place in hydrogenolysis reactions are discussed in more detail in the following paragraphs.

Carbon-Carbon Linkages. Such linkages are frequently cleaved by hydrogen in the presence of hydrogenation catalysts. Thus, the carbon rings of cyclopropane and cyclobutane and their derivatives are readily opened when passed with hydrogen over nickel at 80–180°C. Cyclopropane under these conditions and at 80°C yields propane, while cyclobutane gives *n*-butane. Isopropyl cyclopropane on treatment with hydrogen at 150°C and 1,250 psig over a nickel-on-kieselguhr catalyst gives 2,3-dimethylbutane.[1]

Cyclic hydrocarbons containing five- and six-membered rings are stable and do not undergo change except the usual degradative decompositions at higher temperatures. However, isomerization of the six- to five-membered rings and vice versa can occur.

Cycloheptane and cyclooctane at 200–250°C when hydrogenated over nickel undergo changes to methyl and dimethyl derivatives of cyclopentane and cyclohexane. Thus, methylcyclohexane in the presence of a nickel-silica-alumina catalyst at 290–370°C and in the presence of hydrogen gives a mixture of 1,1-, 1,2-, and 1,3-dimethylcyclopentanes and some ethylcyclopentane.[2]

Paraffin and aromatic hydrocarbons, depending on the length of the chain or branching in the chain or the ring structure, under the combined action of hydrogen catalysts and heat, undergo certain cleavages that involve the splitting off of groups or molecular fragments or the opening of ring structures. The resulting products are then usually smaller molecules, are of a more stable type, and usually contain a higher percentage of hydrogen than the original material. The opening of the ring may first involve the reduction to a hydroaromatic of naphthene structure, followed by the opening of the ring with the formation of a chain or paraffin structure. These reactions are also of great technical importance, for they are probably the type of reaction occuring in the hydrogenation of heavy petroleum residues or asphaltic or aromatic-base oils, whereby conversion takes place in high yields to stable, more volatile petroleum products such as gasoline and kerosene.

Hydrocarbons also demethylate in the presence of hydrogen over nickel or cobalt catalysts at 260°C and pressures of 100–500 psig to yield methane and a hydrocarbon containing fewer carbon atoms. Thus, neohexane gives neopentane (77 per cent), methane, butanes, and pentanes.[3]

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[1] Van Volkenburgh, Greenlee, Derfer, and Boord, *J. Am. Chem. Soc.*, **71**, 172, 3595 (1949).

[2] Ciapetta, *Ind. Eng. Chem.*, **45**, 159 (1953).

[3] Haensel and Ipatieff, *Ind. Eng. Chem.*, **39**, 853 (1947); *J. Am. Chem. Soc.*, **68**, 345 (1946).

Carbon-Oxygen Linkages. Such linkages in alcohols, ethers, heterocyclic compounds, and in many other oxygenated compounds may be cleaved by hydrogen in the presence of catalysts to give a variety of products, as indicated by the following discussion.

Alcohols undergo catalytic hydrogenolysis according to the equation: $ROH + H_2 \rightarrow RH + H_2O$ to give the corresponding hydrocarbon.[1] When R contains a benzyl, pyrryl, or furyl group, the reaction takes place readily. For the case of the benzyl group the reductive cleavage (debenzylation) occurs so readily that the reaction is employed widely in organic syntheses.[2]

Phenol, polyphenols, and cresols yield aromatic hydrocarbons on hydrogenolysis over nickel catalysts at temperatures above 250°C.

1,3-Glycols are more susceptible to hydrogenolysis than, 1,2- or 1,4-glycols. Thus, cyclohexanediol-1,3 undergoes hydrogenolysis in the presence of copper chromium oxide at 175 atm pressure of hydrogen and at a temperature of 200°C to give cyclohexanol in a 95 per cent yield. Under these same conditions cyclohexanediol-1,4 does not react.

2-Methylpentanediol-2,4 and diacetone alcohol cleave so readily in the presence of nickel that the latter compound cannot be hydrogenated to the glycol without producing an appreciable amount of isopropyl alcohol. However, if the nickel catalyst contains no alkali, an 89 per cent yield of the glycol can be obtained from diacetone alcohol.[3]

Carbonyls undergo hydrogenolysis at temperatures above about 250°C over nickel catalysts to yield hydrocarbons. Thus, acetone and benzaldehyde yield propane and toluene (plus benzene), respectively.

Ethers, in general, are quite stable to hydrogenolysis even over Raney nickel at temperatures as high as 250°C. However, ethyl ether slowly reacts above this temperature over nickel to give ethane and ethyl alcohol.[4] If the ether contains an aromatic nucleus, complete hydrogenation of the latter will occur at a lower temperature than is required for carbon-oxygen cleavage.

Lactones undergo hydrogenolysis to give glycols, acids, or tetrahydrofurans.[5]

Acetals are similar to ethers in their stability to hydrogenolysis. Thus, the diethyl acetal of furfural yields furfuryl ethyl ether when reacted at 175°C over Raney nickel.

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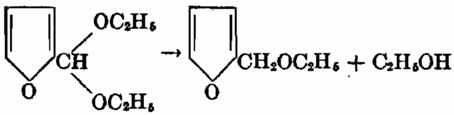
[1] KOMAREWSKY, PRICE, and COLEY, *J. Am. Chem. Soc.*, **69**, 238 (1947); IPATIEFF, MONROE, FISCHER, and MEISINGER, *Ind. Eng. Chem.*, **41**, 1802 (1949); IPATIEFF et al., *J. Am. Chem. Soc.*, **73**, 553, 4098 (1951).

[2] HARTUNG and SIMONOFF, "Organic Reactions," vol. 7, p. 263, 1953.

[3] CONNER and ADKINS, *J. Am. Chem. Soc.*, **54**, 4678 (1932).

[4] ELLIS, "Hydrogenation of Organic Compounds," 3d ed., p. 564, D. Van Nostrand Company, Inc., New York, 1930.

[5] WOJCIK and ADKINS, *J. Am. Chem. Soc.*, **55**, 4939 (1933).



Acid anhydrides such as succinic anhydride and phthalic anhydride give lactones on hydrogenolysis.[1] Other oxygenated compounds on hydrogenolysis yield a variety of products, as illustrated by the data of Table 10-12.

Carbon-Sulfur Linkages. Compounds having such linkages can be cleaved by hydrogen in the presence of hydrogenation catalysts (hydrodesulfurization), and this reaction is of particular importance in the petroleum industry. Thiophenes, mercaptans, and sulfides behave as follows on hydrogenolysis to give hydrocarbons and hydrogen sulfide:

$$\text{RSH (mercaptan)} + H_2 \rightarrow H_2S + RH$$
$$\text{RSR}' \text{ (sulfide)} + 2H_2 \rightarrow H_2S + RH + R'H$$
$$C_4H_4S \text{ (thiophene)} + 4H_2 \rightarrow H_2S + C_4H_{10}$$

Carbon-Nitrogen Linkages. Such linkages also cleave on hydrogenolysis. Thus, pyridine and pyrrole give ammonia and hydrocarbons. Pyridine homologues are frequently found in naphthas high in nitrogen content, and the denitrogenation of such feedstocks is important in the petroleum industry.

$$C_5H_5N \text{ (pyridine)} + 5H_2 \rightarrow NH_3 + C_5H_{12}$$

Benzylamine and dibenzylamine, unlike benzyl alcohol, are resistant to hydrogenolysis even at high temperatures over a nickel catalyst.[2]

Amides react with hydrogen in the presence of copper chromium oxide at 250°C and about 3,000 psig hydrogen pressure to yield a mixture of the corresponding primary, secondary, and sometimes tertiary amines. Thus, lauramide gives a mixture of dodecylamine (48 per cent) and didodecylamine (49 per cent).[3]

Carbon-Metallic Linkages. Compounds containing such linkages may be cleaved by hydrogenolysis to give the metal and hydrocarbons. Thus, lead tetraphenyl on treatment with hydrogen at a pressure of 1,000 psig and a temperature of 200°C yields lead and benzene.[4] Tin tetraethyl on similar treatment is converted to tin and ethane.

Carbon-Halogen Linkages. Compounds of this type also may cleave with hydrogen. Thus, 2-chlorolepidine at 70°C and a hydrogen pressure of

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[1] Austin, Bousquet, and Lazier, *J. Am. Chem. Soc.*, **59**, 864 (1937).

[2] Hartung and Simonoff, "Organic Reactions," vol. 7, p. 263, 1953.

[3] Wojcik and Adkins, *J. Am. Chem. Soc.*, **56**, 2419 (1934).

[4] Gershbein and Ipatieff, *J. Am. Chem. Soc.*, **74**, 1540 (1952).

TABLE 10-12. HYDROGENOLYSIS OF HETEROCYCLIC COMPOUNDS

Compound	Catalyst	Temperature, °C	Pressure, psig	Product	Ref.*
Tetrahydrofurfuryl alcohol	Copper chromium oxide	255–300	3,500	1,5-Pentanediol (45%)	1
2,2-Dimethylethylenimine	Nickel	60	40–60	*t*-Butylamine	2
2-Thio-6-methyluracil	Nickel	100	0	4-Methyl-6-hydroxypyrimidine	3
Furfural	Copper chromium oxide on charcoal	250	...	Methylfuran	4
Furan	Platinum	50	20–60	*n*-Butanol	5
Methylfuran	Nickel on celite	150	1,200	1,4-Pentanediol (62%) and methyltetrahydrofuran (30%)	4
Methylfuran	Nickel on celite	...	...	Acetopropyl alcohol and methyltetrahydrofuran	4
Methylfuran	Nickel	200	...	2-Pentanone	6
2,3-Dihydropyran	Nickel	200	...	Cyclopentanone, butene, butane	6
Tetrahydrofurfuryl alcohol	Platinum	50	20–60	1,5-Pentanediol	5
2-Benzyl-cyclopentanone	Platinum oxide	25	50	Benzylcyclopentane	7
1-Furyl-propanol-3	Nickel on celite	210	3,000	1,4,7-Heptanetriol and 1-tetrahydrofurylpropanol-3	8
5-Methyl-furoic acid	Platinum	50	20–60	5-Hydroxyhexanoic acid	5

* (1) KAUFMAN and REEVE, "Organic Syntheses," vol. 26, p. 83, John Wiley & Sons, Inc., New York, 1946; (2) CAMPBELL, SOMMERS, and CAMPBELL, "Organic Syntheses," vol. 27, p. 12, 1947; (3) FOSTER and SNYDER, "Organic Syntheses," vol. 35, p. 80, 1955; (4) SCHNIEPP, GELLER, and VONKORFF, *J. Am. Chem. Soc.*, **69,** 672 (1947); (5) SMITH and FUZEK, *J. Am. Chem. Soc.*, **71,** 415 (1949); JONES and TAYLOR, *Chemistry & Industry,* **1951,** 1075; (6) WILSON, *J. Am. Chem. Soc.*, **70,** 1311, 1313 (1948); (7) PHILLIPS and MENTHA, *J. Am. Chem. Soc.*, **78,** 140 (1956); (8) RUSSEL, ALEXANDER, ERICKSON, HAFNER, and SCHNIEPP, *J. Am. Chem. Soc.*, **74,** 4543 (1952).

30 psig gives lepidine while using palladium as the catalyst.[1] Hexadecyl iodide over palladium and in the presence of hydrogen gives *n*-hexadecane.[2]

Selective Hydrogenation

The term *selectivity* as recognized in catalytic hydrogenations refers either to the partial or stepwise reduction of a single molecule (such as the reduction of acetylene to ethylene) or to the preferential reduction of one or more functional groups with respect to others present. In the latter case the groups may be as different as a nitro group and an ester group or as closely related as an olefinic and an aromatic double bond. Further, the groups may be identical parts of different molecules such as the carbonyl group in a mixture of an aldehyde and a ketone, or they may be parts of the same molecule as in the case of allylbenzene, for example.

Selective hydrogenation is of importance industrially. It is used in the manufacture and in the purification of ethylene, in removing substituted acetylenes from butadiene, in lowering the olefin content of cracked naphthas while leaving the aromatics unchanged, and in various other petroleum-processing reactions such as hydrodesulfurization.

Selective hydrogenations are accomplished either by making the proper choice of catalyst, temperature, pressure, and solvent (and thereby attaining a difference in reaction rate) or by interrupting the reaction when the desired amount of hydrogen has been absorbed. In the case of the hydrogenation of acetylene to ethylene and ethane, the latter is only loosely held on the catalyst surface compared with the two former molecules, and as soon as all the acetylene is reduced the absorption of hydrogen increases because of the ease with which ethane is released from the catalyst.[3]

An increase of hydrogen pressure generally decreases selectively; and an increase of temperature appears to increase it.

"Inactive" catalysts appear to be more useful than "active" ones and are obtained either by "poisoning" (adding mercury to palladium, for example) or by greatly diluting a catalyst with an inert carrier. Further, palladium catalysts are relatively inactive to aromatic nuclei, nitriles, and aldehydes which makes this catalyst useful in certain selective hydrogenations. Platinum and nickel catalysts are alike in activity, and both under suitable conditions are effective against all types of carbon-carbon unsaturated linkages, carbonyls, nitriles, oximes, and nitro compounds; however, the addition of triethylamine to Raney nickel retards the reduction of aromatic nuclei so that it is possible to reduce carbonyl groups

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[1] NEUMANN, SOMMER, KASLOW, and SHRINER, "Organic Syntheses," vol. 26, p. 45, 1946.

[2] CAREY and SMITH, *J. Chem. Soc.*, **1933**, 346.

[3] FARKAS and FARKAS, *J. Am. Chem. Soc.*, **61**, 3396 (1939).

without hydrogenating an aromatic nucleus.[1] Copper chromium oxide may be used in reducing olefins and carbonyls without effecting aromatic nuclei.

Many additional examples of selective hydrogenation may be found elsewhere in this chapter. Other examples have been reported.[2]

In general, the choice of catalyst and conditions necessary for a desired selective hydrogenation must be determined experimentally for each individual problem.

IV. KINETICS AND THERMODYNAMICS OF HYDROGENATION REACTIONS

The Reaction Must Be Possible.* Since catalysts affect only the rate or speed of a reaction and have nothing to do with the inherent tendency of a reaction to proceed, it is obviously of real importance to know whether or not the reaction is at all possible for the conditions of temperature and pressure chosen. The concern is then with chemical affinity; and since the free energy change of a definite, specific reaction is a quantitative measure of such chemical forces, it is desirable to have free-energy data on the substances in question if such data can be had. If reliable free-energy data show the reaction to be possible, then experimental work may be started in order to find suitable catalysts that will enable the reaction to proceed at a reasonable rate.

It is difficult to get accurate free-energy data on a large number of organic compounds, but a reasonable amount of fairly reliable data are now available.[3] Figures 10-2*a* to *h* give free-energy values for a few compounds of industrial importance. The values are for the free energy of formation from the elements of the substance in question in the gaseous

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* Examples of the use of free-energy data may be extended into a long list. Such is not the intention of this discussion. Applications have been made to only the four types of reduction that this chapter is concerned with, viz., ethylenic, carbonyl, and carboxyl linkages and hydrogenolysis or destructive hydrogenation. The purpose has been to show the method of applying free-energy data to such reductions and the nature of the results and conclusions that are possible therefrom. It should be pointed out that free-energy data on organic compounds are a comparatively recent development in the field of organic chemistry. Consequently, the data given here may in many cases be found to be wanting in accuracy. Nevertheless, rather than to ignore their usefulness and possibilities, it is believed to be better to show that at least semiquantitative conclusions may be drawn from them that would not otherwise be possible. On this basis alone, their use is justified. For excellent data and tables on the thermodynamic properties of a wide variety of hydrocarbons, see Selected Values of the Properties of Hydrocarbons, *Nat. Bur. Standards* (*U.S.*), *Circ.* *C*461, 1947.

[1] ADKINS and BILLICA, *J. Am. Chem. Soc.*, **70**, 695 (1948).

[2] JONES and TAYLOR, *Chemistry & Industry*, **1951**, 1075; ELSNER and PAUL, *J. Chem. Soc.*, **1953**, 3156; ADKINS, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937.

[3] PARKS and HUFFMAN, "Free Energies of Some Organic Compounds," Reinhold Publishing Corporation, New York, 1932.

state at 1 atm pressure. Values are given for two temperatures: 100 and 400°C. It is permissible to make linear interpolation between these temperatures; i.e., a value at 250°C will lie midway between the 100 and 400°C values. To point out the relationships that exist in these straight-chain aliphatic compounds, the free-energy content per carbon atom is plotted. Therefore, to get the molal value, these values (ordinates) must be multiplied by the number of carbon atoms in the straight-chain aliphatic compound in question. Figures 10-2*a* to *c* give, respectively, the free-energy values for carbon monoxide, water, and carbon dioxide, all in the gaseous state at 1 atm pressure. Figures 10-2*d* and *e* give free-energy values for the straight-chain olefins and paraffins.

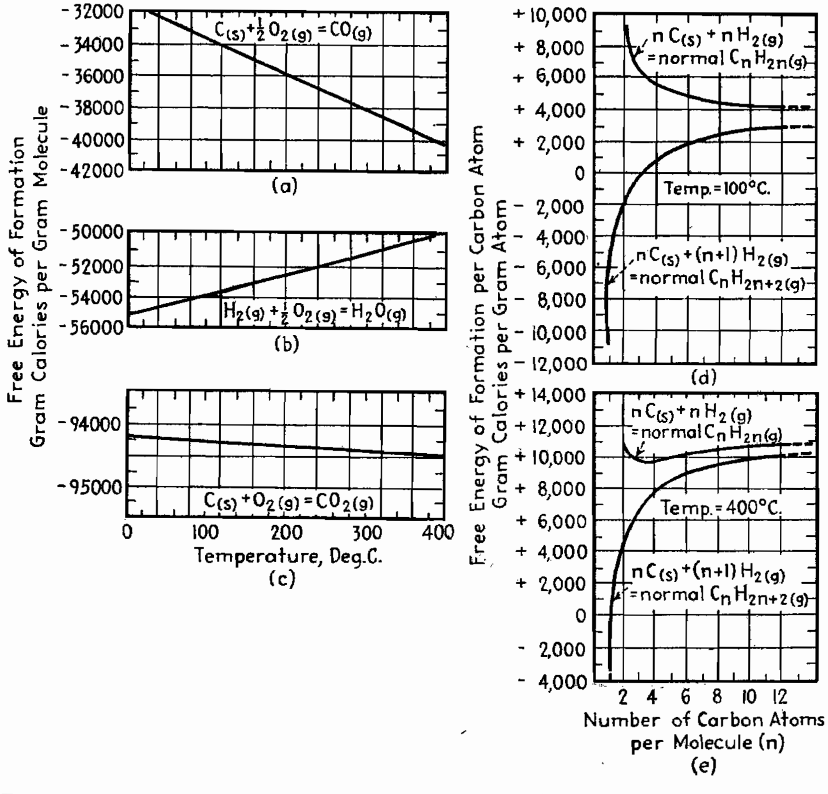
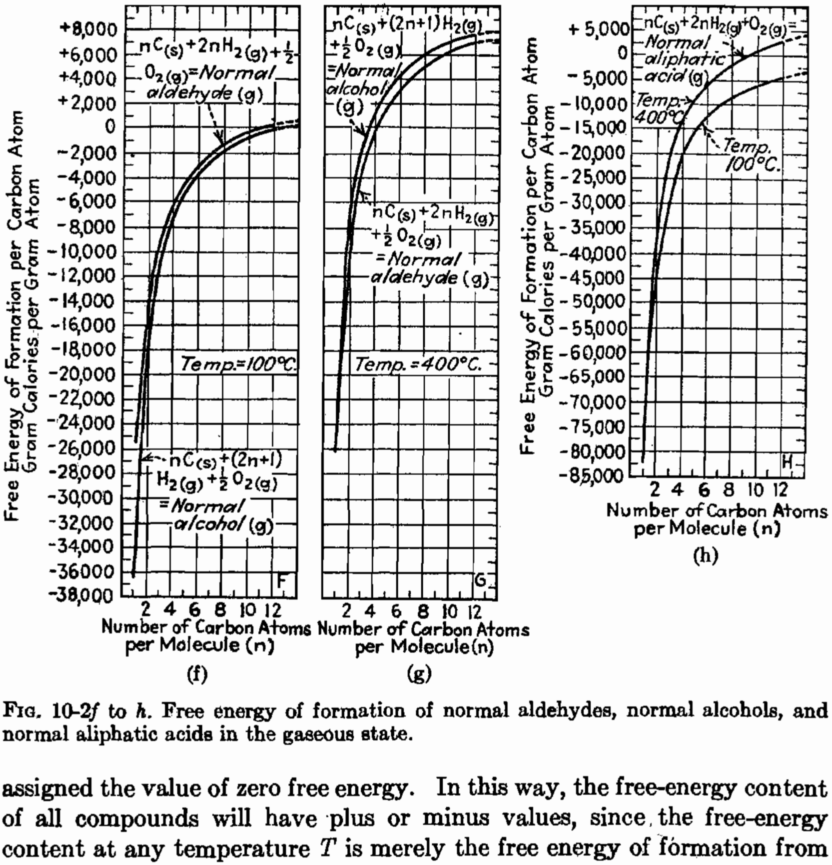


FIG. 10-2*a* to *e*. Free energy of formation of CO, H_2O, CO_2, normal olefins, and normal paraffins in the gaseous state.

When all the reactants and products are in the gaseous state at a partial pressure of 1 atm, then the well-known relationship exists:

$$-\Delta F = 4.57T \log k \tag{1}$$

The term $-\Delta F$ is the free-energy decrease in calories for the reaction as it proceeds from left to right. It represents the difference in free-energy content of all the reactants and all the products. On the basis used here for free-energy values, all elements in their normal state of aggregation at 1 atm pressure and at any particular temperature T are arbitrarily assigned the value of zero free energy. In this way, the free-energy content of all compounds will have plus or minus values, since the free-energy content at any temperature T is merely the free energy of formation from the elements at T. In Eq. (1), T is the absolute temperature in degrees Kelvin, and k is the equilibrium constant for the reaction, with the products appearing in the numerator and the reactants in the denominator in terms of the individual partial pressures expressed in the unit of atmospheres. In making calculations, this system of units must be definitely adhered to in using Eq. (1). From the equilibrium constant of a chemical reaction, it is of course possible to calculate in the usual way the ultimate yields that may be expected and also to determine quantitatively the effect of pressure on the equilibrium conversion for those reactions affected by



(f) (g) (h)

FIG. 10-2*f* to *h*. Free energy of formation of normal aldehydes, normal alcohols, and normal aliphatic acids in the gaseous state.

pressure, viz., those attended by a change in the number of gaseous moles. And if the equilibrium conversion at another temperature is wanted, then the free-energy change at that temperature only need be evaluated.

All spontaneous reactions, i.e., those proceeding of their own accord and in the absence of any electrical influences, such as magnetic or electrostatic forces, or various forms of radiation, are attended by a free-energy decrease. If a reaction involves only one compound and an element, e.g., hydrogen, yielding as the product only one other compound of the same number of carbon atoms, then the compound with the lower free energy is the more stable of the two under the experimental conditions chosen. Thus, it is seen in connection with Fig. 10-2*d* that the normal paraffins at 100°C have lower free-energy values than the normal olefins; i.e., at this temperature, all normal olefins are capable of being hydrogenated to normal paraffins with good equilibrium yields. However, at 400°C (Fig. 10-2*e*), it is seen that the free-energy difference is not so large and, for the higher olefins, the free-energy decrease on hydrogenation is very small and approaches zero. From Eq. (1), if $\Delta F = 0$, then the equilibrium constant is unity, and so it follows that the reverse reaction at this temperature is capable of proceeding to a reasonable degree. Such reactions occur in the cracking or pyrolysis of hydrocarbons, and it is well known that these pyrolytic reactions are carried out at temperatures in the vicinity of 400°C.

From Figs. 10-2*d* and *e*, it can be calculated that at 400°C in the case of a larger paraffin, e.g., hexane, there is a spontaneous tendency to decompose or crack, yielding a smaller paraffin and smaller olefin, e.g., propane and propylene. At 100°C, such a reaction does not tend to occur. Therefore, if a relatively large olefin were to be hydrogenated to a paraffin of the same molecular weight, apparently it would be desirable to carry out such a reduction at lower temperatures for two pertinent reasons: (1) the equilibrium yield is better, (2) decomposition or side reactions are less likely to be troublesome. Because of this preferred lower-temperature operation, catalysts must be available to operate at these lower temperatures. Such hydrogenation catalysts are known, as was pointed out elsewhere in this chapter.

Inspection of Figs. 10-2*f* and *g* shows that the reduction of aldehydes to alcohols parallels, in many respects, that of olefins to paraffins. At 100°C, it is seen that the normal alcohols have lower free-energy values than the corresponding aldehyde. Hydrogenation is, therefore, feasible if catalysts can be found to effect the reduction with reasonable speed. At higher temperatures, e.g., 400°C, the aldehyde is seen to possess a lower free-energy value than the alcohol. In other words, the normal spontaneous tendency at this temperature is for the alcohols to dehydrogenate to yield aldehydes. Since the reduction goes with a volume decrease, it is possible to carry it out at this temperature by the application of pressure; but without pressure, reduction would not be feasible at 400°C. Further studies will show that, as in the case of the paraffin hydrocarbons, there is the tendency at the higher temperatures to crack or decompose into lower-molecular-weight hydrocarbons and that also, at all temperatures, there is the decided tendency to continue the reduction to the hydrocarbon stage (hydrogenolysis). In other words, these few observations indicate that the reduction of aldehydes is apt to be beset with side reactions, and, in general, unless carefully chosen conditions are used, this is the actual fact.

The data of Fig. 10-2 may be applied to some of the various reductions of carbon monoxide. The simplest may be indicated by the following reaction at 400°C:

$$\begin{aligned} CO\ (g) + 3H_2\ (g) &= CH_4\ (g) + H_2O\ (g) \\ -40{,}500 + 0 + \Delta F &= -3{,}600 - 50{,}000 \\ \Delta F &= -13{,}100 \text{ cal at } 400°C \end{aligned} \tag{2}$$

This free-energy decrease shows that, at this temperature, reduction of carbon monoxide to methane is a very complete reaction as judged by the equilibrium yield that is possible. However, as indicated elsewhere, most hydrogenation reactions are reversible; if the above reaction is considered in the reverse direction, then it is seen to be the reaction indicated for obtaining hydrogen from hydrocarbons by causing them to react with steam at temperatures of about 1000°C where the reverse of reaction (2) is possible.

In this connection, it might be proposed to carry out a reaction as follows:

$$\begin{aligned} CH_4\ (g) + H_2O\ (g) &= CH_3OH\ (g) + H_2\ (g) \\ -3{,}600 - 50{,}000 + \Delta F &= -26{,}000 + 0 \text{ at } 400°C \\ \Delta F &= +27{,}600 \text{ cal at } 400°C \end{aligned} \tag{3}$$

Although it would be highly desirable to carry out such a reaction, thereby making natural gas into a more valuable product, the magnitude of this free-energy increase indicates the impossibility of so doing at any practical temperature level. It is useless, therefore, to expend any effort in this direction. The reverse reaction is obviously predominating.

Instead of the complete hydrogenation of carbon monoxide, the partial reduction to methanol might be considered.

$$\begin{aligned} CO\ (g) + 2H_2\ (g) &= CH_3OH\ (g) \\ -34{,}000 + 0 + \Delta F &= -36{,}500 \text{ at } 100°C. \\ \Delta F &= -2{,}500 \text{ cal at } 100°C \end{aligned} \tag{4}$$

This free-energy decrease indicates that the reaction is possible at 100°C, but, so far, no catalysts have been found sufficiently active to bring about reaction at this relatively low temperature. To get increased reaction rate, it is logical to raise the temperature. If the same calculation is made by means of Figs. 10-2*a* and *g* for 400°C, the free-energy increase is found to be +14,300 cal. Thus, the above reaction is not capable of proceeding to any practical extent at this temperature even though it might be expected that now the reaction velocity might be favorable. However, the reaction as written above and the free-energy value given are for all reactants and products at 1 atm partial pressure. Since the reaction goes with a decrease in the number of gaseous moles, then the equilibrium yield, which is negligible at 400°C and low pressures, can be raised to an appreciable value by working at high pressure. So it is concluded that higher reaction temperatures, i.e., those up to perhaps 400°C, are allowable and so will help the reaction velocity, provided pressure is applied to increase the equilibrium yield. There then remains the problem of finding a particular unusual type of catalyst that will allow the reduction to proceed to only methanol under these rather severe conditions; for, as indicated above, there is a pronounced tendency to reduce carbon monoxide completely to methane. Certain metallic oxide catalysts have been found experimentally to possess this property, thus making the methanol synthesis from water gas a practical reality.

In the same way, and from similar reasoning from the data of Figs. 10-2*c* and *g*, it is apparent that methanol may be synthesized from a carbon dioxide-hydrogen mixture, rather than from carbon monoxide and hydrogen, should this be desired.

The Fischer-Tropsch atmospheric or low-pressure synthesis, from water gas, of hydrocarbons larger than methane may be analyzed by the data given in Fig. 10-2. It is found that such reactions are entirely possible even at atmospheric pressure and temperatures up to 400°C. However, it should again be realized that the higher-molecular-weight hydrocarbons that result from this synthesis are likely to be further reduced to methane, since methane is the most stable hydrocarbon at temperatures below 400°C. This destructive hydrogenation or hydrogenolysis would be more apt to occur at higher temperatures, for all reaction velocities are increased, and the specificity of a catalyst is, in general, markedly reduced. Temperature control has been found to be a highly important factor in the successful operation of this process. Also, in addition to hydrogenating tendencies, it follows that the catalyst must have condensation properties to build up hydrocarbons having higher molecular weights than methane.

It is possible to analyze the mechanism for the higher alcohol synthesis. This may be typified by

$$2CH_3OH\ (g) = C_2H_5OH\ (g) + H_2O\ (g) \qquad (5)$$
$$2(-26{,}000) + \Delta F = 2(-8{,}400) - 50{,}000 \text{ at } 400°C$$
$$\Delta F = -14{,}800 \text{ cal at } 400°C$$

This condensation is entirely possible, for the reaction proceeds with a relatively large free-energy decrease. To carry out such a reaction, catalysts possessing dehydration as well as condensation properties would be desirable. Thus, free-energy data are useful not only in determining whether or not a particular over-all reaction is possible but also in interpreting reaction mechanisms and in aiding in a choice of catalysts for those mechanisms which seem most feasible.

The data of Figs. 10-2*b*, *f*, *g*, and *h* may be used to study the direct hydrogenation of acids to alcohols. For example,

$$\begin{aligned} \mathrm{CH_3CO_2H}\ (g) + 2\mathrm{H_2} &= \mathrm{C_2H_5OH}\ (g) + \mathrm{H_2O} \qquad (6) \\ 2(-37{,}000) + 0 + \Delta F &= 2(-8{,}400) - 50{,}000 \text{ at } 400°\mathrm{C} \\ \Delta F &= +7{,}200 \text{ cal at } 400°\mathrm{C} \end{aligned}$$

Although there is an actual free-energy increase indicated which is not very large, the reaction also proceeds with a decrease in volume so that equilibrium yields can be definitely helped by carrying out the reaction, at relatively high pressures. The equilibrium yield is more favorable at lower temperatures, but here again the slower reaction velocity must be considered. Care must be exercised in the choice of catalysts so that they will have little, if any, dehydrating tendencies, and their hydrogenating ability must not be too violent; otherwise, the hydrocarbon rather than the alcohol will result as the product. These problems have been worked out, and the high-pressure hydrogenation of acids or, more particularly, their simple esters, which are more volatile, is a successful commercial process.

Temperature. For the most part, the temperature for hydrogenation reactions is usually below 400°C, except in reactions where pyrolytic decomposition occurs concurrently with the hydrogenation reactions. In these cases, the temperature may extend to 500°C. Temperature is one of the most important variables affecting a reaction. *Practically every hydrogenation reaction can be reversed by increasing temperature.* It becomes necessary, then, to work at as low a temperature as possible where the rate of reaction will still be satisfactory. Whereas catalysts affect only the speed and course of a reaction, temperature affects the equilibrium position, the speed, and the path, or course, of a reaction. In general, then, increasing temperature adversely affects the equilibrium position, so that the maximum ultimate yield is decreased; but it affects favorably the speed of a reaction, so that in a given time a greater quantity of product can be obtained. It becomes necessary to balance the less favorable equilibrium position with the faster rate of reaction. Fortunately, in recent years, the knowledge of catalysis has been so extended that satisfactory reaction rates are possible at lower temperatures where a more favorable equilibrium position prevails.

In some cases, an increase in temperature may adversely affect a catalyst, so that the reaction rate is decreased or reduced to practically nothing. These are the cases known as *sintering* of the catalyst; i.e., the highly extended and porous surfaces of the catalysts are in some way collapsed or fused together, so that the efficiency of the catalyst is seriously reduced. Here, again, a study of promoters, or substances that catalyze or accelerate the activity of a catalyst, may surmount the difficulties due, at least in part, to sintering.

Finally, a statement is necessary concerning the temperature coefficient of hydrogenation reactions. Barring decrease in activity of the catalyst (such as sintering), few if any hydrogenation reactions fit the generalized statement that the speed of a reaction may be doubled for every 10–15°C increase in temperature. It usually takes 50°C or more to double the speed of a hydrogenation reaction.

In general, the noble-metal catalysts, such as platinum or palladium, are used from room temperatures to 150°C; catalysts of the nickel and copper type, from 150–250°C; and various combinations of metals and metal oxides, from 250–400°C.

Pressure. Pressure, like temperature, can affect the rate of reaction as well as the equilibrium position. The rate of reaction is generally increased by increasing pressure, because a gas phase is usually present, and increased pressure gives increased concentration. In general, increased concentration speeds up a reaction. Pressure increases the equilibrium yield in a hydrogenation reaction when there is a decrease in the volume of the reaction as it proceeds. This is the simple application of the mass-action law, or Le Châtelier's principle. In hydrogenation reactions, there is usually a decrease in volume.

Thus, pressure would have a greater effect on equilibrium yield in the reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

than in the reduction of formaldehyde

$$CH_2O + H_2 \rightleftharpoons CH_3OH$$

for the change in volume is greater in the first case. In simple cases, the effect of pressure on the equilibrium yield can be quantitatively estimated from application of mass-action principles.

The effect of pressure on the reaction rate is not subject to any definite quantitative laws. The results of one reaction may not occur in another. The point is best settled by experimental data. In general, however, increased pressure will result in an increased reaction rate. Thus, Brochet observed that phenol is hydrogenated very slowly at 150°C at atmospheric pressure using a nickel catalyst but that at 15 atm at the same temperature the reaction was complete and rapid.[1] Maxted and Armstrong and

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[1] Brochet, *Bull. soc. chim.* (4), **15**, 588 (1914); *Compt. rend.*, **158**, 1352 (1914).

Hilditch observed the velocity of hydrogenation to be proportional to the pressure.[1] Armstrong reported that the speed of hydrogenation of pyridine to piperidine varied as the square of the hydrogen pressure.[2] In the hydrogenation of acetone to isopropyl alcohol with identical batches of a copper chromite catalyst, Adkins and Connor observed the following conversions in reactions of ½ hr duration.[3]

TABLE 10-13. EFFECT OF PRESSURE IN THE HYDROGENATION OF ACETONE

Pressure, atm	*Conversion, %*
35	17
148	70
212	95

Again, Folkers and Adkins found that an increase in pressure from 100–200 atm increases the rate of hydrogenation of ethyl laurate to lauryl alcohol sevenfold and an increase in pressure from 100–300 atm increases it twenty-eight-fold.[4] Results of hydrogenating acetoacetic ester, benzene, phenol, and aniline at various pressures have also been reported,[5] and there are many other references in the literature to the effect that an increase in pressure usually gives an increased rate of reaction. In general, then, the conclusion that increased pressure results in increased rate of reaction appears well substantiated.

There may be cases, however, where pressures below atmospheric are desirable, particularly when the reaction may need to be stopped at some intermediate stage of hydrogenation. Thus, Grignard observed, in hydrogenating at pressures less than atmospheric with nickel, copper, and platinum catalysts, that hydrogenations could be stopped at the first stage.[6] Phenol was reduced to cyclohexenol; benzaldehyde to benzyl alcohol; benzonitrile to benzaldimine; and phenylacetonitrile, at about 220 mm pressure and 200°C, to phenylacetaldimine.

Time. The time necessary for a hydrogenation reaction may vary from a few seconds to several hours, depending on the materials being hydrogenated, the catalyst, the temperature, and the pressure. In general, the more reactive the compound, the faster the hydrogenation reaction. Thus, simple aldehydes are hydrogenated very readily, whereas the reduction of aromatic rings to saturated cyclic compounds or of esters to alcohols

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[1] MAXTED, *J. Soc. Chem. Ind.*, **40**, 169T (1921); ARMSTRONG and HILDITCH, *Proc. Roy. Soc.* (*London*), **100A**, 240 (1921).

[2] ARMSTRONG, lecture before the British Institute of Chemical Engineers, Oct. 30, 1931.

[3] ADKINS and CONNOR, *J. Am. Chem. Soc.*, **53**, 1093–1095 (1931).

[4] FOLKERS and ADKINS, *J. Am. Chem. Soc.*, **54**, 1153 (1932).

[5] ADKINS, CRAMER, and CONNOR, *J. Am. Chem. Soc.*, **53**, 1403 (1931).

[6] GRIGNARD, *Bull. soc. chim. Belg.*, **37**, 41 (1928).

is a slower reaction. The type of apparatus or equipment used will depend on the speed of hydrogenation and vice versa. The usual type of bomb reactor is admirably suited to slow reactions, while an apparatus where the materials can be continually passed over the catalyst is best for fast reactions.

Ratio of Hydrogen to the Substances Being Hydrogenated. The ratio of hydrogen to the substance being hydrogenated is conveniently expressed in terms of partial pressures. It frequently happens that the speed or path of a certain hydrogenation can be affected by the proportion of hydrogen to the substance. Although no extensive data on this phase of hydrogenation are available in the literature, it has been found that ethyl lactate and malonate are reduced to the corresponding alcohols in good yields in a flow system at pressures of about 1,300 psig, where practically the entire pressure is hydrogen and the partial pressure of the esters is only a few centimeters. Similar results are obtained in the course of other hydrogenations.[1] Usually, such hydrogenations are carried out at considerably higher total pressures, viz., about 3,000 psig. In the examples previously cited, the higher total pressure was lessened, and a higher ratio of hydrogen pressure to the partial pressure of the substance being hydrogenated was employed. This method of operation is, however, somewhat different from that usually employed.

Also, in certain isomerization reactions[2] it has been found that the use of a relatively low hydrogen:hydrocarbon mole ratio favors the minimum conversion to by-products and the maximum conversion to desired product.

Liquid- or Gas-phase Reactions. The hydrogen, the substance being hydrogenated, and the product of hydrogenation may exist entirely in the gas phase; or the substance and the product may exist as a liquid phase. In this latter case, the hydrogen is in contact with the substance, either as a gas phase above or dissolved in it. Hydrogenation reactions obviously cannot occur without intimate contact of the hydrogen with the reacting substance and the catalyst. The type of reaction may differ, depending on whether the hydrogenation is in the gas phase or the liquid phase. Thus, Lush found, in hydrogenating naphthalene, using a nickel catalyst, that tetralin was the principal product formed in the vapor-phase reaction, whereas decalin was produced by the liquid-phase hydrogenation.[3]

In liquid-phase reactions, there must be opportunity for intimate contact of hydrogen with the substance being hydrogenated and the catalyst. This is usually accomplished by some means of shaking, by stirring, or by circulating hydrogen through the liquid. Another factor that greatly facilitates intimate contact is the solubility of hydrogen in the substance

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[1] TRENT, unpublished results, Pennsylvania State University, 1933.

[2] CLARK, MATUSZAK, CARTER, and CROMEANS, *Ind. Eng. Chem.*, **45**, 803 (1953).

[3] LUSH, *J. Soc. Chem. Ind.*, **26**, 454T (1927).

undergoing hydrogenation. Increased pressure favors greater solubility of hydrogen, and an intimate contact comparable to gas-phase reaction is thus possible. The principal difference is the ratio of hydrogen to the substance being hydrogenated. In the gas phase, this ratio may be varied over a very wide range, but, in the liquid phase, it is governed by the solubility of hydrogen.

Solubility of Hydrogen. The effect of the solubility of hydrogen in the reacting substance obviously relates only to liquid-phase reactions. As indicated above, an increase in the pressure of hydrogen increases the solubility in a given liquid, and it has been found that this increase in solubility with pressure follows Henry's law with reasonable accuracy at ordinary temperatures in various liquids, such as methanol, isopropanol, paraffin hydrocarbons, and heavy oils.[1] However, it does not follow that the solubility of hydrogen in liquids will decrease with increasing temperatures, as might be expected. Thus, Grimm, in discussing the catalytic hydrogenation of coal and oil, states that the solubility of hydrogen in oils increases with the temperature, it being three times as great at 300 as at 20°C.[2] The solubility of hydrogen in liquids undoubtedly plays an important, if not the principal, role in liquid-phase hydrogenations.

Exothermic Character of the Hydrogenation Reaction. The values for the heat of reaction are generally obtained from thermochemical data, when data relating specifically to the problem are not available. Depending on the type of hydrogenation reaction, varying amounts of heat may be liberated. Hydrogenations are usually exothermic, and since the reaction occurs only because of the catalyst, local temperatures in the surfaces of the catalyst may reach surprisingly high values. These not only tend to divert the reaction to side reactions such as cracking but are likely to impair the efficiency of the catalyst because of sintering, which is the collapse of the active catalytic surface due to excessive heat. In problems of commercial design, the exothermic character of the reaction must consequently be given careful attention. Uncontrolled temperatures not only influence the course of the reaction and diminish the efficiency of the catalyst but also necessitate materials of construction that can withstand the maximum conditions of temperature and pressure likely to occur. In large units, temperature control is usually best obtained through proper heat interchange with the incoming materials.

V. GENERAL PRINCIPLES CONCERNING HYDROGENATION CATALYSTS

Catalysts are essential to most hydrogenation reactions. Very few hydrogenations occur in the absence of some sort of catalyst. Cases in

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[1] Frolich, Tauch, Hogan, and Peer, *Ind. Eng. Chem.*, **23**, 548 (1931).

[2] Grimm, *Intern. Conf. Bituminous Coal*, **II**, 49 (1931).

which noncatalytic hydrogenations do occur usually involve a separate reaction taking place simultaneously from which extremely active or liberated hydrogen is available in limited amounts. In other cases, the reaction temperature may be high where, in addition to hydrogenation reactions, pyrolytic or cracking reactions are also occuring so that hydrogen gas in the absence of catalysts can add to the molecular fragments produced by the cracking. Thus, the earlier work of Bergius on coal hydrogenation was noncatalytic, but later the process became practically entirely catalytic through the developments of the I.G. Farbenindustrie in Germany.

Excepting these few instances, the large bulk of hydrogenation reactions use hydrogen gas as the source of hydrogen, and the function of the catalyst is to effect the over-all result of chemically combining the gaseous hydrogen with the substance capable of adding hydrogen to its molecular structure. It is the purpose of the catalyst to effect this combination along the desired path as quickly as possible. The following brief discussion is intended to clarify some of the essential features of a catalyst.

Surface. For the most part, hydrogenation catalysts are solids consisting of metals and metal oxides. The hydrogenation is effected at the surface of the catalyst; so a highly extended surface is essential. However, a catalyst surface differs considerably from that produced by simply an extensive mechanical subdivision of matter. Taking a piece of bar nickel or copper and subdividing it mechanically to pass, say, a 50-mesh sieve would not produce an active nickel or copper catalyst. Usually, the preparation of a catalyst is associated with some chemical reaction whereby a highly extended, porous, and honeycombed surface is produced so that the density of the surface metal is far less than that of the bulk metal. Certain surface atoms may become so removed from other adjoining ones that they may approach a gasified state, at conditions far removed from the normal vaporization of the metal. Certain valence bonds of these atoms which normally would be shared with other atoms in the usual dense metallic state are freed, and here is believed to lie the reason for the catalyst's activity. These surface atoms, having varying degrees of unsaturation compared with the bulk metal or metal oxide, will strongly adsorb other substances with which they may come in contact, and active catalysts usually have high absorptive powers. Although absorption is closely related to the successful performance of a catalyst, it may ruin an active catalyst, because other substances called catalyst poisons may be so strongly retained by these active atoms that the substance being hydrogenated can no longer reach the active or catalytic areas.

Two forms of adsorption are now recognized: physical adsorption and chemisorption. It is important to distinguish between them so that the mechanism of any particular heterogeneous catalysis can be identified.[1]

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[1] RIDEAL, *Nature*, **161**, 461 (1948)

The chemisorption of hydrogen on various metals is commonly studied in attempts to understand catalytic activity as well as the complex phenomenon that occurs in the crystal lattices of metals.[1]

Catalyst supports or carriers greatly increase the effective surface area of catalysts, and when the cost is significant this may be of great importance. However, the support often performs a more vital role. For instance,[2] in the isomerization of *n*-pentane to isopentane, an alumina support containing a small proportion of silica was found to be superior to a support consisting of pure alumina alone.

The speed of a hydrogenation will depend on the type and amount of active surface available. Increasing the ratio of catalyst to the substance undergoing hydrogenation usually increases the speed of the hydrogenation, although not necessarily in direct proportion to the increase in amount of catalyst. In batch operations, the catalyst usually is about 1–10 per cent by weight of the substance being hydrogenated.

Mixed-metal Catalysts. Because an apparently small and inappreciable amount of substance might impair or poison the activity of a catalyst, strenuous efforts must be made to prepare the catalyst as nearly chemically pure as possible. It will usually be found that, in this state, activity is either nil or very low. The solution to this dilemma is to recognize more clearly the class of substances to which poisons and promoters belong. Catalyst poisons are usually substances that can react chemically with the catalyst or else, because of their volatility, can condense onto and blot out the active areas of the catalyst. The common poisons are halogens, sulfur, arsenic, and sometimes metals of low melting point such as mercury, lead, and tin.

Promoters, or substances that increase a catalyst's activity, are usually quite stable and frequently exist in physical combination with the catalyst. It frequently happens that they themselves are catalysts for the same or a similar type of reaction. Thus, a small amount of chlorine or sulfur will render a copper catalyst used for the dehydrogenation of methanol entirely inactive,[3] whereas the addition of about 3 per cent of zinc oxide to a pure copper catalyst, when used under exactly the same conditions, will increase the activity threefold.[4]

In those cases where some of the more common poisons, such as sulfur, have to be tolerated, it is possible to utilize catalysts that contain sulfur. The molybdenum sulfides are examples of catalysts of this type. Under proper temperature and pressure conditions, these materials are effective hydrogenation catalysts.

The use of mixed-metal catalysts or promoted catalysts has been rapidly

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[1] Beeck, Ritchie, and Wheeler, *J. Colloid Sci.*, **3**, 505 (1948).

[2] Clark, Matuszak, Carter, and Cromeans, *Ind. Eng. Chem.*, **45**, 803 (1953).

[3] Frolich, Fenske, Perry, and Hurd, *J. Am. Chem. Soc.*, **51**, 187 (1929).

[4] Frolich, Fenske, and Quiggle, *Ind. Eng. Chem.*, **20**, 694 (1928).

extended in recent years. More common mixtures with the well-known types of catalysts are nickel-copper, nickel-alumina, cobalt molybdate, nickel–tungsten sulfide, copper–zinc oxide, copper–chromium oxide, and zinc oxide–chromium oxide.

Stability. The period of activity of a catalyst is a rather indefinite thing. This is because such activity depends not only on the nature of the materials brought in contact with it but also on the stability and permanence of the active areas, which most likely are responsible for the functioning of the catalyst. Loss in activity from contamination with foreign materials is best characterized as poisoning. Loss in activity from a collapse and aggregation of the highly distended surface is best termed sintering. It should be remembered that a catalyst, like any other system, is striving to reduce its surface energy to a minimum for just the same reasons that a droplet of water forms a sphere. Thus, there is always a force tending to bring about the collapse of the extended surface, with the result called sintering. A function of promoters is to maintain and prolong the existence of the active areas of a catalyst.

It is sometimes possible to reactivate a catalyst that has lost its activity, especially when the loss in activity is due to some absorbed materials. Passing hydrogen alone over the catalyst for a period of time may help; or, in some cases, it is possible to reactivate the catalyst by passing a small amount of oxygen over it. In these cases, the adsorbed materials are probably burned off. Oxygen was found to reactivate catalysts used in the synthesis of methanol from carbon monoxide and hydrogen[1] but quite effectively to poison an iron catalyst used in the synthesis of ammonia.[2]

Usually, catalysts of a very high initial activity are short-lived, and it becomes necessary to choose between a high initial rate of hydrogenation and a somewhat lower but better average rate, such as is obtained in a stable catalyst. These stable catalysts are often obtained through the use of mixed-metal or promoted catalysts where the active areas are large. In addition, the mixtures of metals and metal oxides usually afford the best protection against sintering. Then by careful elimination of any foreign materials in the reactor, in the hydrogen, or in the substance being hydrogenated, a reasonable period of catalyst activity can be assured.

The catalyst's life in industrial processes may extend from a month to a year or more; i.e., the catalyst is active for this period, after which it becomes necessary to remove it from the reactor and replace it with fresh material or otherwise to recondition it chemically. However, it is relatively common practice to rejuvenate catalysts periodically by removing deposits, poisons, or other adsorbed and undesirable materials. This is usually accomplished by passing air, steam, or other reactivating gas over the

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[1] FENSKE and FROLICH, *Ind. Eng. Chem.*, **21**, 1052 (1929); NUSSBAUM and FROLICH, *ibid.*, **23**, 1386 (1931).

[2] ALMQUIST and BLACK, *J. Am. Chem. Soc.*, **48**, 2815 (1926).

catalyst without removing it from the reactor. The periods between rejuvenation may range from a day or less to months.

Preparation. Hydrogenation catalysts can be prepared in practically an unlimited number of ways. However, there are again certain generalized or fundamental steps that are quite common to the preparation of any active catalyst. These principles are intended to serve as a guide to catalyst preparation when other more definite information is not available. It may be found later that certain of these steps are not necessary or are relatively unimportant. However, it is believed that if they are recognized a higher average success in catalyst preparations will result. The five most important principles are as follows:

1. To ensure the production and duplication of a reasonably active catalyst, relatively pure materials should be used in its preparation. Because of the small amounts of a substance that may act as either a poison or a promoter, the purity of the starting chemicals should be known; this will be the difference between the building up of successful catalysts by hit-or-miss methods and by a rationalized procedure.

2. Generally the better practice is to prepare the catalyst through a chemical reaction rather than by a mere physical or mechanical method. Thus, in the preparation of a nickel catalyst, it is far better to prepare it by precipitation of nickel hydroxide from nickel nitrate and alkali and convert the hydroxide to oxide and to metallic nickel by hydrogen than to prepare it by subdividing a nickel bar. A finer and more active state of subdivision together with a greater possibility of reproduction of the catalyst generally results by applying rather simple and definitely known chemical reactions.

In mixtures of metal and metal oxide catalysts, generally anything that can be done to promote or bring about more intimate contact between the materials will result in an improved catalyst. Although this may be obvious, sometimes it may not be fully appreciated. This point may be illustrated in the preparation of copper–zinc oxide catalysts.[1] If the efficiency of the coprecipitated hydroxides of copper and zinc is rated as 100, other methods of preparation compare as shown in Table 10-14 when studying the decomposition of methanol.

TABLE 10-14. EFFECT OF METHOD OF PREPARATION ON CATALYST EFFICIENCY

Method of preparation	*Decomposition efficiency, %*
1. Hydroxides precipitated together	100
2. Hydroxide gels mixed	83
3. Zinc hydroxide precipitated on suspended copper hydroxide	75
4. Calcined nitrates	70
5. Copper hydroxide precipitated on suspended zinc hydroxide	67

The activity of nickel catalysts supported on kieselguhr is dependent on

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[1] FROLICH, FENSKE, and QUIGGLE, *Ind. Eng. Chem.*, **20**, 694 (1928).

the method of preparation,[1] and likewise the method of preparing copper oxide–chromium oxide catalysts affects their activity.[2]

3. Precautions should be taken in the course of the preparation of a catalyst to keep it free from any contaminating substances other than those definitely desired in the catalyst. The catalyst should be prepared just as any pure substance is; experience indicates that effort in this direction is well expended. When precipitation of the hydroxide or oxide may occur in the course of preparing a metal catalyst, it is desirable to use the nitrate of the metal and ammonium hydroxide as a precipitant when there are no other conflicting chemical reactions. In this way, any ammonium salts or excess hydroxide is easily volatilized by careful heating.[3]

4. When it is necessary to reduce a catalyst prior to use, precautions must be taken in its reduction. It may be said that catalysts are either made or destroyed in this reduction operation. The reduction of metal oxides by hydrogen is generally exothermic; consequently, the catalyst's activity may be seriously impaired by sintering if reduction temperatures are uncontrolled. Careful measurement and regulation of the temperatures of reduction are important. Sometimes, it is advisable to use hydrogen diluted with nitrogen. In general, the temperatures of reduction should be no higher than necessary to effect a gradual and controlled reduction of the oxide. It is relatively easy to raise the catalyst temperature to incandescence and even to destruction of its activity through carelessness in controlling the temperature during reduction.

5. If the catalysts must be stored, it is generally better to store them in the more stable state. Thus, if the catalyst needs to be reduced prior to use, it is generally better practice to store the oxide and reduce batches of catalyst as needed. These are simple precautions which enable the catalyst to have its maximum activity when used. In addition, storage in containers free from materials that are liable to be poisons is obviously necessary. Cork- or glass-stoppered bottles are preferable to rubber-stoppered ones, as there is danger of sulfur contamination from the latter.

Catalysts for use in industry depend on the following considerations: (1) cost of ingredients, (2) simplicity and reproducibility of preparation, (3) catalyst life, (4) ease of regeneration, (5) resistance to poisoning, (6) physical strength, and (7) resistance to thermal shock. On the other hand, catalysts for use in the laboratory primarily are desired to have high activity and specificity.

Details on the preparation of many catalysts are available in the chemical literature; certain of these are as follows: copper-chromium oxide,[4] Raney

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[1] Covert, Connor, and Adkins, *J. Am. Chem. Soc.*, **54**, 1652 (1932).

[2] Folkers and Adkins, *J. Am. Chem. Soc.*, **54**, 1153 (1932).

[3] Frolich, Fenske, and Quiggle, *J. Am. Chem. Soc.*, **51**, 61 (1929).

[4] Adkins, "Organic Reactions," vol. 8, p. 1, 1954; Lazier and Arnold, "Organic Syntheses," coll. vol. II, p. 142, 1943.

nickel,[1] Raney iron and cobalt,[2] nickel on kieselguhr,[3] nickel-copper,[4] platinum oxide,[5] platinized charcoal,[6] palladium on barium sulfate or on barium carbonate,[7] palladium oxide,[8] molybdenum catalysts,[9] cobalt sulfide,[10] tungsten disulfide,[11] rhenium heptasulfide and disulfide,[12] and chromia-alumina.[13]

Many catalysts for hydrogen-reforming processing of naphthas and other petroleum fractions are used in the form of beads, which have the advantage over pelleted catalysts of greater physical strength and lower resistance to vapor flow. The process for making beaded catalysts is based on the principle that when solutions of sodium silicate and an acid are mixed in the correct proportions a gel forms in which a catalytic material may be chemically bound. The gel may be formed into the desired size and shape, and after removing the water, a porous, active, and durable residue remains.

General Classification of Hydrogenation Catalysts. The number of catalysts capable of effecting hydrogenations is large; in addition, many types of hydrogenation are possible. Practically any type of unsaturation can be hydrogenated catalytically. It has been pointed out that hydrogenation may involve the saturation of a carbon-to-carbon linkage or the reduction of carbonyl or carboxyl or hydroxyl groups and may even involve the breaking of carbon-to-carbon linkages, as in the hydrogenation of coals and mineral oils. In general, however, hydrogenation catalysts may be classified as follows:

Vigorous Hydrogenation Catalysts. These catalysts are usually characterized by the fact that they carry the hydrogenation to the greatest extent possible, so that the maximum addition of hydrogen to compound occurs under the particular operating conditions. Thus, in the case of simple aldehydes, the reduction will pass beyond the alcohol stage and end

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[1] COVERT and ADKINS, *J. Am. Chem. Soc.*, **54**, 4116 (1932); BILLICA and ADKINS, "Organic Syntheses," vol. 29, p. 24, 1949; ADKINS and BILLICA, *J. Am. Chem. Soc.*, **70**, 695 (1948); RANEY, *Ind. Eng. Chem.*, **32**, 1199 (1940).

[2] THOMPSON and WYATT, *J. Am. Chem. Soc.*, **62**, 2555 (1940).

[3] DOUGLAS and RABINOVITCH, *J. Am. Chem. Soc.*, 74, 2486 (1952); COVERT, CONNOR, and ADKINS, *ibid.*, **54**, 1651 (1932).

[4] BEST and RUSSEL, *J. Am. Chem. Soc.*, **76**, 838 (1954).

[5] ADAMS, VOORHEES, and SHRINER, "Organic Syntheses," coll. vol. I, p. 463, 1941; FRAMPTON, EDWARDS, and HENZE, *J. Am. Chem. Soc.*, **73**, 4432 (1951); VANDENHEUVAL, *Anal. Chem.*, **28**, 362 (1956).

[6] BALTZLY, *J. Am. Chem. Soc.*, **74**, 4586 (1952).

[7] MOZINGO, "Organic Syntheses," vol. 26, p. 77, 1946.

[8] STARR and HIXON, "Organic Syntheses," coll. vol. II, p. 566, 1943.

[9] MOORE, TRIMBLE, and GREENSFELDER, *J. Am. Chem. Soc.*, **74**, 373 (1952).

[10] FARLOW et al., *J. Am. Chem. Soc.*, **70**, 1392 (1948).

[11] Technical Oil Mission microfilms, reel 181, frames 06429–06430; reel 212.

[12] BROADBENT, SLAUGH, and JARVIS, *J. Am. Chem. Soc.*, **76**, 1519 (1954).

[13] HUGHES, STINE, and DARLING, *Ind. Eng. Chem.*, **41**, 2184 (1949).

at the saturated hydrocarbon. Even here, the tendency to saturate the carbon atoms may be sufficiently great to cause cracking or to break the carbon-to-carbon bonds so that still more hydrogen can be added, the final result being the formation of the hydrocarbon with the greatest hydrogen: carbon ratio, viz., methane. Cracking tendencies are usually associated with these vigorous hydrogenation catalysts, although through control of the variables of temperature and pressure, the cracking reactions can usually be suppressed. Common catalysts belonging to this class usually consist of the nickel, cobalt, or iron type, as well as molybdenum and tungsten oxides or sulfides. Raney nickel is a generally used catalyst for the hydrogenation of alkyne and alkene linkages, aldehydes, ketones, nitro compounds, nitriles, oximes, and phenyl and pyridyl nuclei.[1]

Mild Hydrogenation Catalysts. The term *mild* should not be confused with activity. These catalysts will effect hydrogenations just as rapidly as the vigorous hydrogenation types, but they are able to carry out only one step at a time in a hydrogenation, or at least they do not permit the reaction to proceed to the hydrocarbon stage. A great many catalysts belong to this class. These catalysts will easily reduce an aldehyde or ketone to the alcohol or an acid or ester to an alcohol. The large number of catalysts developed for the direct synthesis of methanol from water gas belong to this class, and they usually contain copper, zinc oxide, chromium oxide, and manganese oxide and may include some of the rarer elements as promoters. In addition, the noble-metal catalysts such as platinum or palladium or their oxides belong to this class. Vanadium oxide, which is widely used as an oxidation catalyst, is reported to be a sulfur-resistant catalyst for hydrogenating unsaturated hydrocarbons, but temperatures in the range of 400°C are required.[2]

Catalysts with Properties Other than Hydrogenation. The synthesis of higher alcohols from water gas involves a condensation as well as a hydrogenation reaction. These so-called higher-alcohol catalysts are usually of the mild hydrogenating type but contain some more alkaline materials, such as sodium, calcium, or barium carbonates or aluminum or magnesium oxides. Other types of catalysts are capable of splitting out water from a molecule along with the hydrogenation but do not possess any appreciable cracking tendencies. These usually are of the vigorous hydrogenating type but contain considerable and even sometimes preponderating quantities of dehydrating catalysts, such as alumina, thoria, tungstic oxide, or chromium oxide. They can effect such reductions as phenol to benzene and cresols to aromatic hydrocarbons and convert various hydroxy compounds to hydrocarbons, with little or no other changes in the molecular structure.

[1] Adkins and Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

[2] Komarewsky, Bos, and Coley, *J. Am. Chem. Soc.*, **70**, 428 (1948).

Sulfide Catalysts. Molybdenum sulfide and especially tungsten disulfide are active catalysts for hydrogenating at pressures in the range of 3,000 psig. The hydrogenation reactions catalyzed by molybdenum compounds are (1) reduction of unsaturates, (2) cleavage of carbon-to-carbon, carbon-to-sulfur, carbon-to-oxygen, and carbon-to-nitrogen linkages, (3) reduction of nitro compounds to amines, and (4) dehydroisomerization. Since sulfur is a common catalyst poison, these sulfide catalysts are valuable where poisons are likely to be present in the feedstock and where refining or pretreatment of the feed to eliminate the poisons is impractical or too costly. Metal sulfide catalysts also have a remarkable activity and selectivity for hydrogenating certain polyolefins to monoolefins while being essentially inactive toward the latter or to aromatics. Further, such catalysts are active at low temperatures.

VI. APPARATUS AND MATERIALS OF CONSTRUCTION

The trend in hydrogenation practice appears to be toward the use of higher pressures, where the apparatus is smaller. Under such conditions, the reaction velocity is increased; the equilibrium positions are made more favorable; the reaction path is better defined, with fewer side reactions; and heating and cooling and heat interchange are facilitated. The design and construction of equipment for high-pressure work are, however, somewhat more complicated than for low-pressure operations. Alloy steels are by far the most common materials of construction.

The design and construction of small-scale pilot-plant units for processing under extreme conditions of pressure and temperature have been described.[1] This description includes material on constructing barricades, thick-walled pressure vessels, and pumps as well as information on the selection of alloys and the effects of hydrogen on the properties of metals.

Reaction chambers or autoclaves are usually of two types, one in which the contents are agitated or stirred in some way and the other in which the reactor and contents are stationary. The first is used with materials such as solids or liquids to bring intimate contact among the catalyst, the material, and the hydrogen. The second type is used where the substance may have sufficient vapor pressure at the temperature of operation so that a gas- as well as a liquid-phase reaction is possible. It is also most frequently used in continuous operation where larger quantities of material need to be processed than can be done conveniently with batch or autoclave methods. In this case, the reacting material, if liquid, is passed along with hydrogen over the catalyst. A drawing of a small, experimental-scale stirred auto-

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[1] Processing under Extreme Conditions, *Ind. Eng. Chem.*, **48**, 826–919 (1956); COMINGS, "High Pressure Technology," McGraw-Hill Book Company, Inc., New York, 1956.

clave is shown in Fig. 10-3. Here the packing around the stirrer is water-cooled to facilitate a tight joint. Figure 10-4 shows a small-scale type of agitated reaction vessel in which the entire reactor is rocked through a sufficient angle to give intimate mixing of the contents. Autoclaves equipped with magnetic stirrers having no stuffing box are also available.

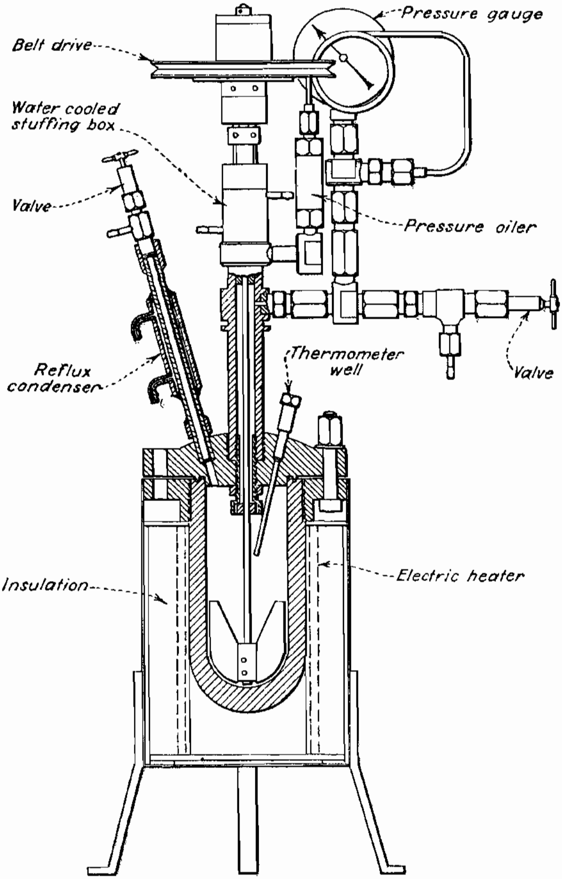

Fig. 10-3. Diagrammatic sketch of high-pressure autoclave.

A convenient small-scale continuous unit is shown in Fig. 10-5. The material to be hydrogenated, if a liquid, is fed into the small high-pressure pump—or, if a solid, it is dissolved in a suitable solvent. All that the pump needs to do is to put sufficient pressure on the liquid to raise it to the pressure on the reactor. Since liquids are relatively incompressible, the work expended in this operation is small. The material is heated near the inlet end of the reactor to the reaction temperature, and then it flows along with the hydrogen over the catalyst contained in the middle or latter half of the reactor. It simply flows or vaporizes through the reactor, the time of contact with the catalyst being dependent on the rate of pumping. Small high-pressure proportioning pumps are readily available, which enable the rate of flow to be accurately maintained as well as readily varied. At the exit end of the reactor, the liquid is condensed, and a trap allows it to be withdrawn from the system without undue loss of hydrogen. Instead of dropping the hydrogen pressure down to substantially atmospheric pressure to measure the amount passing over the catalyst per unit volume or per mole of material being hydrogenated, it is measured at full operating pressure by determining the amount of water displaced from the hydrogen-control tank on the right. This gives an accurate control and measure of the hydrogen passed over the catalyst and avoids reducing the hydrogen pressure—and a corresponding loss of hydrogen. With the use of a two-unit proportioning pump, water can be pumped into the hydrogen-control tank to bring it back to pressure and thus make up for the hydrogen consumed in the reaction. In this way, by careful working, the hydrogen lost is practically only that which is consumed in the reaction. It is also important to note that in this operation the ratio of hydrogen to the substance being hydrogenated is very large. This facilitates the hydrogenation reaction. The substance may flow through the reactor at only a fraction of

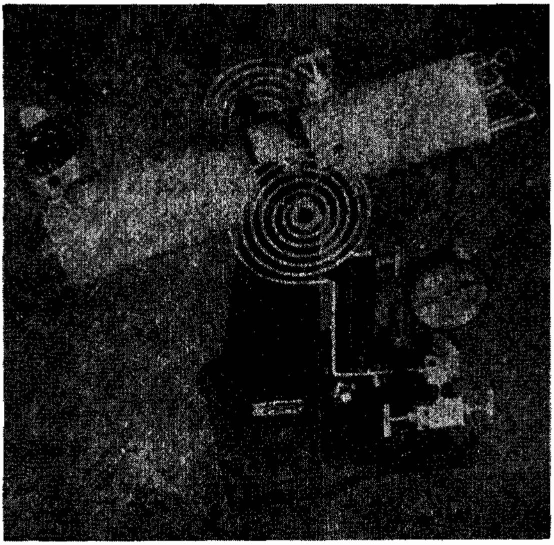

Fig. 10-4. Shaking autoclave for pressures to 15,000 psi.

an atmosphere partial pressure, whereas the partial pressure of hydrogen may be 100 or 200 atm. It has been found that hydrogenations in this type of setup proceed very satisfactorily at considerably lower pressures than when operating in a batch or autoclave type of apparatus. This is undoubtedly because the higher total pressure has been in part replaced by a higher ratio of the partial pressure of hydrogen to the partial pressure of the substance undergoing reduction.

In the operation of large units, heating of the ingoing materials is best accomplished by heat exchange with the outgoing materials and adding additional heat by means of high-pressure pipe coils. A pipe coil is the only convenient and efficient method of heating, for the reactor is usually so large that the heating of it is very difficult. It is usually better practice to add all the heat needed to the materials before they enter the reactor and then simply have the reactor properly insulated thermally. Hydrogenation reactions are usually exothermic, so that once the process is started, the problem may be one of heat removal. This is accomplished by allowing the heat of reaction to flow into the ingoing materials, by heat exchange in the reactor, or if it is still in excess, by recycling and cooling in heat exchangers the proper portion of the material to maintain the desired temperature.

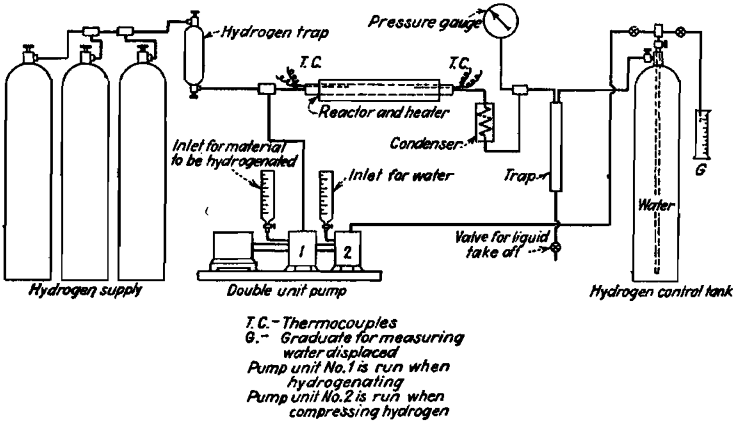

FIG. 10-5. Flow-system apparatus for hydrogenations.

Different types of forgings and tape-wound vessels for use as reactors for commercial operations, along with heat exchangers, types of closures, valves, and instrumentation are described in the literature.[1]

Valves are an important part of any high-pressure operation, and in coal

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[1] DODGE, in PERRY, "Chemical Engineer's Handbook," McGraw-Hill Book Company, Inc., New York, 1950, p. 1234; WILLIAMS, *Chem. Eng.*, **56** (8), 107 (1949); MACCARY and FEY, *Chem. Eng.*, **56** (8), 124 (1949).

hydrogenation they have to withstand hydrogen embrittlement, corrosion, creep at high temperatures, and erosion from solid-liquid mixtures at temperatures of 1000°F and pressures of 10,000 psig. Various special and ingenious designs have been worked out.[1]

VII. INDUSTRIAL PROCESSES

Of the many industrial applications of hydrogenation, only four will be described here: (1) the hydrogenation or hardening of vegetable or marine oils, (2) the synthesis of methanol, higher alcohols, and hydrocarbons from water gas, (3) the reduction of long-chain fatty acids to alcohols, and (4) the hydrogenation of hydrocarbons, mineral oils, and coal. These four processes cover a wide variety of catalysts used in hydrogenation reactions; they deal with the processing of raw materials in the form of solids, liquids, and gases; and they employ practically the entire range of pressures and the temperatures used in any sort of hydrogenation. Many additional industrial applications have been noted in other sections of this chapter.

Hydrogenation or Hardening of Fats

The purposes of the hydrogenation of vegetable and animal oils are (1) to produce a hard fat or one of greater consistency than the original liquid oil and (2) to remove certain impurities that are not removable by any other means, thus rendering the oil useful for purposes for which it could not otherwise be adapted. The process is essentially one of converting the glycerides of the unsaturated fatty acids into glycerides of saturated acids; thus, in the case of olein, the addition of six atoms, or only 0.68 per cent by weight, of hydrogen converts it into stearin:

$$(C_{17}H_{33}\cdot CO\cdot O)_3C_3H_5 + 3H_2 \rightarrow (C_{17}H_{35}\cdot CO\cdot O)_3C_3H_5$$

The reaction is carried out at temperatures from 100–250°C (212–480°F), at pressures usually less than 200 psi, with nickel as a catalyst. The processing of edible oils is usually carried out with considerable care and at lower temperatures in order to minimize undesirable side reactions.

Concurrently with hydrogenation, certain isomerization reactions invariably occur; of these, the one of greatest importance is the conversion of natural low-melting oleic acid which has the *cis* form to elaidic acid or other high-melting *trans* forms generally referred to as "iso-oleic" acids.

A variety of oils may be used in the process. There are glycerides not only of oleic acid but also of linoleic acid, the latter containing two double bonds instead of one, as in oleic acid. Furthermore, there are a number of

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[1] *Crane Valve World*, No. 3, 73 (1949), Crane Co., Chicago, Ill.

TABLE 10-15. PERCENTAGE COMPOSITION OF OILS USED IN HARDENING PROCESSES

Composition or property	Peanut	Cotton-seed	Corn	Soybean	Linseed
Oleic acid, %	50–70	23–33	45–49	21–34	21–38
Linoleic acid, %	13–26	39–48	34–41	49–59	3–23
Linolenic acid, %	Nil	Nil	Nil	2–8	26–58
Myristic acid, %	Nil	0.3–2	2	Nil	Nil
Palmitic acid, %	6–9	19–23	8–11	6–10	4–7
Stearic acid, %	2–6	1–3	2–4	2–4	2–5
Arachidic acid, %	2–5	0.1–1	0.4	0.7–1	0.2–1
Lignoceric acid, %	2–3	Nil	0.2	0.1	0–0.4
Unsaponified matter, %	0–0.3	0.9	2	0.6	0.5–2
Smoke point, °F	464	508	440	492	320
Fire point, °F	692	644	678	673	680
Flash point, °F	632	582	618	618	588
Iodine value	83–95	103–115	116–130	103–152	170–204

isomeric *oleins* in which the unsaturation is at different points in the long chain of carbon atoms. Each of these compounds or isomers behaves a little differently from the others on hydrogenation. In the case of marine oils, fatty acids of 14–24 carbon atoms are known to be present. Table 10-15 gives an approximate analysis of several of the more commonly used vegetable oils.[1]

When these oils are completely hydrogenated, solids result; when the oils are partially hydrogenated, fats of various consistencies or melting points are obtained. The degree of hydrogenation is readily determined for any given oil by the melting point, iodine-absorption number, or refractive index. Table 10-16 gives the melting points of some hydrogenated products.[2]

TABLE 10-16. MELTING POINTS OF COMPLETELY HYDROGENATED OILS

Oil	*Mp, °C*
Coconut	43–45
Whale	52–56
Cottonseed	62–63
Olive	68–69
Soybean	69–71
Castor	86–90

The process of hydrogenating a mixture of olein with more unsaturated glycerides such as linolein is selective; i.e., the linolein, or fatty acids con-

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[1] *Chem. Eng. News*, **23** (13), 1169 (1945).

[2] HILDITCH, "Catalytic Processes in Applied Chemistry," p. 226, D. Van Nostrand Company, Inc., New York, 1929.

taining two double bonds, is practically entirely converted into olein before this, in turn, is hydrogenated to stearin. In other words, during the hydrogenation of the more highly unsaturated oils, the reaction mixture passes through a stage where it is practically equivalent to an oleinic oil before it proceeds to complete saturation. This technique is also employed in the selective hydrogenation of small amounts of linoleic and linolenic acid constituents of tallow soaps that are used in conjunction with the production of butadiene-styrene copolymers.

This selectivity is not so apparent in the hydrogenation of whale and menhaden oils. In the hardening of these oils, a more abrupt change occurs at an iodine value of about 84, at which time nearly all the acids of more than two double bonds have disappeared. Below this point, hydrogenation results both in the formation of saturated acids and in the conversion of the C_{20} and C_{22} acids containing two double bonds to corresponding acids of one double bond. Thus, the hydrogenation of these marine oils is different from that of typical vegetable oils, in which substantial increases in the quantity of saturated acids present is coincident with the almost complete disappearance of acids containing more than one double bond.[1]

The oils to be hydrogenated should be reasonably free from materials likely to poison the catalyst. Impurities that may be present and that are poisonous to nickel are, in decreasing order of toxicity, organic sulfur compounds; oxidized unsaturated fatty compounds; colloidal suspensions of protein, of mucilage, etc.; moisture; and free higher fatty acids. Free fatty acids, up to about 3 per cent, do not seriously interfere. Moisture should preferably be kept low, because certain nickel catalysts tend to absorb water in preference to oils, and in the preparation of palatable oils, moisture is apt to produce undesirable materials through saponification. Organic sulfur compounds, although difficult to remove, are fortunately very seldom present in amounts to impair seriously the activity of the nickel. Oxidized materials and other colloidal and high-molecular-weight compounds can be removed either with an aqueous alkali wash or by adsorption, using certain earths or charcoals.

Nickel is by far the most commonly used catalyst in oil hardening. The catalyst problem consists of three phases: (1) preparation of a suitable catalyst, (2) maintenance of its activity as long as possible, and (3) recovery and reactivation of the spent catalyst. Nickel catalysts are of different types, depending upon the operation in which they are used. They may be in a relatively fine state, particularly in those processes where stirring or other agitation of the oil is used, or they may be supported on inert materials such as clays, kieselguhr, charcoal, or pumice, which extend the surface of the catalyst and facilitate the filtration of the catalytic mass from the oil. The decomposition of nickel formate produces a finely divided,

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[1] RICHARDSON, KNUTH, and MILLIGAN, *Ind. Eng. Chem.*, **17**, 80 (1925).

active, and practical catalyst.[1] Finally, in continuous processes, the nickel may be in a massive form, i.e., as turnings, wool, or screen which has previously been activated by special processes involving alternate oxidation and reduction to produce an active nickel surface.

There are numerous patents pertaining to apparatus and processes for hydrogenating oils. For the most part, these may be divided into three types: (1) a vessel nearly full of oil containing the catalyst in suspension through which hydrogen is circulated by mechanical means, possibly also with circulation of the oil to maintain the suspension of the catalyst, (2) a vessel full of hydrogen and oil in which an intimate mixture is attained without moving parts or stirrers, and (3) continuous processes in which the catalyst is maintained stationary and through which oil and hydrogen are continuously circulated.

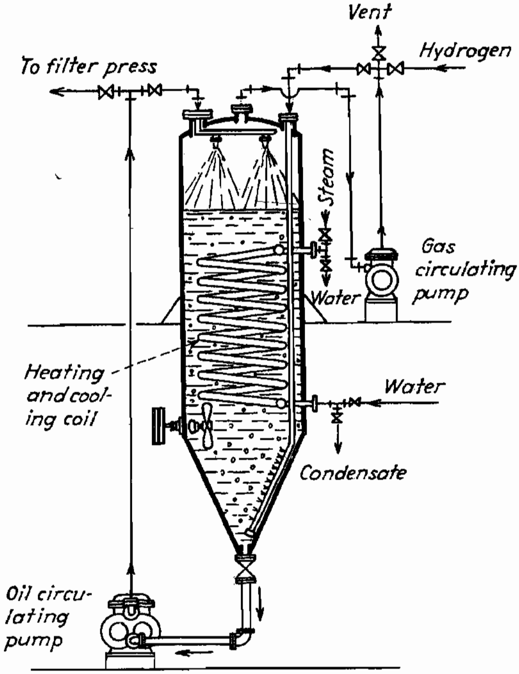

FIG. 10-6. Oil-hydrogenating unit with internal heating and cooling coil, gas-circulating pump, oil- and catalyst-circulating pump, and propeller-type mechanical agitator.

Apparatus belonging to the first type is shown in Fig. 10-6. It consists of a cylindrical tank, containing a helicoid, or spiral, propeller, driven by a pully. Hydrogen is admitted through a perforated pipe, and internal coils

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[1] WURSTER, *Ind. Eng. Chem.*, **32**, 1193 (1940).

provide ample means for heating or cooling the charge of oil contained in the vessel.[1]

Another apparatus pertaining to the second type is shown in Fig. 10-7. Here there are no moving agitators and consequently no stuffing boxes to leak.[2] This apparatus is built in various sizes, sometimes 20–30 ft tall. The essential features are intimate contact of the liquid and gas phases and the maintenance of this intimate contact over as large a portion of the whole bulk of oil as is practicable. The catalyst is suspended in the oil in a finely divided state. The oil and gas flow countercurrently through the tall mixing column, intimate contact being caused by the action of fixed propellerlike baffle plates, causing the oil and gas mixture to rotate alternately in opposite directions. In addition, the inclination of the baffles is such that they exert, along with the rotating motion, such an action on the hydrogen-oil mixture that this is alternately thrown toward the center of the column and its periphery.

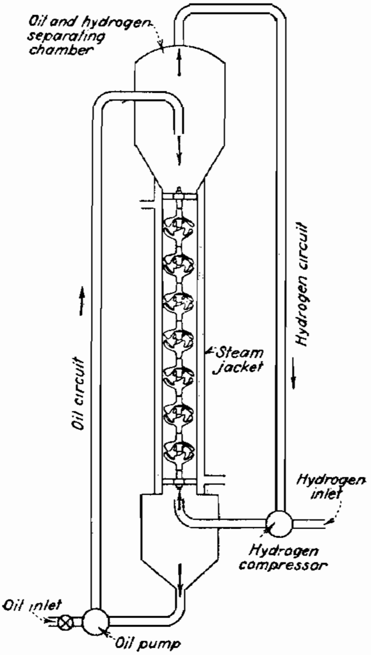

FIG. 10-7. Recycling apparatus for hydrogenating oils.

In operation, the column (Fig. 10-7) is filled with oil. It enters at the top and is recirculated by the pump. The enlarged section at the top serves to effect a separation of the intimate hydrogen-oil mixture so that hydrogen may be withdrawn at the top of the apparatus, repressured by the gas compressor, and then returned at the bottom of the column. The degree of mixing of hydrogen and oil may be varied by the rate at which the gas compressor and oil pump operate. A steam jacket serves to heat the charge and maintain suitable temperatures. This process is said to effect very rapid hydrogenation, for instance, of peanut or cottonseed oil, in 15–25 min, with an initial temperature of 130°C. Because of the rapid reaction at low temperature, this process is particularly applicable to hardening of oils for edible purposes, where the product must possess a good flavor. The usual working pressure is about 60 psig.[3]

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[1] *Ibid.*

[2] Maxted, U.S. 1,313,407 (1919).

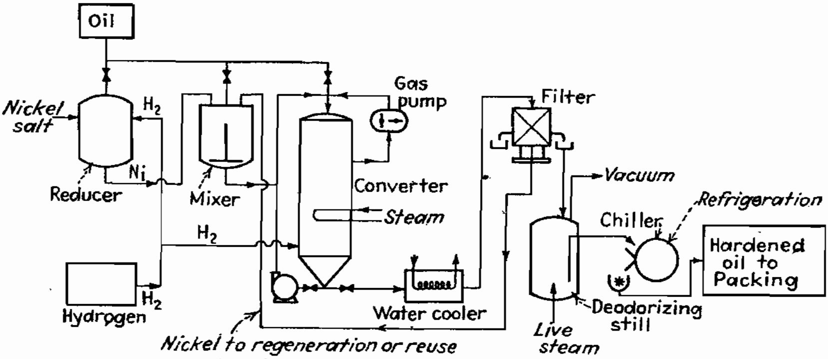
[3] ELLIS, "Hydrogenation of Organic Substances," 3d ed., p. 421, D. Van Nostrand Company, Inc., New York, 1930.

TABLE 10-17. VARIOUS PROCESSES FOR THE HYDROGENATION OF CARBON MONOXIDE*

Process	Catalysts	Pressure, atm	Temperature, °C	Products
Methanol	Zinc oxide, copper, chromia, manganese oxide	100–500	250–400	Largely methanol
Higher alcohol	Same as above except with alkali oxides or carbonates as promoters	100–500	300–400	Methanol, isobutyl alcohol, and others
Iso	Thoria with alumina and potassium carbonate	100–500	350–400	Alcohols as above plus small yields of branched hydrocarbons
Iso	Thoria with alumina and potassium carbonate	100–500	400–475	Branched hydrocarbon plus small yields of alcohols
Fischer-Tropsch	Iron + promoters	10–30	220–300	Olefins 90%; paraffins, alcohols, acids, ketones, and aldehydes 10%
Fischer-Tropsch	Fluidized iron	10–50	300–400	Olefins 90–75%, oxygenated compounds 10–25%
Fischer-Tropsch (Synol)	Iron + promoters	20	190–220	Olefins 50%, alcohols 50%
Fischer-Tropsch	Nitrided iron	10–30	190–200	Olefins + paraffins 40%, alcohols 60%
Fischer-Tropsch	Nickel	1	170–200	Largely methane
Fischer-Tropsch	Cobalt	1	250–450	Largely methane
Fischer-Tropsch	Cobalt	1–15	170–210	Largely paraffins hydrocarbons
Fischer-Tropsch	Ruthenium	1–15	170–200	Largely solid paraffin wax

* ANDERSON, FELDMAN, and STORCH, *Ind. Eng. Chem.*, **44**, 2418 (1952).

The third type, or continuous process, involves the use of a massive or rigid catalyst over which the hydrogen-oil mixture passes. This procedure obviates the use of filtration for removing the catalyst from the oil and, with respect to its capacity, usually makes the plant more compact. The nickel catalyst is in the form of a wire screen or turnings contained in tubes or reactors. The hydrogen-oil mixture may flow in the same or in countercurrent directions. Generally, more than one reactor is used, and these are provided with suitable connections so that they may be operated in series or in parallel with one another. This permits either the capacity or extent of hydrogenation to be varied readily. The process developed by Bolton and Lush uses a nickel catalyst in the form of turnings or wire, prepared in a special way.[1] In order to get active nickel, the nickel metal is oxidized by means of anodic oxidation; i.e., the nickel wires or turnings are made the anode, an electrolyte such as sodium carbonate being used. This does not allow the nickel to pass into solution but converts the surface into nickel oxides, which are then subsequently reduced by hydrogen under carefully controlled conditions. The conditions of operation during hydrogenation are about 180°C and 60–100 psig hydrogen pressure. The catalyst maintains its activity for relatively long periods of time, but when it needs reactivation the anodic oxidation is again used, the activity of the catalyst being restored on reduction.



Requirements per Pound of Hardened Oil

Refined cottonseed oil	*0.134 gal.*	*Cooling water*	*0.6 gal.*
Nickel	*0.00075 lb.*	*Steam*	*0.5 lb.*
Hydrogen	*0.75 cu. ft.*	*Electricity*	*0.1 kw.-hr.*
Direct labor	*0.0006 man hr.*		

Fig. 10-8. Flow sheet for hydrogenation of cottonseed oil.

In all the various processes for oil hardening, the quantity of nickel used is generally less than 1 per cent by weight of the oil hardened. In those operations where the nickel catalyst needs to be removed from the oil, it is

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[1] *Ibid.;* Bolton, *J. Soc. Chem. Ind.*, **41**, 384R (1922); **46**, 444T (1927); Lush, *ibid.*, **42**, 219T (1923); **43**, 53T (1924); **44**, 129T (1925); **46**, 454T (1927).

usually done by filtration of the hot liquid fat. The catalyst is then washed, redissolved, and reused in preparing fresh catalyst. Thus, except for small mechanical losses, the catalyst is continually reused.

The total nonequipment cost for hydrogenating fats and oils amounts to about $3.60 per ton; this value represents about 25 per cent of the total project cost.[1]

Figure 10-8 is a flow diagram for the hydrogenation of cottonseed oil.

Synthesis of Methanol, Higher Alcohols, and Hydrocarbons

Carbon monoxide may be hydrogenated to produce either alcohols or hydrocarbons, depending on the catalysts used and the reaction conditions. Temperatures ranging from 100–400°C and pressures as high as 1,000 atm have been studied. Different catalysts yield radically different types of products. Important processes for such reactions consist of the methanol synthesis, the higher-alcohol synthesis (or the variation termed the iso synthesis), the Fischer-Tropsch reaction (or the version called hydrocarbon synthesis), and the methanation reaction. These syntheses were discovered in the period 1920–1925, at which time the methanol and higher-alcohol syntheses developed rapidly. A brief summary of processes and conditions used for the hydrogenation of carbon monoxide is presented in Table 10-17.

The Methanol Synthesis. The synthesis of methanol from carbon monoxide and hydrogen is a reversible reaction and has been the subject of several investigations. The following values of the equilibrium constant are available:[2]

$$K_p = \frac{P_{\mathrm{CH_3OH}}}{P_{\mathrm{CO}} \times P^2_{\mathrm{H_2}}}$$

TABLE 10-18. EQUILIBRIUM CONSTANT (K_p) FOR THE METHANOL SYNTHESIS

Temperature, °C	K_p
260	1.5×10^{-3}
300	3.1×10^{-4}
340	8.7×10^{-5}
380	2.7×10^{-5}

These data show that the equilibrium constant is small and that it decreases rapidly with temperature. Consequently, the temperature interval over which the synthesis is operative from a practical viewpoint is not very large. At temperatures much below 300°C (572°F), the rate of reaction is slow, so that the capacity of the apparatus is small. Above

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[1] KISTEN, CAMERON, and CARTER, *Chem. Eng.*, **60**, 191 (November, 1953).

[2] NEWTON and DODGE, *J. Am. Chem. Soc.*, **56**, 1287–1291 (1934).

400°C (752°F), the equilibrium becomes too unfavorable. Despite the small values of the equilibrium constant, very satisfactory conversions are obtained. This is because of the decrease in volume attending the reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

so that by the application of pressure, the reaction is driven to the right, or to higher conversions. Thus, at 300°C and 3,500 psig, using the theoretical mixture, i.e., 1 vol. of carbon monoxide to 2 of hydrogen, the equilibrium yield is above 60 per cent, whereas under exactly the same conditions but working at 150 lb pressure, the yield is less than 2 per cent. The pressures used in this synthesis are usually 3,000–4,000 psig.

Along with the synthesis of methanol, other side reactions, or parasitic reactions, are possible. Some of these are

$$CO + 3H_2 \rightarrow CH_4 + H_2O + 50{,}000 \text{ cal}$$
$$2CO + 2H_2 \rightarrow CH_4 + CO_2 + 60{,}280 \text{ cal}$$
$$2CO \rightarrow C + CO_2 + 41{,}950 \text{ cal}$$
$$xCO + yH_2 \rightarrow \text{high-molecular-weight alcohols, hydrocarbons, etc.}$$

The first of the above reactions is called *methanation* and is important in removing small quantities of carbon monoxide (or carbon dioxide) from a hydrogen stream. The reaction proceeds almost quantitatively so that the carbon monoxide removal is essentially complete in one pass. Since the reaction consumes 3 vol. of hydrogen and produces methane, it is not used with hydrogen containing more than a few tenths of a per cent of carbon monoxide. Carbon monoxide is an active poison for nickel catalysts used in hydrogenation and for this reason must be removed. Although synthesis gas can be converted to methane, the process is not economical at present and may not be until the demand for natural gas substitutes increases.

Methane also results from the reduction of carbon dioxide by hydrogen, according to the reaction[1]

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

This equilibrium has been studied.[2] Using a catalyst consisting of 73 per cent charcoal and 27 per cent nickel, which resulted from carbonizing a mixture of sugar and nickel acetate, the decomposition of carbon monoxide into carbon and carbon dioxide was entirely suppressed and the catalyst maintained its activity for months in producing methane. Ferric oxide, vanadium pentoxide, and cerium oxide are promoters for the nickel-charcoal catalyst. Studies have also been made of the various reactions involved in the reduction of carbon monoxide and dioxide.[3]

The second of the four reactions listed above takes place at about 250°C

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[1] Sabatier and Senderens, *Compt. rend.*, **134**, 514, 689 (1902).

[2] Randall and Gerard, *Ind. Eng. Chem.*, **20**, 1335 (1928).

[3] Hightower and White, *Ind. Eng. Chem.*, **20**, 10 (1928).

over a nickel catalyst when the ratio of hydrogen to carbon monoxide is lower than that needed for the synthesis of methanol. With even less hydrogen and at higher temperatures, carbon monoxide reacts according to the third equation to form carbon dioxide. Consequently, there is carbon deposition on the catalyst and loss in activity.

Not only do the above reactions consume carbon monoxide and hydrogen, but they also make control more difficult, for they are more exothermic than the methanol reaction. Such reactions as the last of the four listed above tend to build up heavy nonvolatile materials, which impair the catalyst's activity. In this synthesis, a catalyst is selected that causes reduction principally to methanol, and a variety of materials are now known to do this surprisingly well, with practically complete exclusion of the side reactions.

The carbon monoxide–hydrogen mixture traditionally was generated from coke, steam, and air by the water-gas method, but this process has been supplanted by steam-hydrocarbon reforming and by the partial oxidation of natural gas. More recently, processes for producing synthesis gas by the partial oxidation of pulverized coal have been introduced.

The cost of synthesis gas is a major item. It is generally believed that the synthesis step should be conducted at a pressure of several hundred pounds and that it is most economical to generate the gas under pressure rather than at atmospheric pressure followed by compression.

In instances where carbon dioxide–hydrogen mixtures are available, methanol is made from these under practically the same conditions as would be used for carbon monoxide–hydrogen mixtures. The reaction

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

produces a methanol-water solution instead of pure methanol. Despite the apparent simplicity of the raw materials, a large variety of complex organic products can be readily obtained by only minor changes in the catalyst and operating conditions. This is because condensation as well as hydrogenation reactions occur.

The catalyst is contained in special reactors (Fig. 10-9) designed to withstand the pressures and temperatures used. By heat interchange either in the reactor or in special heat exchangers, the heat of the reaction—some 24,620 cal per g mole of methanol formed—is absorbed. Some of this is used to heat the entering gas to reaction temperature. By proper choice of the space-time yield or, in other words, the amount of methanol produced per volume of catalyst per hour and the amount of heat removed in the heat exchangers, the temperature of the catalyst can be kept reasonably constant. Once started, the reaction is self-supporting; i.e., the problem is one of heat removal and not addition.

The methanol-containing gases leave the reactor and, after passing through heat exchangers (not shown in Fig. 10-9), are finally led through condensers where the methanol is condensed, usually under full operating pressures (3,000–4,000 psig). This procedure frees the gas more completely of methanol than if the condensation took place at lower pressure. Any drop in pressure in the reactor and cooling system is repressured by *booster compressors.* If a gas mixture other than the 1:2 ratio of carbon monoxide: hydrogen is used, the composition of the gases must be continually adjusted as it is recycled, and provision must also be made for venting inert or other gaseous side-reaction products. It has been found that the partial pressure of carbon monoxide is the dominant factor upon which the rate of fouling of the catalyst depends owing to adsorption of high-molecular-weight nonvolatile compounds. For this reason, a higher hydrogen:carbon monoxide ratio than the theoretical one of 2:1 is sometimes used.

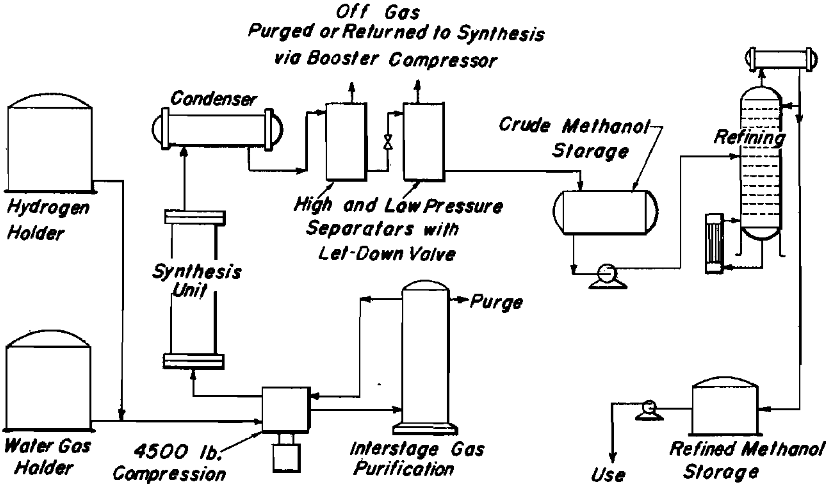

FIG. 10-9. Flow sheet for the synthesis of methanol from carbon monoxide and hydrogen.

The catalysts usually consist of metal and metallic oxide mixtures, the most common constituents being copper with oxides of zinc, chromium, manganese, and aluminum.[1] Zinc chromate is typical of the catalysts used.[2]

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[1] FROLICH, FENSKE, and QUIGGLE, *Ind. Eng. Chem.*, **20**, 694 (1928); FENSKE and FROLICH, *ibid.*, **21**, 1052 (1929); LAZIER and VAUGHEN, *J. Am. Chem. Soc.*, **54**, 3084 (1932); LEWIS and FROLICH, *Ind. Eng. Chem.*, **20**, 285 (1928); FROLICH, FENSKE, TAYLOR, and SOUTHWICK, *ibid.*, **20**, 1327 (1928); CRYDER and FROLICH, *ibid.*, **21**, 867 (1929); AUDIBERT and RAINEAU, *ibid.*, **20**, 1105 (1928); HUFFMAN and DODGE, *ibid.*, **21**, 1056 (1929); BROWN and GALLOWAY, *ibid.*, **20**, 960 (1928); SMITH and BRANTING, *J. Am. Chem. Soc.*, **51**, 129 (1929); NEWITT, BYRNE, and STRONG, *Proc. Roy. Soc. (London)*, **123A**, 236 (1929); HIRST, Methanol Synthesis from Water Gas, chap. XL in LOWRY, "Chemistry of Coal Utilization," vol. II, pp. 1846–1868, John Wiley & Sons, Inc., New York, 1945.

[2] *F.I.A.T. Final Rept.* 888 (Field Information Agency Technical).

For the synthesis of methanol alone, contact of the hot gases with iron should be avoided. In this case, the reactors are lined, usually with copper or some other material not affecting the catalyst. The catalysts for pure methanol are usually susceptible to iron carbonyl, formed when carbon monoxide is in contact with iron. This impairs the activity of the catalyst or else induces undesirable side reactions. Practical operations usually involve the production of other alcohols along with methanol. In this case, a somewhat different type of catalyst is used; the presence of iron is not particularly objectionable, since it also catalyzes the formation of higher alcohols from carbon monoxide–hydrogen mixtures.

The methanol synthesis is a striking case of the selectivity, or preferential character, of catalysts. The methanol catalysts readily reduce carbon monoxide to methanol with only a trace of methane, even though the temperature is 375°C and pressures are as high as 4,000 psig. On the other hand, carbon monoxide in contact with an active nickel catalyst results in a violent reduction to methane at temperatures of 200°C and atmospheric pressure. The methanol type of catalyst, for some reason, is incapable of carrying the reduction to completion, viz., to methane. Consequently, they are finding extensive application where mild hydrogenation conditions are needed.

With the proper catalyst and the exclusion of sulfur and iron, methanol of a purity of 99 per cent or better can be produced. As an alternative, methanol may result as part of the synthesis of other valuable higher alcohols, where the exclusion of iron is no longer necessary. The largest single use of methanol is for the preparation of formaldehyde, this product consuming some 45 per cent of the production. About 40 per cent of the production is used as an antifreeze, about 5 per cent as a denaturant, about 5 per cent in the manufacture of dimethylaniline and dimethylamine, and about 5 per cent as a solvent and for miscellaneous uses.

Higher alcohols are produced when operating temperatures are slightly higher (350–475°C) than those used in the methanol synthesis and with methanol catalysts containing alkalies or else iron-base catalysts containing alkalies. The reaction product may be so complex that complete separation and identification of the constituents are very difficult. Of course, the lower-molecular-weight alcohols are more readily separated and identified, and for this reason, this synthesis has been one of the principal sources of solvents for nitrocellulose and resinous products.

Although the mechanism of the formation of these higher alcohols is not entirely understood and several theories have been suggested, the following method of formation appears the most probable. Certain steps in it have been demonstrated experimentally.[1] This scheme involves three simple assumptions: (1) higher alcohols result from intermolecular dehy-

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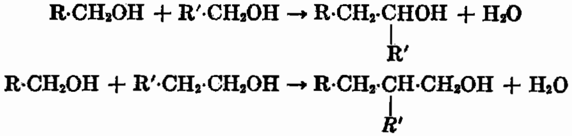
[1] GRAVES, *Ind. Eng. Chem.*, **23**, 1381 (1931); FROLICH and CRYDER, *ibid.*, **22**, 1057 (1930).

dration of two lower alcohol molecules, (2) dehydration involves removal of hydrogen either from the hydroxylated carbon atom, thus producing secondary alcohols (except in the case of methanol), or from the carbon atom adjacent, producing primary alcohols, (3) hydrogen separates most readily from a $>CH_2$ group, with more difficulty from a $-CH_3$ group, and not at all from a $\equiv CH$ group. For example,



$$R{\cdot}CH_2OH + R'{\cdot}CH_2OH \rightarrow R{\cdot}CH_2{\cdot}\underset{\displaystyle R'}{\underset{|}{C}}HOH + H_2O$$

$$R{\cdot}CH_2OH + R'{\cdot}CH_2{\cdot}CH_2OH \rightarrow R{\cdot}CH_2{\cdot}\underset{\displaystyle R'}{\underset{|}{C}}H{\cdot}CH_2OH + H_2O$$

The higher alcohol mixture has been found to contain the following primary alcohols: *n*-propanol, isobutanol, 2-methyl-1-butanol, 2-methyl-1-pentanol, 2,4-dimethyl-1-pentanol, 4-methyl-1-hexanol; and the following secondary alcohols: isopropanol, 3-methyl-2-butanol, and 2,4-dimethyl-3-pentanol. In addition, there are definite indications of 2,4-dimethyl-1-hexanol, 4 or 5-methyl-1-heptanol, 3-pentanol, 2-pentanol, and 2-methyl-3-pentanol.[1]

The iso synthesis, which is a variation of the higher-alcohol process, produces in addition to the higher alcohols, branched-chain and cyclic hydrocarbons. The catalyst used consists chiefly of thoria. When promoted with alkali, the catalyst is useful in increasing the average molecular weight of the products. At 400°C the iso synthesis produces a mixture of alcohols and hydrocarbons, whereas at 450°C hydrocarbons (largely isobutane) are the principal products.

Synthesis of Liquid Hydrocarbons by the Reduction of Carbon Monoxide. When carbon monoxide–hydrogen mixtures are passed over cobalt, iron, nickel, and some copper catalysts that are promoted with certain metallic oxides, particularly oxides of the alkali metals, at temperatures in the range from about 200–300°C and pressures from about 1–25 atm, various hydrocarbons are formed according to the following type of reactions:

$$xCO + \left(x + \frac{y}{2}\right) H_2 = C_xH_y + xH_2O$$

$$2xCO + \left(\frac{y}{2}\right) H_2 = C_xH_y + xCO_2$$

These hydrocarbons may contain 1–50 or more carbon atoms in varying degrees of saturation with hydrogen. They may comprise chain or ring systems that are saturated or unsaturated. These reactions, known as the Fischer-Tropsch synthesis of hydrocarbons, are important and have great potentialities. It is estimated that nearly a million tons of fuel

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[1] GRAVES, *Ind. Eng. Chem.*, **23**, 1381 (1931).

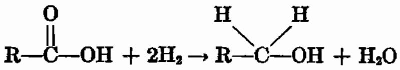
was produced annually in Germany in 1940–1943 by this method. This procedure enables coals, coke, tars, and refinery and natural gas to be converted into gasoline, diesel fuel, and wax as the main products. The olefinic products can be polymerized to synthetic lubricating oils or utilized by the Oxo process to make alcohols, or the paraffinic materials can be oxidized to produce fats and detergents. The fuels can have a wide range of octane or cetane numbers.

The original German process gave a product containing less than 1 per cent of oxygenated compounds. However, modifications of the process used in this country are referred to as "hydrocarbon synthesis," and generally the process is conducted to yield considerable proportions of oxygenated compounds as well as hydrocarbons. Full details on the process are presented in Chap. 11.

Hydrogenation of Acids or Esters to Alcohols

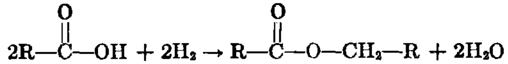
The direct reduction of the carboxyl group to an alcohol by means of molecular hydrogen and catalysts occurs at temperatures usually from 300–400°C (570–750°F) and with hydrogen pressures of about 3,000 psig. The acids or esters may be of the long straight-chain type such as occur in vegetable oils and fats, or they may be of the shorter-chain type, with more complicated groupings or branchings. The oil-hardening processes use long-chain acids and esters and saturate only the olefinic linkages in the carbon chain; in the reductions to be described here, the carboxyl group (—COOH) is changed to an alcohol group (—CH_2OH), and the olefinic bonds in the chain may or may not be reduced at the same time. This is again an illustration of the remarkable specificity of catalysts; normally, the olefinic bonds would be considered far more reactive in hydrogenations than a carboxyl group. Yet they may not be reduced while the carboxyl group is being converted to an alcohol.

The earlier methods of reducing acids or esters to alcohols involved the use of metallic sodium with anhydrous alcohols; also, an acid derivative, such as the acid chloride, could be reduced by direct hydrogenation to an aldehyde by palladium catalysts. The direct reduction, using molecular hydrogen at high pressure, involves 2 moles of hydrogen per mole of acid reduced, as shown in the following reaction:



$$R-\overset{\overset{O}{\|}}{C}-OH + 2H_2 \rightarrow R-\overset{H\quad H}{C}-OH + H_2O$$

where R represents a group preferably of the aliphatic or the hydroaromatic series. A secondary reaction consists of esterfication of a portion of the alcohol formed with a portion of the unchanged acid. The proportion of ester present in the product depends chiefly on the completeness of the hydrogenation. When the reaction is conducted under conditions that yield only partial reduction of the acid, the process may be altered to give esters as the main products, according to the equation:



$$2R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 2H_2 \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-R + 2H_2O$$

If R in these formulas contains an unsaturated or olefinic bond, partial reduction of the carbon-carbon unsaturation may occur. It is sometimes more suitable to conduct the reaction to favor alcohol or ester formation and then further reduce the olefinic bonds at lower pressures and temperatures with nickel catalysts in the same manner as that used in hardening oils. This brings all the reaction products to the same completeness of hydrogenation, yielding new compositions—usually solids—from which alcohols and esters may be separated if desired. The stability of high-molecular-weight acids and alcohols under high-pressure hydrogen at high temperatures is very different from that which would be expected when heating these compounds in air. Decarboxylation of the acid to form carbon dioxide and a hydrocarbon of fewer carbon atoms does not occur in hydrogenation. The dehydration of the alcohol to an olefin, or the more complete reduction of the—CH_2OH to a—CH_3 group, occurs only slightly. However, this is dependent on the other groups near the alcohol group; with straight hydrocarbon chains, these decompositions occur to a very minor extent.

The reductions may be carried out in a batch system or in a flow system, the latter being preferable. The catalyst in granular form is held in place in a heated tube capable of withstanding the pressure and temperature. The acid or ester, if solid, may be melted or may be dissolved in a solvent such as normal butyl alcohol or ethyl alcohol, and it is then pumped into the reactor and over the catalyst. The use of acids or esters of the acids and simple alcohols is preferable to the use of the glycerides, because the presence of glycerol and its decomposition products makes the separation of the reaction products difficult. The acid or ester is pumped through the reactor at the rate of 2–8 vol. of material per volume of catalyst per hour, a considerable excess of hydrogen being passed along with the material over the catalyst. From 2–10 moles of hydrogen is used per mole of acid hydrogenated.[1] The proportion of esters to alcohols produced in the hydrogenation will depend on the ratio of hydrogen to the acid being reduced.

An active catalyst for hydrogenating the lauryl ester of coconut oil fatty acid is made by decomposing copper-ammonium chromate at 350–400°C. A 90 per cent hydrogenation is obtained in 2 hr by operating at 275°C and 3,000 lb hydrogen pressure.[2] Coconut oil is one of the vegetable oils commonly hydrogenated to produce alcohols. In this case, the result-

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[1] Lazier, U.S. 1,839,974 (1932).

[2] Reiner, *J. Am. Chem. Soc.*, **71**, 1130 (1949).

ant alcohols comprise octyl, decyl, lauryl, myristyl, cetyl, and stearyl. They are valuable chemicals used in the manufacture of detergents, petroleum additives, solvents, and plasticizers.

Hydrogenation of Hydrocarbons, Petroleum, Tar, and Coal

The purposes of hydrogenating hydrocarbons, petroleums, tars, and coals are (1) to improve existing petroleum products or develop new uses and products, (2) to convert inferior or low-grade materials such as heavy oils and tars into valuable petroleum products, and (3) to transform solid fuels such as lignites and coals into liquid fuels. The distinguishing feature of these operations is that both the raw materials and finished products are very complex mixtures of relatively unknown composition. All types and sizes of molecules are present along with a variety of contaminating impurities. Thus, in the hydrogenation process, a variety of reactions may be occuring simultaneously and to varying extents, and yet the final product may be very satisfactory, meeting all the required specifications.

These complicated mixtures are identified and recognized by certain properties, sometimes more physical than chemical in character. Thus, gasoline specifications are concerned with sulfur content, gum-forming materials, general stability and resistance to chemical change or oxidation, and detonation and volatility characteristics. Kerosenes are identified by their sulfur content, specific gravity, burning qualities, and volatility. Lubricating oils are judged by their stability toward heat and oxidation, their carbon-forming tendencies, lubricating qualities, viscosity characteristics, color, and volatility. Tars are recognized by their aromatic and phenolic hydrocarbon content, their specific gravity, volatility, and viscosity. Coals are classified according to their age; ash content; the carbon, hydrogen, nitrogen, oxygen, and sulfur analysis; and the volatile matter. Hydrogenation of fuels is a relatively old art and may result in an upgrading of one or all of the properties of the material. In processing petroleums, tars, and coals, the operation is far more complex than in working with pure or relatively pure materials.

Catalysts must not only speed up these hydrogenations but also must guide and direct the desired reactions and effect a balancing and harmonizing of many factors so that the correct over-all result is attained. They must also be able to operate on liquid, solid, or gaseous materials and, in addition, cause impurities that are common catalytic poisons, such as sulfur, oxygen, and nitrogen, to be detached from their molecular linkages and removed as hydrogen sulfide, water, or ammonia. All these things the hydrogenation catalysts must do rapidly and at relatively low temperatures. Although at first it may seem incredible, catalysts are now known that perform all these functions satisfactorily.

The extent to which these catalysts increase the velocity of hydrogenation is indicated in the case of effecting improvements in lubricating oils.[1] At 200 atm pressure, there was no improvement without catalysts; and even at 1,000 atm without catalysts, the improvement, if any, was very slight. The hydrogenation velocity in the presence of catalysts and about 200 atm pressure is, however, about 100 times greater than without catalysts. In the conversion of heavy, nonvolatile materials into lighter products such as gasoline, the catalyst must favor cracking reactions as well as hydrogenation reactions. Yet these two must be in the proper balance. Cracking must not proceed faster than the hydrogenation of the cracked products; condensation and polymerization of unsaturated or reactive molecular fragments must not proceed faster than their hydrogenation. Otherwise, high-molecular-weight products would accumulate on the surface of the catalyst, decreasing or completely destroying its activity. With the conditions of temperature, pressure, and catalyst delicately coordinated, complex hydrogenations proceed with surprising smoothness.

TABLE 10-19. EXOTHERMIC HEAT OF REACTION OF DIFFERENT HYDROGENATION REACTIONS

Reaction	Raw material	
	Cal/g	Btu/lb
Hexane + $H_2 \rightarrow$ methane	730	1315
Bituminous coal + $H_2 \rightarrow$ light oil	450	810
Middle oil from bituminous coal + $H_2 \rightarrow$ gasoline	400	720
High-boiling crude-oil fraction + $H_2 \rightarrow$ lubricating oil	50	90
N_2 + $H_2 \rightarrow$ ammonia	750	1350
CO + $H_2 \rightarrow$ methanol	700	1260

Hydrogenations are usually exothermic, but the amount of heat liberated depends on the proportion of hydrogen consumed and the nature of the process. In petroleum reforming and hydrotreating processes in which the hydrogen consumption is low, heat is usually supplied to the reaction. Table 10-19 sets forth some of the approximate quantities of heat liberated by different hydrogenations.[2]

The hydrogen consumed in the process obviously depends on the difference in hydrogen content of the raw material and finished product and on the extent to which gases containing methane and other low-boiling hydrocarbons are formed. In the hydrogenation of bituminous coals and tars derived from such coals, 8–16 cu ft of hydrogen is required per pound of

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[1] GRIMM, *Intern. Conf. Bituminous Coal*, II, 49 (1931).

[2] SCHLATTMANN and KOPPENGERG, *Natl. Petroleum News*, **28** (37), 24E (1936); HOLLADAY, ALBRIGHT, APJOHN, and STEFFENS, *Petroleum Processing*, **4** (11), 1233 (1949).

coal. In crude oils, poor in hydrogen, the consumption is about 3–6 cu ft of hydrogen per pound of oil, but in oils rich in hydrogen, 0.5–2 cu ft per lb is consumed. These data are for reductions in which no gaseous products form.

The additional hydrogen consumption for gasification depends on the extent of the hydrogenation, whether paraffinic or aromatic products are formed, and the hydrogen content of the raw materials. In processing coal or coal tars, the hydrogen consumed in making gaseous products such as methane and its homologues is about 0.3–0.4 cu ft per lb of charging stock for each 1 per cent of gaseous products; in processing petroleum, brown-coal tars, and the light oils, the gaseous products use about 0.15–0.25 cu ft of hydrogen per pound of material charged.

The yield of liquid reaction products will depend on the amount of gasification during hydrogenation. A yield of 55 per cent by weight or more of marketable gasoline appears possible by hydrogenating brown coals or lignites. With suitable bituminous coals, it may be 65 per cent by weight or more. These figures are for the ash-free dry coal. In the case of tars, the yield may be 80–85 per cent by weight, which is over 100 per cent yield by volume.

In operating hydrogenation processes, it has been found advantageous to divide them into two parts: (1) liquid-phase reactions, where pulverized coal and *pasting* oil or heavy oils are contacted with hydrogen, and (2) gas-phase reactions, where the light oil exists practically entirely in the gas phase during hydrogenation. It has been found, in processing heavy oils or in processing coals in one step, that the extent of hydrogenation was insufficient and the yield low because heavy materials tended to be preferentially adsorbed, thus excluding the light oils from hydrogenation. Under these conditions, the latter accumulate; instead of being hydrogenated to gasoline, uncontrolled cracking and polymerization reactions take place. The polymerization of unstable materials produced by cracking builds up high-molecular-weight compounds, resulting in low yields of gasoline. These difficulties are avoided in the two-step operation for producing gasoline. Materials with normal boiling points below about 300–350°C (570–660°F) are used in the gas-phase operation; those boiling higher than this are hydrogenated in the liquid phase.

Petroleum Hydrogenation. Hydrogenation processes for the conversion of petroleum oils and petroleum products may be classified as destructive and nondestructive. Destructive hydrogenation (hydrogenolysis or hydrocracking) is characterized by the cleavage of carbon-to-carbon linkages accompanied by hydrogen saturation of the fragments to produce lower boiling products. Such treatment requires severe processing conditions and the use of high hydrogen pressures to minimize polymerizations and condensations leading to coke formation. Many other reactions such as isomerization, dehydrogenation, and cyclization occur under the drastic conditions employed. Processing under these severe conditions is generally referred to as "catalytic reforming." Many commercial reforming processes are in operation under such names as Hydroforming, Catforming, Houdriforming, Hyperforming, Platforming, Ultraforming, Powerforming, etc.

Nondestructive or simple hydrogenation is generally used for the purpose of improving product quality without appreciable alteration of boiling range. Mild processing conditions are employed so that only the more unstable materials are attacked. Thus, nitrogen, sulfur, and oxygen compounds undergo hydrogenolysis to split out ammonia, hydrogen sulfide, and water, respectively; olefins are saturated; unstable compounds such as diolefins, for example, which might lead to the formation of insolubles are converted to more stable compounds; and any heavy metals present are removed. Treatment under such mild conditions is generally called "hydrotreating" or "hydrofining." Commercial processes for hydrotreating are Hydrofining, Unifining, Hydropretreating, Hydrodesulfurization, Hydrotreating, Gulfining, etc.

Hydrotreating is being employed extensively in the petroleum industry for processing a variety of feedstocks.[1] Both straight-run and cracked petroleum products such as naphthas, kerosenes, middle distillates, gas oils (atmospheric and heavy vacuum types), cycle stocks, residues, asphalts, crudes, and shale oils may be so treated. The process primarily is employed as a "pretreat" previous to catalytic reforming or catalytic cracking.

Hydrotreating of feeds intended for further processing is desirable to the extent that the principal contributors to poor product quality or refining characteristics are eliminated; this assures protection of the expensive catalysts employed in reforming and cracking reactions. Undesirable effects produced by certain types of contaminates are itemized below:

Unsaturates: poor fuel stability, color degradation, lower catalytic cracking efficiency.

Sulfur: poor odor, decreased tetraethyllead susceptibility in gasoline, corrosion of processing equipment, deactivation of catalysts.

Oxygen: poor fuel-storage stability.

Nitrogen: lower catalytic cracking efficiency, poor odor, color degradation, corrosion of processing equipment.

Metals: deactivation of catalysts.

Hydrotreating is carried out by charging the feed to the reactor together with a portion or all of the hydrogen produced in the catalytic reformer. Catalysts suitable are tungsten-nickel sulfide, cobalt-molybdenum-alumina, nickel oxide-silica-alumina, and platinum-alumina. Most processes employ

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[1] *Petroleum Processing*, **11** (11), 116 (1956).

cobalt-molybdena catalysts which generally contain about 10 per cent of molybdenum oxide and less than 1 per cent of cobalt oxide supported on alumina. The temperatures employed are in the range of 300–450°C, while the hydrogen pressures are about 500–1,000 psig. The volume yields usually are 100 per cent or greater.

The reaction generally takes place in the vapor phase but, depending on the application, may be a mixed-phase reaction. The reaction products, after leaving the reactor, are cooled in a heat exchanger and led to a high-pressure separator where hydrogen gas is separated for recycle. Liquid product from the high-pressure separator flows to a low-pressure separator or stabilizer where dissolved light gases such as hydrogen sulfide are removed. The product then may be fed if desired to a reforming or cracking unit. Generally, it is more economical to hydrotreat high-sulfur feedstocks prior to catalytic cracking than to hydrotreat the products from catalytic cracking. The advantages are (1) the products require less finishing, (2) since sulfur is removed from the catalytic cracking feedstock corrosion is reduced in the latter unit, (3) carbon formation during cracking is reduced and higher conversions result, and (4) the catalytic cracking quality of the gas-oil fraction is improved. Typical results obtained by hydrotreating are given in Table 10-20.

TABLE 10-20. HYDROTREATING OF TYPICAL NAPHTHAS*
(Operating Pressure, 400 psig)

	Virgin charge	Naphtha product	Thermal charge	Naphtha product
Gravity, °API	52.9	52.8	47.9	50.4
Gravity, specific at 60°F	0.767	0.768	0.789	0.778
ASTM distillation, °F:				
Initial boiling point	....	.....	264	260
10%	289	280	278	276
50%	320	309	302	301
90%	366	355	350	352
End point	384	384	382	384
Composition, vol. %				
Paraffins	64	63	25	45
Olefins	1	1	43	2
Naphthenes	20	21	17	38
Aromatics	15	15	15	15
ASTM octane No. (research method):				
Clear	23.5	33.5	70.0	46.8
With 3 ml TEL†	46.1	58.5	83.3	63.6
Sulfur content	0.10	0.003	0.116	0.003
% Desulfurization	.....	97	.....	97

* STEVENSON and MILLS, *Proc. Am. Petroleum Inst.*, **35** (III), 328 (1955).

† TEL = tetraethyllead.

The data of Table 10-20 clearly show that the most important change produced by hydrotreating is the reduction in sulfur content. Olefins if present also are reduced, but aromatics are unaffected. Further, the boiling point of the feedstock is essentially unchanged.

Hydrogenation of the olefinic constituents of catalytically cracked gasolines to the corresponding paraffins without hydrogenation of aromatic constituents to naphthenes produces a gasoline improved in stability and in lean-mixture octane number after the addition of tetraethyllead, with no sacrifice in rich-mixture rating, thus permitting this product to be used in aviation gasoline. Product yields are essentially 100 per cent with little loss due to light end formation.

Fuel oil high in sulfur and aromatic content on mild hydrogenation at 300–450°C and a hydrogen pressure of 500–3,000 psig while circulating 500–3,000 standard cu ft of hydrogen per barrel of feed and using commercial catalysts, such as cobalt molybdate, was completely desulfurized, freed of objectionable odor, and improved in sooting tendency. The sulfur content was lowered from 0.6 to 0.01 or 0.02 per cent with essentially no change in boiling range.[1]

Catalytic hydrogenation of crude oils also is a proved means of reducing the sulfur and metallic content and increasing the yield of distillate fractions. The process operates at 430–450°C and at 500–1,000 psig, using hydrogen gas for recycle over the catalyst at a rate of 2,500–10,000 cu ft per bbl of charge.

Other stocks which may be upgraded by hydrotreating are thermally and catalytic cracked naphthas, straight-run naphthas abnormally high in contaminants, and coker gasolines. The latter are produced by the high-temperature pyrolysis of reduced fuel to coke and distillate fractions. Naphthas to be used as specialty solvents also are treated to obtain premium products with respect to color, odor, and stability.

Lubricating oils and waxes can be improved in color, reduced in carbon residue, and decreased in sulfur content by hydrogenation. Middle distillates on mild hydrogenation give diesel oils and heating oils superior in burning characteristics, storage stability, and color.

The cost of hydrodesulfurizing a barrel of a catalytic cracked naphtha has been estimated[2] to be as shown in Table 10-21.

The cost of hydrodesulfurizing crude oils totals about $0.60–$1.00 per barrel of daily capacity on the basis of a 20,000 bbl-per-calendar-day fixed-bed unit operating at 430–450°C and at a hydrogen pressure of 500–1,000 psig. The plant would require an investment of approximately $500 per barrel of daily capacity. This cost includes complete facilities

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[1] ZIMMERSCHIED, HUNT, and WILSON, *Proc. Am. Petroleum Inst.*, **35** (III), 308 (1955).

[2] ABBOTT, LIEDHOLM, and SARNO, *Proc. Am. Petroleum Inst.*, **35** (III), 345 (1955); HEMMEN, KELLEY, STERBY, and READ, *ibid.*, **35** (III), 234 (1955).

for hydrogen manufacture; costs would be reduced considerably if by-product hydrogen were available.[1]

Increasing interest is being shown in utilizing selective hydrogenation as a means for improving the stability and counteracting gum-forming tendencies of cracked motor gasoline fractions. Fractions containing more than 2–3 per cent of diolefins require high inhibitor concentrations and render alkylation impractical because of high acid consumption. Polymerization can be used to remove the diolefins but is uneconomical because of the losses incurred. Selective hydrogenation thus offers a solution. For this purpose, nickel sulfide and tungsten–nickel sulfide supported catalysts may be used.[2] Such a process operates at a hydrogen pressure of about 75 psig and at about 300°C. In addition to the selective hydrogenation of conjugated diolefins, the catalyst also is useful in desulfurizing the feed and in isomerizing monoolefins. Thus, 1-octene yields 82 per cent 2-octene, 12 per cent 3- and 4-octenes, and 5 per cent unconverted 1-octene on such treatment.[3]

TABLE 10-21. HYDRODESULFURIZATION OF A CATALYTIC CRACKED NAPHTHA, CAPITAL AND OPERATING COSTS.
(Plant Cost, \$2,000,000; Plant Capacity, 10,000 Bbl per Stream Day; On Stream Time, 93 Per Cent)

	Cost, cents/bbl
Utilities	3.2
Chemicals and catalyst	1.1
Hydrogen	0.6
Labor (including benefits)	1.7
Maintenance (labor plus material)	2.4
Overhead (taxes, insurance, laboratory)	4.1
Total	13.1

Catalytic reforming or mildly destructive hydrogenation was developed during World War II to produce aromatics for high-octane aviation gasoline and toluene for TNT. Eight such plants were built in this period, and one of the plants alone produced more than half of the toluene used in TNT production. After the war the process gained momentum as the demand for motor gasolines high in octane number increased. By the end of 1956 more than 1 million bbl per day of petroleum products was being fed to catalytic reformers; at the end of 1951 the daily reforming capacity was

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[1] MCAFEE, MONTGOMERY, SUMMERS, HIRSCH, and HORNE, *Proc. Am. Petroleum Inst.*, **35** (III), 312 (1955).

[2] ANDERSON et al., *Ind. Eng. Chem.*, **40**, 2295 (1948).

[3] CASAGRANDS et al., *Ind. Eng. Chem.*, **47**, 744 (1955); MEERBOTT and HINDS, *ibid.*, **47**, 749 (1955).

only 100,000 bbl, which indicates the rapid rate at which the process has grown.

Catalytic reforming has brought with it the problem of expensive catalysts. About 70 per cent of the capacity in the United States employs platinum catalysts. These catalysts are especially susceptible to poisoning by sulfur, arsenic, and other contaminants, and if the catalyst is to have a long active life and remain selective, the charge should contain less than 0.1 per cent sulfur. Fortunately, however, cheap hydrogen is available from the reformers and is used to pretreat the feed prior to reforming (see above under hydrotreating). Such pretreatment using cobalt molybdate catalysts of long life, highly resistant to poisoning, and easily regenerated has provided the means of upgrading feedstocks in high yield. Recent developments in reforming combine aromatic separation and raffinate recycle to achieve higher octanes.

The phenomenal growth of reforming is directly related and responsive to the need for fuels suitable for engines having a high compression ratio. Thus, each increase in compression ratio created a demand for higher octane gasolines which, in turn, meant more severe refinery processing.

Catalytic reforming usually is carried out by feeding a naphtha (after pretreating with hydrogen if necessary) and hydrogen mixture to a furnace where the mixture is heated to the desired temperature (about 450–520°C) and then passed through fixed-bed catalytic reactors at hydrogen pressures of 100–1,000 psig. Normally more than one reactor is used in series, and reheaters are located between adjoining reactors in order to compensate for the endothermic reactions taking place. Sometimes as many as four or five are kept on stream in series while one or more is being regenerated. The on-stream cycle of any one reactor may vary from several hours to many days, depending on the feedstock and reaction conditions. Product issuing from the last catalytic reactor is cooled and sent to a high-pressure separator where the hydrogen-rich gas is split into two streams—one stream goes to recycle while the remaining portion represents excess hydrogen available for other use. The excess hydrogen is vented from the unit and used (1) in hydrotreating, (2) as a fuel, or (3) for manufacture of chemicals (ammonia, etc.). The liquid product (reformate) is stabilized (by removal of light ends) and used directly in motor gasoline or extracted for aromatic blending stocks for aviation gasoline.

A simplified diagram of a typical combination hydropretreating-reforming unit is shown in Fig. 10-10, which illustrates both of the processes described above using fixed-bed type reactors. In such reactors the catalyst as granules or tablets is held in a vessel of suitable size and the reactants are passed through the bed. Fixed-bed reactors have the advantage of being simple to construct and are satisfactory for reactions which do not involve large heating or cooling effects. As it is virtually impossible to utilize heating or cooling coils in fixed-bed reactors, adequate temperature

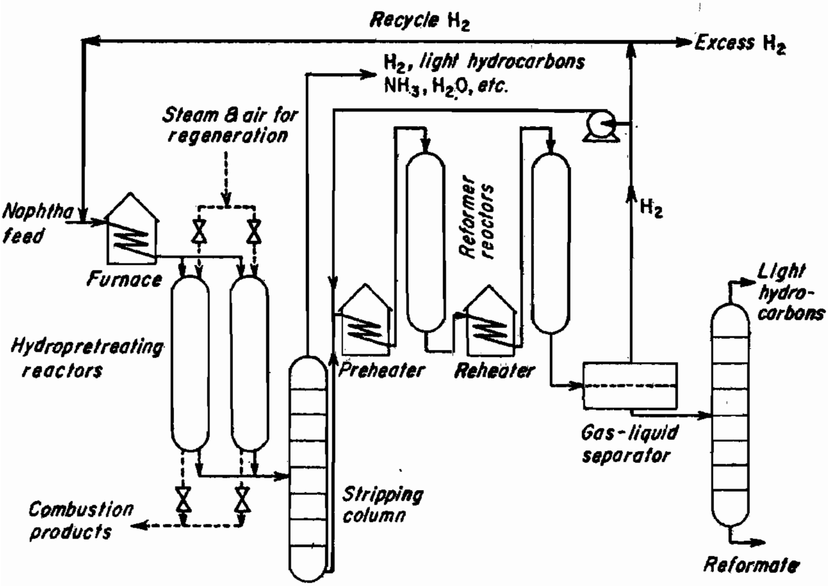

FIG. 10-10. Combination hydropretreating-hydroforming process for upgrading naphthas, using fixed-bed reactors.

control cannot be maintained for either highly exothermic or endothermic reactions.

Another version of a reactor suitable for reforming is shown in the simplified diagram in Fig. 10-11 in which a fluidized-bed type is illustrated. In fluidized-bed operation the finely divided catalyst, behaving much like a fluid, is suspended in a stream of reacting vapors. By regulating the gas velocity and pressure, the catalyst can be maintained either as a stationary bed or as a moving bed. In fluidized-bed reactors a portion of

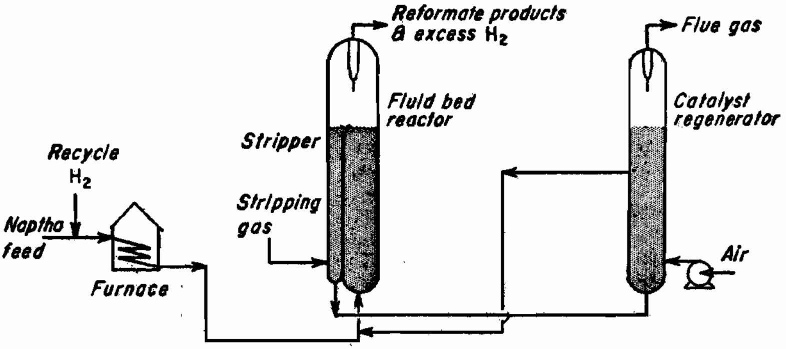

FIG. 10-11. Fluidized-bed reactor and catalyst regenerator for hydroforming.

TABLE 10-22. CATALYTIC REFORMING OF PETROLEUM NAPHTHAS

	Naphtha				Heavy naphtha*		Light naphtha*	
	Feed	Expr. 1	Expr. 2	Expr. 3	Feed	Expr. 4	Feed	Expr. 5
Yield: vol. % of charge (product) C_5+	...	93.8†	90.6†	87.5†	...	69.0	...	72.5
C_4, vol. %	...	...	...	...	...	11.5	...	10.5
$C_1 - C_3$, wt %	...	...	...	...	...	16.5	...	12.5
Gravity, °API	52.6	48.0	46.8	44.8	54.0	...	61.9	
Gravity, specific at 60°F	0.769	0.788	0.794	0.803	0.763	...	0.732	
ASTM distillation, °F.:								
Initial boiling point	230	144	140	132				
10%	255	200	191	173	276	...	216	
50%	308	285	281	272	326	...	241	
90%	372	366	366	365	370	...	282	
End point	397	410	412	413				
Research clear octane No.	32.4	85.0†	90.0†	95.0†	29.7	100	39	95
Research octane No. with 3 ml TEL‡	56.4	95.5†	98.5†	100+†§	...	103	...	100.5
Motor clear octane No.	...	...	...	...	...	88.5	...	85.5
Motor octane No. with 3 ml TEL‡	...	...	...	...	...	93.5	...	92

* *Petroleum Refiner*, **35** (9), 212 (1956).

† Product contains added butanes to give 10 lb Reid vapor press.

‡ TEL = tetraethyllead.

§ Product possessed an octane number equivalent to isooctane + 0.12 ml TEL.

the catalyst can be continuously withdrawn from the reactor for regeneration in a separate chamber and then returned to the reaction zone. In operation, the preheated naphtha or other feedstock enters the bottom of the reactor where it meets a hot bed of catalyst. The reformed products then pass through the fluidized bed (which behaves much like a boiling liquid) and through cyclone separators where entrained catalyst is removed and returned to the reactor. The overhead "reformate" products pass to heat exchangers, are cooled and separated into liquid and gaseous products.

Carbon deposits on the catalyst during the reaction and is burned off with air in the regenerator. This combustion reaction generates much heat which is used to preheat fresh feed or to produce steam.[1] The catalyst, usually a chromia-base type, is finely divided and must be cheap, rugged, and not susceptible to poisoning by sulfur or water. In commercial installations of 40,000 bbl per day capacity, the catalyst circulating from reactor to regenerator and return may amount to as much as 30,000 tons per day.

Examples of the octane improvement and change in boiling range produced by reforming typical petroleum naphthas are given in Table 10-22. As the data show, catalytic reforming increases the octane value but produces material boiling lower than the feed.

A combination hydrodesulfurization-reforming unit of 10,000 bbl per day capacity operates at a cost of about $0.26–$0.35 per bbl when processing heavy naphthas.[2]

The reactions taking place during catalytic reforming are summarized in Table 10-23 for a variety of pure hydrocarbons.[3] As the data show, olefins principally hydrogenate to the corresponding paraffins. Olefins, however, also can cyclize to naphthenes, dehydrogenate to diolefins, and then cyclize to aromatics, polymerize, crack, or undergo hydrogen transfer by disproportionation to produce molecules of more or of less saturation.[4]

The application of reforming to the production of aromatics[5] is presently being carried out on a large scale in many refineries in this country.

At temperatures above 250–300°C, nickel catalysts cause extensive degradation of hydrocarbons with the formation of methane and hydrogen and the deposition of carbonaceous materials on the catalyst surface. However, on combining a hydrogenation catalyst such as nickel with a cracking catalyst such as silica-alumina so that the final catalyst contains 4–6 per cent by weight of nickel, a complex catalyst results which is quite active and

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[1] Winslow and Hanker, *Petroleum Refiner*, **34** (11), 214 (1955).

[2] Stanford, *Petroleum Refiner*, **34** (9), 190 (1955); **35** (9), 214 (1956).

[3] Haensel and Donaldson, *Ind. Eng. Chem.*, **43**, 2102 (1951); Connor, Ciapetta, Leum, and Fowle, *ibid.*, **47**, 152 (1955); Hettinger et al., *ibid.*, **47**, 719 (1955).

[4] Heinemann et al., *Ind. Eng. Chem.*, **45**, 130, 134 (1953); **47**, 735 (1956).

[5] Beyler and Stevenson, *Ind. Eng. Chem.*, **47**, 740 (1955).

TABLE 10-23. PRODUCTS FROM THE CATALYTIC REFORMING OF A VARIETY OF PURE HYDROCARBONS

Conditions: 500 psig; 460°C; platinum-type catalyst; 3–10 vol. of hydrogen per volume of hydrocarbon; 2–6 vol. of liquid feed per volume of catalyst per hour.

Feed	Products	
	Material	Weight % of feed
n-Heptane (hydrogen consumption: 2 wt % of feed)	Unreacted heptane	12
	Methane, ethane, and propane	13
	Butanes (65% as isobutane)	16
	Pentanes (60% as isopentane)	4
	Hexanes	3
	Branched heptanes	52
	Higher boiling end	2
		102
n-Pentane	Unreacted pentane	60
	Isopentane	38
	Butanes	2
		100
Isopropylbenzene (cumene)	Unreacted cumene	16
	Methane, ethane, and propane	21
	Butanes	2
	Methylcyclopentane	10
	Cyclohexane	3
	Benzene	19
	Toluene and xylenes	2
	Isomeric naphthenes	5
	C_9 aromatics	25
		103
Methylcyclohexane	Unreacted methylcyclohexane	6
	Methane, ethane, and propane	4
	Butanes, pentanes, and hexanes	1
	C_7 cyclopentanes	33
	Toluene	57
		101
Pentenes	Pentanes	100

selective in isomerizing saturated hydrocarbons in the presence of molecular hydrogen. In the absence of hydrogen, the catalysts show no activity. The role of hydrogen appears to be primarily to keep the catalyst surface clean of hydrocarbon residues and maintain its activity.

n-Hexane on hydroisomerization[1] over such a catalyst at 385°C and 25 atm hydrogen pressure gives 23 per cent of unreacted *n*-hexane, 57 per cent of methylpentanes, 11 per cent of dimethylbutanes, and 9 per cent of paraffin hydrocarbons ranging from methane through pentane.

By regulating the temperature and partial pressure of hydrogen, supported nickel catalysts can be used in controlling demethylation reactions.

Hydrogenation of Heavy Oils. Asphalt[2] or residua[3] from petroleum processing apparently are composed of a complex colloidal system of asphaltenes (high-molecular-weight aromatics) dispersed in heavy oils. It is believed that this complex system is stabilized by compounds containing polar groups such as those involving oxygen, nitrogen, and sulfur. Hydrogenation at relatively low pressures (200–1,000 psig) and at tempertures of 380–440°C over cobalt molybdate cleaves the polar compounds and produces smaller, less complex molecules. The process also improves the quality of the products by increasing the ratio of hydrogen:carbon in the average hydrocarbon molecule and by desulfurizing the asphalt to the extent of 80–85 per cent.

Typical yields resulting from asphalt hydrogenation are as follows: methane, ethane, and propane, 2.3 weight per cent; gasoline (butane to 430°F), 12.1 volume per cent; heating oil (430–650°F), 16.4 volume per cent; gas oil (650–1000°F), 31.2 volume per cent; residuum (above 1000°F), 45.2 volume per cent. Total yield: 107.2 volume per cent.

Colorado shale oils are normally high in sulfur and nitrogen content and do not respond well to petroleum processing. However, hydrogenation at cracking temperatures offers a means of removing sulfur and nitrogen and giving a product suitable for normal catalytic processing. The reaction may be carried out at hydrogen pressures of 3,000 psig and temperatures of about 480°C.[4]

If high-molecular-weight petroleum fractions are simply pyrolyzed, i.e., if no hydrogenation occurs, then progressive cracking and polymerization generally lead to the final products: (1) gaseous and low-boiling liquid compounds of high hydrogen content, (2) liquid material of intermediate

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[1] Ciapetta et al., *Ind. Eng. Chem.*, **45**, 147–162 (1953).

[2] Gwin et al., Division of Petroleum Chemistry *ACS Preprints*, **1** (4), 73 (September, 1956).

[3] Heinemann and Stevenson, Division of Petroleum Chemistry, *ACS Preprints*, **1** (4), 65 (September, 1956).

[4] Cottingham et al., Division of Petroleum Chemistry, *ACS Preprints*, **1** (4) 97 (September, 1956); *Ind. Eng. Chem.*, **48**, 1146 (1956); Carpenter et al., *ibid.*, **48**, 1139 (1956).

molecular weight and a hydrogen:carbon ratio differing more or less from that of the original feedstock, depending on the method of operation, and (3) liquid material of high molecular weight, such as tar and petroleum coke, possessing a lower ratio of hydrogen:carbon than the starting material. Highly aromatic or refractory cycle stocks or gas oils contain varying proportions of highly condensed aromatic structures of the naphthalene, phenanthrene, pyrene, etc., types and on cracking in the absence of hydrogen yield tars and coke.

An essential difference between pyrolysis and hydrogenolysis of petroleum is that in pyrolysis a certain amount of polymerized heavier products, such as tar and coke, is always formed along with the light products, such as gas and gasoline; whereas, in hydrogenolysis or destructive hydrogenation, polymerization may be partly or even entirely prevented, so that only light products are made. The prevention of tar and coke formation usually results in an increased gasoline yield. The condensed type of molecule, such as naphthalene or anthracene, is one that is closely associated with the building up of tar and coke, but in an atmosphere of hydrogen and in contact with catalysts, these condensed molecules are changed over into lower-molecular-weight compounds which are more saturated and boil within the gasoline range. Figure 10-12 shows the pronounced effect of temperature and hydrogen partial pressure on the hydrogenation-dehydrogenation equilibriums of a few condensed types of hydrocarbons. These data show that it is possible to get varying degrees of hydrogenation. At low temperatures and high hydrogen pressures (200 atm), the product can be completely saturated; if the temperature is raised and the partial pressure of hydrogen lowered, a more aromatic product can be made. These factors are important in producing motor fuels of varying antiknock qualities. The aromatic content, which is related to the antiknock properties of a fuel, can be retained under conditions wherein sulfur compounds and resinous and asphaltic materials are hydrogenated and thus removed or converted into more valuable products.

Catalytically cracked cycle stocks on hydrogenation at 3,000 psig and 300–400°C over sulfur-resistant catalysts yield materials greatly improved in quality to the point where they are more desirable cracking stocks than the original virgin feeds. Such an operation gives the highest possible yield of gasoline from virgin charging stocks.[1]

Hydrogenation of Olefins. Figure 10-13 shows a flow sheet for the hydrogenation of a mixture of branched-chain olefins containing seven and eight carbon atoms per molecule.[2] The hydrogenation may be accomplished in one or two stages. Where the cost of the hydrogen is relatively high and it is desired to make the most effective use of it, two-stage hydro-

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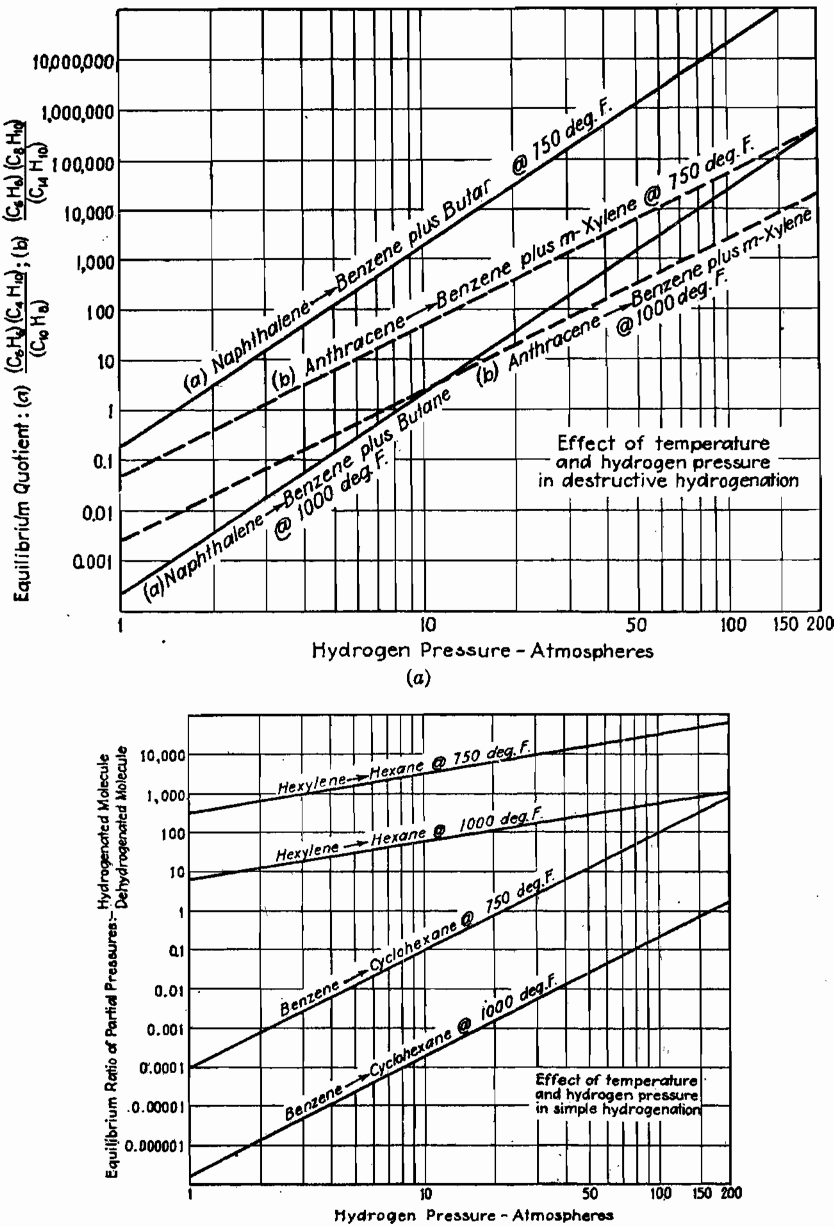
[1] Brown, Voorhies, and Smith, *Ind. Eng. Chem.*, **38**, 136 (1946).

[2] *Heat Engineering*, **14**, 71 (May, 1939), issued by Foster-Wheeler Corp., New York.



(a)

(b)

Fig. 10-12. Effect of temperature and pressure on the hydrogenation-dehydrogenation equilibriums.

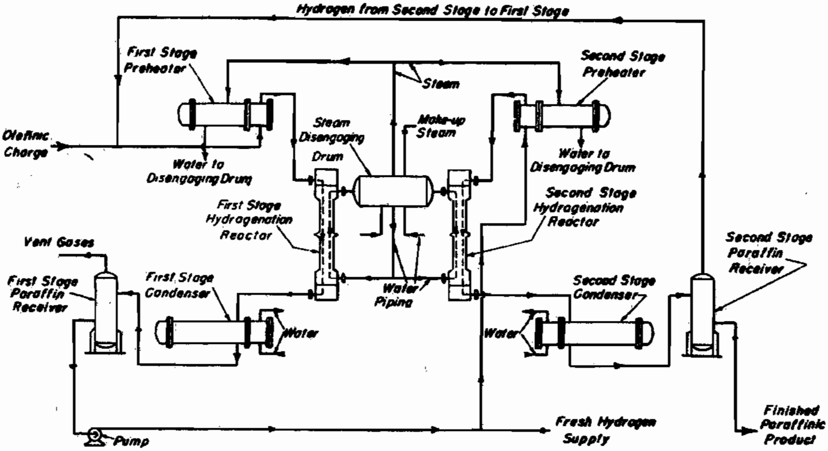


FIG. 10-13. Flow sheet for the low-pressure hydrogenation of olefins to paraffins.

genations are employed; in this way, about 95 per cent of the hydrogen may be utilized.

The olefinic charge is combined with unreacted hydrogen from the second stage, and both are passed through a steam-heated preheater and then into the top of the first-stage hydrogenation reactor. Here the olefin-hydrogen mixture intimately contacts the catalyst, which induces saturation of the olefinic linkage.

The reactor consists of a steel shell containing a multiplicity of tubes filled with catalyst. Since this hydrogenation reaction is exothermic, water is maintained in the shell of the reactor and in the space around the catalyst tubes to limit the reaction temperature and to pick up the heat of the reaction. This is accomplished by allowing the water to vaporize under pressure to generate steam. This high-pressure steam is then used in the preheaters to heat the incoming olefin-hydrogen mixture.

The vaporized olefins are partially hydrogenated as they flow downward through the first-stage reactor. They are withdrawn at the bottom of the reactor, condensed in a conventional type of shell-and-tube condenser, and collected in the first-stage paraffin receiver. Noncondensable gases, resulting from side reactions, are vented from the receiver into the atmosphere.

A pump draws the partially hydrogenated product from the first-stage receiver and feeds it to the second-stage preheater. At this point, a fresh supply of hydrogen is introduced into the hydrocarbon stream, and the mixture is preheated as before in the second-stage preheater. From here, the mixture flows downward through the catalyst in the tubes of the second-stage reactor. As in the first stage, water in the shell of the reactor removes the heat liberated during the hydrogenation, and the resulting steam is used to provide the proper preheating.

The paraffin hydrocarbons and excess hydrogen pass from the bottom of the reactor through a condenser where the hydrocarbons condense. In the second-stage paraffin receiver, the hydrogen is separated for return to the first-stage reactor, while the fully hydrogenated paraffinic product is sent to storage, thereby completing the operation. This same type of equipment is suitable for hydrogenating phenols. For example, phenol upon hydrogenation yields cyclohexanol. This in turn is oxidized to adipic acid, an important component of nylon.

Hydrogenation of a Gas Oil. The destructive hydrogenation of gas oil fractions carried out during World War II for the manufacture of aviation base gasoline was the beginning of the reforming process which has been discussed in detail above. Table 10-24 gives some experimental results on hydrogenating a gas oil with various catalysts. The gas oil used had a density at 20°C of 0.894, 73.4 per cent by weight distilling over between 234–280°C and 22.2 per cent between 280–310°C.[1] It is evident that molybdenum and tungsten sulfides are effective catalysts for converting gas oil into lower-molecular-weight and more saturated products. Such catalysts are not poisoned by sulfur compounds in the oils. When the materials are free of sulfur, nickel-type catalysts are frequently used. Otherwise, metal sulfide or oxide types that are sulfur-resistant have to be employed.

Figure 10-14 is a flow sheet of the hydrogenation of a heavy gas oil. The oil to be hydrogenated is fed to the system by high-pressure pumps. It is mixed with fresh hydrogen that has been separately compressed to the desired operating pressure, which is usually in the range of 100–250 atm. Additional hydrogen is added in the form of recycle gas which has been separated from the liquid hydrogenated product. This hydrogen is recycled by a booster compressor which essentially makes up the pressure drop through the system. The incoming oil is brought to reaction temperature, usually in the range of about 400–540°C, by specially designed heat exchangers and by heating in a direct-fired high-pressure coil or heater. The hydrogenation takes place in high-pressure reaction chambers containing the catalyst. There is a net evolution of heat, for the reaction is exothermic. To control the temperature, intermediate cooling is sometimes effected by adding cold recycle gas at suitable points in the reactors. After exchanging its heat with the entering mixture of oil and hydrogen, the reaction product passes through a cooler to a high-pressure gas separator where the recycle gas, consisting mainly of hydrogen, is removed. In a low-pressure system following the separator, the products are fractionally distilled as desired to make gasoline, kerosene, etc. The catalysts employed in the reaction chambers are very stable physically and chemically and are

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[1] SWEENEY and VOORHIES, *Ind. Eng. Chem.*, **26**, 195 (1934).

TABLE 10-24. HYDROGENATION OF GAS OIL
Temperature, 440°C (825°F); Time, 1 Hr

Catalyst	H_2 pressure, psi			Yields of reaction products, wt % of gas oil used				Fraction up to 230°C, wt %				Fraction 230–270°C, wt %				Liquid reaction products, wt %	
	Initial at 20°C	Maximum	Final at 20°C	Gaseous hydrocarbons, %	Liquid hydrocarbons		Loss	Gas oil used	Liquid reaction products	D_4^{20}	Iodine No.	Gas oil used	Liquid reaction products	D_4^{20}	Iodine No.	Residue above 270°C	Gas + loss
					%	D_4^{20}											
No catalyst	1,160	2,800	1,100	3.2	92.4	0.8691	4.4	21.1	22.9	0.800	86.8	40.2	43.5	0.893	39.7	32.1	1.5
MoO_3	1,160	2,800	990	3.3	91.3	0.8675	5.4	20.6	22.6	0.796	42.7	41.7	45.7	0.895	....	30.2	1.5
MoO_3 (reduced by H_2 at 600°C)	1,160	2,900	1,670	3.6	88.4	0.8650	8.0	22.8	25.8	0.795	....	39.4	44.6	0.897	....	27.8	1.8
MoS_3	1,150	2,600	870	5.5	89.2	0.8324	5.3	43.9	49.3	0.791	20.9	30.0	33.7	0.890	25.3	14.5	2.5
$(NH_4)_2MoS_4$	1,160	2,800	880	4.5	86.8	0.8128	8.7	55.3	64.0	.....	....	22.5	26.0	.....	....	6.4	3.6
$(NH_4)_2MoS_4$ (reduced by H_2 at 500°C)	1,150	2,600	960	2.9	91.2	0.8523	5.9	32.9	36.2	0.801	....	35.5	39.0	0.886	....	22.9	1.9
Molybdenite (MoS_2)	1,150	2,800	1,050	4.9	88.4	0.8641	6.7	27.0	30.7	0.793	....	38.2	43.4	0.899	....	24.9	1.0
$MoSe_3$	1,160	2,800	1,020	4.6	92.5	0.8520	2.9	32.4	35.0	0.798	....	41.3	44.7	0.892	....	23.3	
WS_3	1,160	2,700	820	5.3	82.7	0.8098	12.0	44.4	54.1	0.765	21.9	24.4	29.7	0.883	....	15.8	0.4
NiS	1,160	3,200	1,020	4.9	93.4	0.8482	1.7	38.0	40.8	0.800	57.1	34.1	36.6	0.893	....	20.5	2.1
ZnS	1,160	2,900	1,050	1.8	90.6	0.8611	7.6	26.4	29.4	0.795	....	37.5	41.8	0.834	....	27.0	1.8

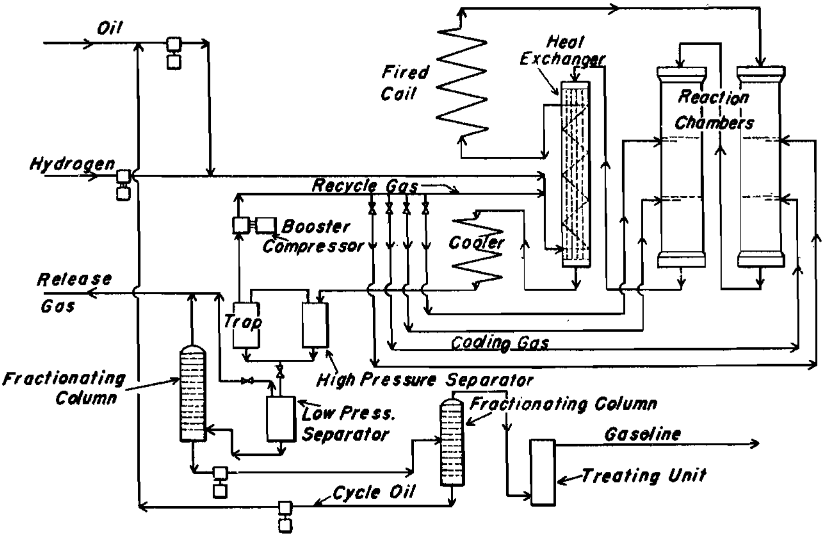

FIG. 10-14. Flow chart for the hydrogenation of heavy oil.

not harmed by the normal constituents of petroleum oils, including sulfur compounds. The life of these catalysts may extend to a year or more.

Tar Hydrogenation. The manufactured-gas and coke-oven industries produce large quantities of tars, and these can be hydrogenated to produce satisfactory motor or diesel fuels. In Europe, coals are subjected to low-temperature carbonization where the tar yield is considerable, and these tars are then hydrogenated to produce fuels instead of directly hydrogenating the coal. The processing of tar is much easier than that of coal, and the operation is more closely related to petroleum hydrogenation than coal hydrogenation. Practically twice as much motor fuel can be produced by hydrogenating the tars than by cracking them to produce similar products. Molybdenum oxide has been found to be a suitable catalyst, and an even greater activity is shown by molybdenum sulfide. Temperatures of 450–500°C (840–930°F) are used, and the pressures are approximately 250 atm. In addition to the catalysts effecting cleavages of hydrocarbons of high molecular weight and hydrogenating these into stable, more volatile products, they must also be able to effect the reduction of phenolic and organic nitrogen compounds to hydrocarbons.

In Great Britain a creosote fraction boiling from 200–340°C and obtained from coal tar by high-temperature carbonization processes is hydrocracked to give a 75 per cent yield of gasoline having a research octane number of 94.5 (+1.5 ml tetraethyllead per gallon) and a motor octane number of 87 (+1.5 ml tetraethyllead per gallon). The process is carried out at 3,000 psig hydrogen pressure and at about 400°C over a nickel-on-alumina catalyst. The process was initiated in about 1935 and has undergone many process changes since that time. In 1944 the process produced aviation, pursuit grade, gasoline. The creosote feedstock contains about 0.5–0.7 per cent nitrogen, 0.7–0.9 per cent sulfur, up to 2.0 per cent oxygen, and only 8–8.5 per cent hydrogen. The average molecular weight is 160–170. Further, the feedstock contains only about 70 per cent of hydrocarbons (substituted benzenes, naphthalene, naphthalene derivatives, and more highly condensed aromatics), the remainder being phenols, nitrogen bases, and sulfur compounds. The main reactions taking place appear to be hydrogenolysis of the phenols, nitrogen compounds, and sulfur compounds to lower-molecular-weight (gasoline-range) hydrocarbons. The aromatics undergo partial saturation followed by cleavage of the molecule to yield lower-molecular-weight fragments.[1]

Coal Hydrogenation. The hydrogenation of coal is a special application of the liquid-phase process. Coal is a complex mixture of very high-molecular-weight compounds which apparently exist as an elaborate network of carbon rings. These rings are cleaved during hydrogenation, and the fragments formed yield open-chain and cyclic hydrocarbons. Depending on the reaction conditions, coal may be hydrogenated either for chemicals or for fuels.

The successful hydrogenation of coal to produce high yields of liquid motor fuels depends not only on high-pressure hydrogen but also to a very great extent upon catalysts that facilitate and accelerate the entry of hydrogen into coal or its decomposition products.

In general, the coal is first mixed with a high-boiling oil, called a *pasting oil,* and this mixture is forced into the high-pressure reaction chamber. The coal paste, which is made up of about equal parts of finely ground bituminous or brown coal (about 80 per cent through 65 mesh on the Tyler scale) and a high-boiling oil, is mixed also with a finely divided catalyst, and this highly viscous liquid is pumped through pipes and heat exchangers into the reaction chamber. The catalyst may also be added at successive stages in the operation, or the coal may be soaked with a solution of the catalyst.

The reaction is highly sensitive to changes in temperature because of the high-molecular-weight compounds present in the coal. Great care must be taken to avoid overheating, particularly during the preheating operations; otherwise, the components of the coal that still have their original molecular structure will tend to form coke and inert products not suitable for further hydrogenation. Another difficulty lies in completing the hydrogenation reaction, for although the coal is finely ground, the particles are

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[1] CLOUGH, Division of Petroleum Chemistry, *ACS Preprints*, 1 (4), 83 (September, 1956).

solid, and contact with hydrogen is possible, therefore, only on the surface. After partial hydrogenation and reduction of oxygen compounds in the coal have occurred, the particles, aided by the action of the heavy oil, swell and partly dissolve, resulting in an almost completely liquid mass. The oil also serves to maintain the temperature uniform throughout the reaction chamber. The reaction is usually carried out in two stages. The first is in the liquid phase, the second usually in the vapor phase. The primary hydrogenation products are heavy, high-boiling oils, which crack, if maintained at temperatures of 450°C (840°F) or above, into lighter oils, gasoline, and gas. If the time of hydrogenation is controlled, the liquefied product from the coal may be obtained as light oils, gasoline, or gas, with the heavy pasting oil recovered unchanged.

For the case of brown or young coals or those high in lignin content, different temperature and pressure conditions are usually employed in the liquid- and the vapor-phase hydrogenation steps. For example, for the liquid-phase operation, hydrogen pressures up to 700 atm may be employed, whereas in the vapor-phase step, the pressures may be confined to around 300 atm. The coal is first dried, then crushed, ground, and screened so that the bulk of the coal particles are below 0.1 mm in size. It is then mixed with catalyst and a nonvolatile oil (one boiling above about 350°C, atmospheric pressure) and made into a paste in the paste mill. High-pressure reciprocating pumps or injectors force this paste, which may contain about 35–50 per cent coal, into the liquid-phase hydrogenation unit. The latter consists of a heat exchanger, a gas-fired furnace, and reaction chambers or converters where sufficient time and temperature are provided for the interaction between the coal and the hydrogen. In the converters, the bulk of the coal is changed into liquid and gaseous products and the reaction is exothermic (Table 10-22). The average residence time in the reaction zone is 1–2 hr (about 10–15 lb coal per cubic foot of reaction space per hour) for about 95 per cent carbon conversion to gaseous and liquid products suitable for subsequent processing. The solids consisting of ash, coke, catalyst, and any other nonconvertible materials are separated from the bulk of the other products in the catchpot. A final separation of the solids from the liquid is usually made by centrifuges in the sludge-recovery unit. The chemical composition of the ash is important, for it affects the formation of deposits in the converters and the ease with which the solids can be cleanly separated from the liquid products.

In the liquid-phase hydrogenation, the catalyst may comprise about 5 weight per cent of the dry coal, and it is commonly composed of sulfur-containing and promoted iron- and iron oxide-containing catalysts on special clays. Another common catalyst is 2 per cent ammonium molybdate on 98 per cent fuller's earth. About 1 per cent of this catalyst, based on the coal, is mixed into the paste going to the converters. The residue or nonliquefiable portions may be 10–15 per cent of the coal. This liquid-phase hydrogenation commonly occurs at about 450–500°C (840–930°F) and, as indicated, the hydrogen pressures range from about 300–700 atm. About one-third to one-half of the coal may be converted in this step to hydrocarbons boiling below approximately 400°C. A portion of this product boiling in the range of about 200–400°C is commonly termed *middle oil*, and it may contain 10–20 per cent of phenols. Products boiling above the middle oil are recycled to the liquid-phase hydrogenation step.

The middle oil is further hydrogenated in a second, or vapor-phase, hydrogenation to convert it into hydrocarbons in the gasoline boiling range, i.e., those which boil to about 200°C at atmospheric pressure. This vapor-phase step is similar in certain respects to the liquid-phase operation except that a fixed-bed type of catalyst is used; the temperatures are usually in the range of 350–400°C; and the hydrogen pressures are commonly between 200 and 300 atm, although 700 atm is sometimes used. Since all the material used in this vapor-phase operation has been distilled, there is no problem with respect to solid handling and disposal. The distillation tower removes the hydrocarbons in the gasoline or diesel-fuel range, and the higher boiling portions can be recirculated through the vapor-phase converter to be changed ultimately into lower boiling fuels. Any basic or nitrogen-containing compounds are removed by an acid wash. Similarly, any remaining phenolic constituents are eliminated from the fuel by a caustic-soda wash.

In hydrogenations of this type, five to ten times as much hydrogen may be circulated as consumed. For processing young or brown coals, this consumption may be 10–20 cu ft of hydrogen per pound of coal. For bituminous coals, such as Illinois No. 6, the consumption is about 20–25 cu ft per lb of coal.

For 100 tons of dry and ash-free bituminous coal hydrogenated, there can be produced 62 tons of motor gasoline, 13 tons of liquified petroleum gases, and 11 tons of residual oils. Also, 98 tons of additional coal is used to generate the power needed and to supply all the other energy requirements of the process. Thus, the thermal efficiency of coal hydrogenation is reported to be as high as 55 per cent, although in German practice it has been much lower.[1]

A plant making 30,000 bbl per day of liquid fuel by hydrogenating Illinois coal yields the quantities of products shown in Table 10-25.

The hydrogenation of coal gives about ten times as much refined aromatic chemicals per ton of coal as does high-temperature carbonization.

Extensive information has been obtained from Germany on the processing of coals and tars to chemicals and liquid fuels, and much of this knowledge is available from the U.S. Department of Interior, Bureau of

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[1] Skinner, Dressler, Chaffee, Miller, and Hirst, *Ind. Eng. Chem.*, **41**, 87 (1949).

TABLE 10-25. CHEMICALS AND FUELS FROM A 30,000-BBL-PER-DAY COAL HYDROGENATION PLANT*

Chemicals and fuels	Production		Composition, wt % of total product
	Lb/day	Bbl/day	
Tar acids:			
Phenol	157,400	428	1.9
o-Cresol	17,600	48	0.2
m- and *p*-cresols	192,000	530	2.4
Xylenols	136,000	374	1.6
Aromatics:			
Benzene	....	2,210	8.2
Toluene	....	3,770	13.9
Xylene	....	4,190	15.4
Mixed aromatics	....	1,780	6.8
Ethylbenzene	....	750	2.8
Naphthalene	316,000	790	3.7
Liquefied petroleum gas	....	7,300	16.4
Gasoline:			
Motor	....	5,260	15.6
Aviation	....	3,660	11.1
Total	....	31,090	100.0
Others:			
Ammonium sulfate	900,000		
Sulfuric acid	178,000		

* DONATH, *Ind. Eng. Chem.*, **46**, 2032 (1954).

Mines,[1] from the U.S. Technical Oil Mission,[2] and from other sources.[3]

Catalysts for the vapor-phase step have to be sulfur-resistant and be able to convert sulfur-, oxygen-, and nitrogen-containing compounds to hydrocarbons. A typical catalyst is 0.7 per cent molybdenum sulfide, 2 per cent chromium oxide, 5 per cent zinc oxide, and 10 per cent sulfur on fuller's earth. Tungsten disulfide is also a good catalyst.

A plant to make 30,000 bbl per day of liquid fuel by coal hydrogenation was reported in 1952 to have amounted to an investment of about 400–500 million dollars—about $13,000–$17,000 per barrel per day of liquid fuel.[4] The corresponding investment for a plant to synthesize liquid fuel in 1952

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[1] RHODES, *U.S. Bur. Mines, Inform. Circ.* 7490, February, 1949; HIRST, SKINNER, CLARKE, DOUGHERTY, and LEVENE, *U.S. Bur. Mines, Rept. Invest.* 4413, November, 1948; HOLROYD, *U.S. Bur. Mines, Inform. Circs.* 7370 and 7375, 1946; *U.S. Bur. Mines, Repts. Invest.* 4456, 4457, and 4458, January, 1949.

[2] See Technical Oil Mission microfilm reels 177, 181, and 201.

[3] SHERWOOD, *Petroleum Refiner*, **28** (12), 97 (1949); **29** (1), 119 (1949).

[4] *Chem. Eng.*, **59**, 159 (June, 1952).

from carbon monoxide and hydrogen was about $3,000–$5,000 per barrel per day of product. In contrast to these data, the cost of a refinery for processing crude oil to high-quality liquid fuels was about $2,000 in 1952 per barrel per day of oil refined.

All types of lignite and most bituminous coals, except those which have progressed too far in the coalification process, such as anthracite, are satisfactory raw materials for liquefaction. Young coals, which at present have the least value, are suitable for high-pressure hydrogenation.

In 1952, a "pilot plant" processing 300 tons of coal per day was started by Union Carbide Chemicals Company for producing chemicals. This new process apparently uses only about 3–6 per cent by weight of hydrogen (half the amount of hydrogen needed in a synthetic-fuels process) and cleaves the coal molecules so that they come apart in fairly large pieces. The coal molecules are regarded as multiple hexagon lattices which look much like a chicken-wire fence, and for this reason the process is called "chicken-wire chemistry." The Carbide process apparently is able to accomplish the first-step hydrogenation in a very short time as compared with the usual coal-hydrogenation procedure. Since higher retention of the ring structures present in the coal is achieved by the process, increased yields of chemicals result. Thus, cresols are recovered in 100–200 times the amount obtained from coking operations. The recovery of quinolines is enhanced by a factor of 300–500, phenol by a factor of 60–80. Substantial quantities of indole, quinaldine, and carbazole also are formed.[1]

Recent developments in the hydrogenation of bituminous coal and of low-cost residual oils at temperatures of 650–730°C and pressures of 1,400–3,200 psig indicate that a gas rich in methane can be produced at thermal efficiencies of 60–70 per cent without heat recovery.[2] The process is said to occur in two stages. In the initial stage pyrolysis and hydrogenolysis of the more reactive coal constituents occur; in the second stage the cokelike residue reacts with hydrogen to give methane. The potential value of the operation depends on the use of cheap hydrogen such as that available from reforming. The gas from such a process is suitable as a replacement for pipeline gas, and if 10 per cent of the present high Btu pipeline gas were made from coal, about 100 million tons of coal per year would be required. Interest in such a substitute gas results from the increasing cost of natural gas and the need to supplement local peak demands.

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[1] *Chem. Eng. News*, **30**, 1954 (1952); *Chem. Eng.*, **59**, 152 (June, 1952).

[2] CHANNABASAPPA and LINDEN, *Ind. Eng. Chem.*, **48**, 900 (1956); SHULTZ and LINDEN, *ibid.*, **48**, 895 (1956).

CHAPTER 11

HYDROCARBON SYNTHESIS AND HYDROFORMYLATION[1]

By W. C. Schroeder, H. E. Benson, and J. H. Field

I. INTRODUCTION

Aliphatic hydrocarbons and oxygenated compounds can be synthesized from mixtures of hydrogen and carbon monoxide by reaction over suitable catalysts. Since Franz Fischer and Hans Tropsch first synthesized liquid hydrocarbons over an alkalized iron catalyst in 1923, considerable research and process development has been done in many parts of the world. Because the synthesis reaction is highly exothermic, many methods have been investigated for removing heat liberated in a catalyst bed. The various methods of heat transfer and the basic design of the reactors are discussed in this chapter. Also, a brief description is given of recently constructed commercial plants and some information concerning the economics of the synthesis.

Usually, hydrocarbons are the principal products of the Fischer-Tropsch synthesis, with about 5–15 per cent of the total products being oxygenated hydrocarbons. However, by use of selected catalysts and operating conditions, the yield of oxygenated hydrocarbons can be increased considerably. Production of oxygenated compounds (other than water and carbon dioxide) without hydrocarbon by-products has been attained only in the hydroformylation reaction in which an olefin is reacted with a mixture of hydrogen and carbon monoxide. In the Oxo process, hydroformylation of the olefin to an aldehyde occurs by addition of a hydrogen atom and a formyl group to the double bond. A discussion of the chemistry of the hydroformylation reaction and its commercial applications is included. Other variations of the basic Fischer-Tropsch synthesis described are the Synol process for the production of relatively high concentrations of alcohols and the Isosynthesis process for the production of branched-chain hydrocarbons.

Background. Concern over the greatly increasing consumption of petroleum has, since World War II, created new interest in the synthesis

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[1] Contribution from Central Experiment Station, Bureau of Mines, U.S. Department of the Interior, Bruceton, Pa.

of liquid and gaseous fuels from coal. During the 1930's, synthetic-fuel processes utilizing coal as a raw material were established in Germany and became firmly entrenched in the German economy. By the time of World War II, Germany was self-sufficient in so far as liquid fuels were concerned owing in part to development of synthetic fuels. During the past few years, only a limited resumption of synthesis from coal has occurred. Primarily oxygenated chemicals and waxes are produced in these plants.

In the United States interest in synthetic fuels increased after World War II, partially because of a desire for self-sufficiency in time of emergency, as well as the greatly increasing demand for liquid fuels. Research and development were intensified by petroleum companies and the U.S. Bureau of Mines. Several companies organized the Carthage Hydrocol Company in 1945 to make motor fuel and chemicals at Brownsville, Tex., from carbon monoxide and hydrogen, using cheap natural gas as a raw material. Because of equipment and design difficulties, the plant never reached full production during the first few years of operation. In addition, new discoveries of oil in the Southwest, the Dakotas, and Canada decreased interest in synthetic fuels. Vast discoveries of oil in the Middle East also decreased interest in synthetic fuels abroad. In 1954, Stanolind Oil and Gas Company became the sole owner of the plant at Brownsville and the company was renamed Hidalgo Chemical Company.[1] The main purpose of the plant is to produce chemicals, even though a greater quantity of fuels will be produced.

Although nearly any combustible fuel can be used as a source of Fischer-Tropsch synthesis gas, coal is by far the most common. A long-term agreement made prior to construction made available a supply of natural gas at $0.05 per thousand cubic feet for the Carthage Hydrocol Company plant.[2] With greatly increasing demand for natural gas, however, it is unlikely that plants producing purely synthetic liquid fuels will be based on natural gas in the United States. New supplies of natural gas at the well are currently about 15–20 cents per thousand cubic feet, and the price will inevitably continue to increase.

Reserves of natural gas in the United States are presently estimated at 223,697 billion cu ft.[3] At the production rate during 1955 of 10,118 billion cu ft, a 22-year supply of gas is indicated at present. Domestic petroleum reserves, including natural-gas liquids, are estimated at 35,461 million bbl. The domestic petroleum production, including natural-gas liquids, in 1955 was 2,737 million bbl, indicating a 13-year supply at the present consumption rate.[4] Estimates of the reserves of oil shale range from the

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[1] *Oil Gas J.*, **52** (48), Apr. 5, 1954.

[2] KEITH, *Natl. Petroleum News*, **38** (27), R-506-511 (1946).

[3] *Petroleum Processing*, April, 1956, p. 12.

[4] *Oil Gas J.*, **52** (48), Apr. 5, 1954.

equivalent of 100 billion–1,000 billion bbl of oil, and oil or tar sands may contribute some supplemental supplies.[1]

The estimated recoverable reserves of coal and lignite (949,870 million tons),[2] on the other hand, are 1,700 times the present yearly consumption and constitute the major portion of our domestic fossil energy reserves. The role of coal since the turn of the century in the over-all energy picture is shown graphically in Fig. 11-1. The percentage of total energy supplied by coal has been shrinking steadily. The annual consumption of lignite and bituminous coal has varied between 300 and 600 million tons during the last twenty-five years.

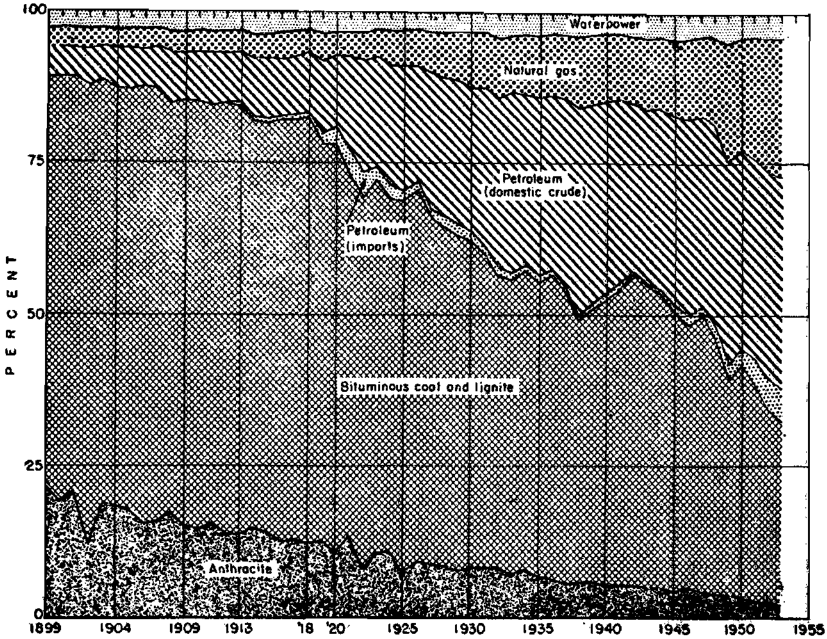

FIG. 11-1. Percentage of total Btu contributed by several sources of energy.[3]

In 1954, coal production reached its lowest postwar level of 392 million tons. In 1955, production climbed to 470 million tons,[3] and in 1956 the estimated production was 545 million tons. Barring major economic upheavals, there is strong reason to believe that coal production will increase steadily in the future.

Past history has shown that new discoveries of natural gas and petroleum have been able to keep the ratio of reserves to yearly production fairly

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[1] AYRES, *Sci. American*, **195** (4), 43–49 (October, 1956.)

[2] *U.S. Bur. Mines Inform. Circ.* 7754, May, 1956.

[3] *Ibid.*

constant. However, recent estimates indicate that petroleum consumption will double in the next ten years and that it may be necessary to utilize coal in the future for synthetic-fuels production.

An informative discussion of the liquid-fuel situation indicating the time when synthetic liquid fuels would be required was published by Ayres in 1953,[1] followed by a reappraisal published in 1956.[2] Current production and discovery trends were extrapolated in the 1953 paper, resulting in the graph shown in Fig. 11-2. His estimate is that commercial production of synthetic liquids from oil shale will begin just before the year 1960, and just after 1960 synthetics will be produced from coal. Regardless of the exact year in which synthetic liquid-fuel production will begin, it is obvious that our domestic oil and gas reserves eventually must be supplemented by fuels derived from oil shale and coal to fill the gap between supply and demand for liquid and gaseous fuels.

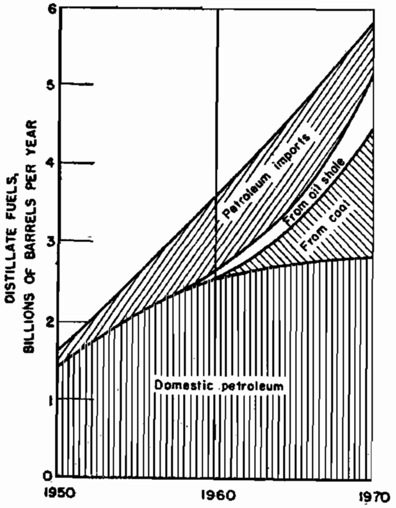

FIG. 11-2. Production of distillate fuels.

The course of synthetic-fuel development, as well as domestic petroleum, will be greatly influenced by oil from abroad. At the present time the proved reserves of oil in the free foreign world are over forty times production. Barring adverse political situations, it is probable that oil can be imported into the United States at comparatively low cost for many years. On the other hand, there is very serious question as to whether any world power can safely rely on oil supplies which are not under immediate control.

II. TECHNOLOGY OF FISCHER-TROPSCH OPERATION

General Synthesis Scheme. A schematic diagram of a plant producing synthetic liquid fuels and chemicals from coal via the Fischer-Tropsch synthesis is shown in Fig. 11-3. Gasification of coal with steam and oxygen is followed by a purification step to eliminate solids, sulfur compounds, and most of the carbon dioxide. Two stages of synthesis are employed to attain a high conversion of the synthesis gas. Recovery and treatment of primary

[1] AYRES, *Petroleum Refiner*, **32** (8), 90–93 (August, 1953).

[2] AYRES, *Sci. American*, **195** (4), 43–49 (October, 1956).

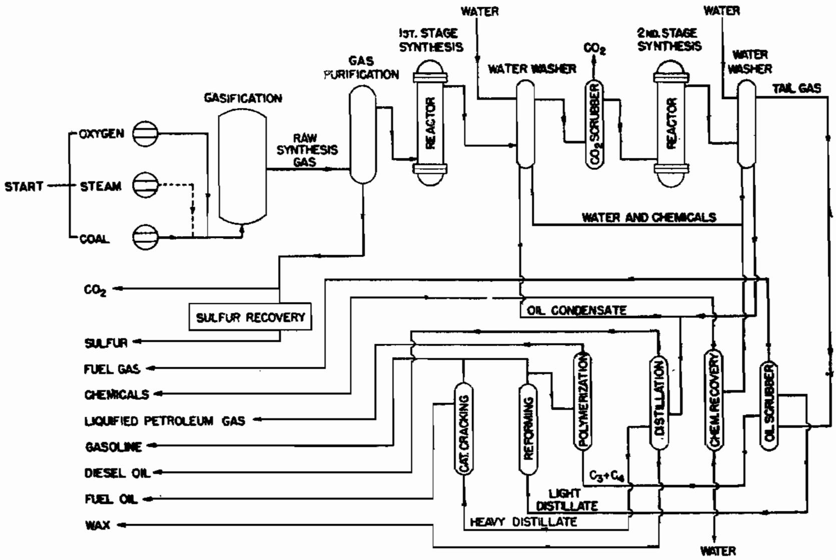

FIG. 11-3. Flow diagram of Fischer-Tropsch process.

products to refined products is carried out in several conventional steps.

Production of Synthesis Gas. Synthesis gas for the Fischer-Tropsch reaction consists of mixtures of hydrogen and carbon monoxide in ratios of from $0.7H_2:1CO$ to $2.5H_2:1CO$. Mixtures of hydrogen and carbon monoxide have been made in the past by water-gas generators operated cyclically, usually using coke as a fuel. The coke is first heated by an air blow (1) to heat the bed, and then, during the make cycle, steam is blown through the hot coke bed (2) to produce hydrogen and carbon monoxide:

$$C + O_2 = CO_2 \qquad \Delta H = -94{,}555 \text{ cal } (1500°\text{K}) \tag{1}$$

$$C + H_2O = H_2 + CO \qquad \Delta H = +32{,}265 \text{ cal } (1500°\text{K}) \tag{2}$$

Reaction (2) is endothermic; when the temperature of the coke bed becomes too low, the make cycle is ended and air is blown to heat the bed to high temperatures again.

Water-gas generators have been widely used to make heating gas of about 300 Btu per cu ft as well as gas for the production of hydrogen to be used in ammonia synthesis. Because of the cyclic nature of this method, the high cost of coke in relation to coal, and the relatively low productive capacity, water-gas generators are not sufficiently economical to be considered for the manufacture of synthetic fuels.

Other processes are available for the continuous production of synthesis gas from natural gas, liquefied petroleum gas, high-boiling oils, or solid fuels. Natural gas and liquefied petroleum gas can be reformed with steam and carbon dioxide over a nickel catalyst at high temperatures. Recently, processes have been developed for producing synthesis gas by the partial combustion of gaseous and liquid hydrocarbons or solid fuels with commercially pure oxygen (95–98 per cent oxygen) and steam. Coal, which costs only one-fourth as much as coke on a Btu basis, is readily converted to synthesis gas in this manner. The partial combustion can be carried out at a pressure of 400–450 psi, with the advantage that synthesis gas is produced at a pressure preferable for synthesis, thus avoiding the expense of compressing the gas. In addition, gasification of coal under pressure allows considerably greater throughputs in a given piece of equipment, thereby decreasing capital costs.

Pressure gasification can be accomplished with fine coal in suspension and in fluidized beds or with lump coal in fixed beds. Reactions (1) and (2) occur continuously, and at the high temperature attained by the use of oxygen, reaction (3) occurs:

$$CO_2 + C = 2CO \qquad \Delta H = +39{,}460 \text{ cal } (1500°\text{K}) \tag{3}$$

The heat required for reactions (2) and (3) is supplied by reaction (1). Other reactions occur in the gasification zone, but the three shown are the principal ones involved.

Where pulverized coal is gasified with oxygen and steam, the gases leave the combustion zone at a high temperature; a typical analysis of the gas produced is shown in the first column of Table 11-1.

TABLE 11-1. COMPOSITION OF CRUDE SYNTHESIS GAS FROM COAL GASIFICATION WITH STEAM AND OXYGEN

Composition	Pulverized coal	Fixed bed—Lurgi* (lump coal)
H_2	35	41.1
CO	50	22.4
CO_2	10	24.6
H_2S	1.5	0.5
N_2	1.7	3.5
CH_4	0.9	7.6
O_2	....	0.1
Illuminants	....	0.2

* COOPERMAN, DAVIS, SEYMOUR, and RUCKES, *U.S. Bur. Mines Bull.* 498, 1951.

The second set of data in Table 11-1 is an analysis of a raw gas produced by a coal-gasification process developed by Lurgi Gesellschaft. This process employs a noncaking type of coal in a pressurized fixed bed. Fresh coal is charged to the top of the bed by a pressurized hopper arrangement, and steam and oxygen are fed to the bottom of the gasifier. Coking of the coal occurs at the top of the bed, producing by-product tar. The gases have a relatively high content of methane, as its formation is favored in fixed-bed high-pressure gasification. This gasification process is employed in the 5,000-bbl per day synthesis plant in South Africa.

Purification of Synthesis Gas. The raw synthesis gas must be purified to remove solids such as unburned carbon and fine ash. This is generally done by water washing the gas in packed or spray towers, cooling as well as cleaning the gas.

Hydrogen sulfide and organic sulfur are catalyst poisons and must be removed to an extremely low value, generally less than 0.1 grain of total sulfur per 100 cu ft of gas. Carbon dioxide is harmful to the catalyst in high concentrations, and in addition is a diluent. Up to about 2 per cent of carbon dioxide usually can be tolerated in the purified gas.

Acidic constituents of raw synthesis gas, carbon dioxide and hydrogen sulfide can be removed either by water or Rectisol scrubbing or by an alkaline wash such as monoethanolamine, diethanolamine, or a hot potassium carbonate solution. Regeneration of these alkaline solutions is accomplished by steam stripping of the spent solution in the regenerator column. The main cost is that for steam required in the regeneration step, the hot-carbonate process requiring less steam than the amine-scrubbing operation. The latter process has the advantage also in removing carbonyl sulfide, usually the only organic sulfur compound present in the gas, when the exit temperature of gasification is relatively high, such as is the case in gasification of pulverized coal.

Because the synthesis gas is under pressures of 300–450 lb, it can also be scrubbed with water. Inasmuch as water scrubbing depends upon physical solubility of carbon dioxide and hydrogen sulfide in water, rather than upon chemical reaction, several times the rate of solvent circulation rate is required. No heating steam is required, but the main disadvantage of water washing is that 3–5 per cent of the carbon monoxide and hydrogen is lost by solution in water. Investment costs for water washing are considerably higher than for the alkaline-wash processes.

Another method of gas purification is the Rectisol process used in the South African plant. This process is based on the physical solubility of impurities in a methanol solution at −40 to −60°C. The solution is regenerated by pressure let-down for the most part. A small amount of methanol is thoroughly regenerated by heating for the final purification. Although the investment cost of the Rectisol plant is higher than those of other purification plants, the process does remove other constituents, such as organic sulfur compounds and gum-forming molecules in gas made by Lurgi fixed-bed gasification.

In connection with water washing and hot-carbonate or amine scrubbing, iron oxide boxes are usually added in the purification train, similar to those long used for purifying coke-oven gas. Iron oxide impregnated on wood shavings effectively reduces the concentration of hydrogen sulfide to trace amounts acceptable for Fischer-Tropsch synthesis. Iron oxide is converted to sulfide, which is then oxidized by small amounts of oxygen in the gas; free sulfur is formed.

When organic sulfur is not removed with the carbon dioxide and hydrogen sulfide, it must be eliminated by hot alkalized iron oxide, as was done in the German synthesis plants, or—probably more advantageously—by adsorption on activated carbon. The latter method was quite effective at the U.S. Bureau of Mines demonstration plant at Louisiana, Mo.

III. CATALYSTS

Nickel, cobalt, and iron catalysts are commonly used for the Fischer-Tropsch synthesis. Nickel catalysts have been prepared by precipitation from a nitrate solution with potassium carbonate in the presence of thoria and kieselguhr in the proportions $100Ni:18ThO_2:100$ kieselguhr.[1] It is not desirable to employ nickel catalysts at low temperatures and elevated pressures because the formation of nickel carbonyl is excessive. In the temperature range of 170–220°C at low pressures, both liquid and gaseous products are obtained. As the temperature is increased to 300–350°C and the pressure increased to 300–400 psi, nickel catalysts produce only methane. Thus, these catalysts can be used for making a gas from coal comparable in heating value to natural gas.

Cobalt catalysts are preferable to nickel when greater yields of liquid products are desired. The standard German cobalt catalyst during World War II had a composition of $100Co:5ThO_2:8MgO:200$ kieselguhr. Insoluble metal carbonates or hydroxides were precipitated by addition of sodium carbonate to the solution of the nitrate. Kieselguhr was then added, the slurry filtered, and the cake formed into granules of 1–3 mm in diameter. The dried granules were reduced with a mixture of 75 per cent hydrogen and 25 per cent nitrogen (ammonia synthesis gas for convenience) at about 400°C for about 50 min at a space velocity (volumes of gas/hr/volume of catalyst) of 10,000. The catalyst was used at atmospheric pressure or at 7–10 atm and at 180–200°C.

Because of the expense and scarcity of cobalt, emphasis has shifted to the use of iron. Iron catalysts may be prepared for commercial applications by precipitation from solution, from magnetite (Fe_3O_4) ore, or from magnetite obtained by fusion of iron oxides, or by oxidation of metallic iron with steam. An active catalyst prepared at the U.S. Bureau of

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[1] Fischer and Meyer, *Brennstoff-Chem.*, **12**, 225–232 (1931).

Mines laboratories by steam oxidation of steel lathe turnings is an example of the latter type. Mill scale, a product recovered from rolling and scaling operations in steel mills and composed predominantly of magnetite, has been employed with good results. The catalyst used for ammonia synthesis performs quite well in the Fischer-Tropsch synthesis. Additions of small amounts of potassium oxide, in the range of 0.1–0.5 per cent, are effective in increasing the activity and change the selectivity of the catalyst. Many other promoters have been added to iron catalysts, but their effect upon product distribution or activity has been relatively minor.

The magnetite catalysts are generally reduced to metallic iron with pure hydrogen at space velocities of 2,000 hr^{-1} and at 400–500°C. The time required for reduction depends upon catalyst size, a finely powdered catalyst requiring several hours, and coarser catalysts of 6–20 mesh requiring about 48 hr. The rate of reduction can be accelerated by increasing the temperature; however, if the temperature is too high, sintering of the catalyst surface reduces the surface area, resulting in lower activity. Precipitated iron catalysts usually are not reduced with hydrogen but are treated with synthesis gas at temperatures of 200–300°C.

Upon exposure of freshly reduced iron catalyst to synthesis gas, the metallic iron is converted to iron carbide, having the approximate composition Fe_2C, during the first few hours of synthesis. During the life of the catalyst, iron carbide is slowly oxidized to Fe_3O_4 by water vapor, a by-product of the synthesis, and deposition of free carbon occurs. Below about 280°C the main carbon-forming reaction is $3Fe_2C + 4H_2O = 2Fe_3O_4 + 3C + 4H_2$ (assuming the carbide to have the composition Fe_2C).

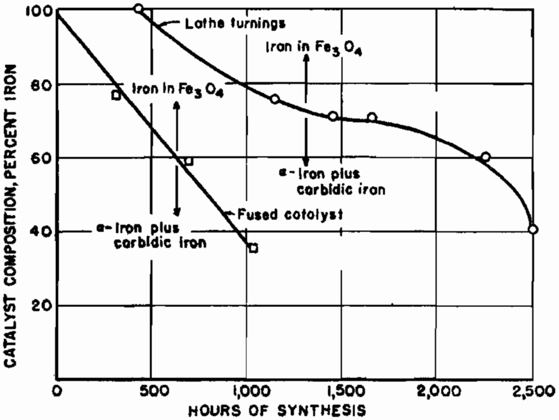

FIG. 11-4. Change in catalyst composition during synthesis. (*U.S. Bur. Mines Inform. Circ.* 7754, *May,* 1956.)

Carbon deposition at temperatures above about 300°C results mainly from the reaction $2CO = CO_2 + C$. This reaction becomes rapid at about 300°C, but can be controlled to some extent by employing synthesis gas having a ratio of $H_2:CO = 2$ or higher, thereby lowering the partial pressure of carbon monoxide. Figure 11-4 illustrates the rates of oxidation of fused iron oxide and of lathe turnings from low-carbon steel whose outer surface (20 per cent of the iron) was oxidized, impregnated with potassium carbonate, and reduced before synthesis. These data were obtained in pilot-plant investigations of the oil-circulation process at the U.S. Bureau of Mines laboratories.[1]

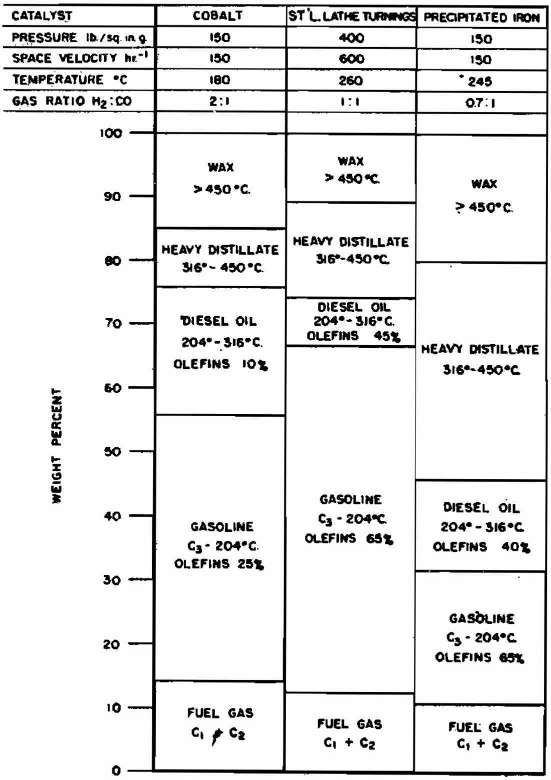

FIG. 11-5. Product distribution; cobalt and iron catalysts.

Iron catalysts operate over a considerably wider temperature range, 200–350°C, than do cobalt catalysts. The space velocity of operation is almost directly proportional to the pressure; however, pressures above 450

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[1] BENSON, FIELD, BIENSTOCK, and STORCH, *Ind. Eng. Chem.*, **46**, 2278 (November, 1954).

psi are not used for prolonged operation because of the danger of forming iron carbonyl, resulting in deterioration of the catalyst.

Product distributions obtained with precipitated iron with steel lathe turnings and with cobalt are shown in Fig. 11-5. As the olefin content of products from iron was considerably greater than from cobalt, the octane rating of the gasoline was higher.

The temperature of operation greatly affects the product distribution obtained with iron, as shown in Fig. 11-6. The gasoline yield increases as the temperature increases, while the yield of heavier products decreases. A similar shift of products to lighter material occurs when the alkali content of the catalyst is decreased. Thus, the two main factors affecting product distribution are temperature and alkali.

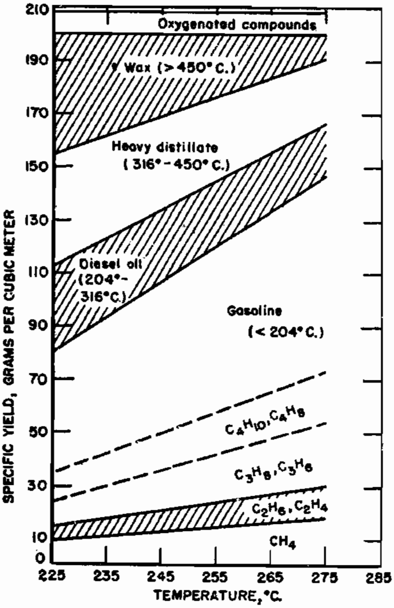

FIG. 11-6. Effect of temperature on specific yields with $0.7H_2 + 1CO$ synthesis gas.

IV. THERMODYNAMICS AND KINETICS OF THE FISCHER-TROPSCH REACTION

The Fischer-Tropsch synthesis may be represented by the following reactions to produce paraffins and olefins. Two sets of reactions are shown; water is formed as a by-product in the first set, carbon dioxide in the second.

$$(2n + 1)H_2 + nCO = C_nH_{2n+2} + nH_2O$$

$$2nH_2 + nCO = C_nH_{2n} + nH_2O$$

$$(n + 1)H_2 + 2nCO = C_nH_{2n+2} + nCO_2$$

$$nH_2 + 2nCO = C_nH_{2n} + nCO_2$$

The first two equations can be converted to the corresponding equations in the second set by addition of the water-gas shift:

$$CO + H_2O = CO_2 + H_2$$

In Table 11-2 heats of reaction, logarithms of equilibrium constants, and standard-state free energies are shown at 250 and 350°C for typical products of the synthesis (carbon numbers of 1, 6, and 20).[1] Data are

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[1] STORCH, GOLUMBIC, and ANDERSON, "The Fischer-Tropsch and Related Syntheses," John Wiley & Sons, Inc., New York, 1951.

TABLE 11-2. THERMODYNAMIC DATA PERTAINING TO FISCHER-TROPSCH REACTION

	ΔH, kcal/g mole				$\Delta F°$, kcal/g mole*				$\log_{10} k$			
	H_2O formed		CO_2 formed		H_2O formed		CO_2 formed		H_2O formed		CO_2 formed	
	250°C	350°C	250°C	350°C	250°C	350°C	250°C	350°C	250°C	350°C	250°C	350°C
Methane	−51.47	−52.7	−60.93	−61.45	−22.3	−15.8	−26.2	−18.6	9.3	5.5	10.95	6.5
n-Hexane	−236.8	−239.35	−293.7	−294.7	−55.6	−19.1	−83.3	−40.5	23.2	6.7	34.8	14.2
1-Hexene	−206.0	−208.35	−262.75	−263.55	−41.9	−9.4	−69.7	−31.1	17.5	3.3	29.1	10.9
n-Eicosane ($C_{20}H_{42}$)	−762.0	−769.8	−951.6	−954.1	−154.5	−31.7	−254.0	−106.1	64.5	11.2	106.0	37.2
1-Eicosene ($C_{20}H_{40}$)	−731.5	−739.0	−920.8	−923.0	−142.6	−20.0	−236.0	−86.5	59.5	7.0	98.5	30.3

* $\Delta F°$ is standard-state free energy.

given for the formation of water and carbon dioxide, corresponding to the two sets of reactions. The difference in the heats of reaction of about 9 kcal per g mole per carbon atom of the hydrocarbon is equivalent to the heat of reaction of the water-gas shift reaction.

The highly exothermic character of the synthesis is shown by the data. Except for formation of methane which is even more exothermic, about 38–42 kcal per carbon atom is liberated in the synthesis of the paraffins when water is the oxygenated product and 47–50 kcal when carbon dioxide is formed. Slightly less heat is liberated in the synthesis of olefins. The heat of reaction amounts to about 70 Btu per cu ft of synthesis gas reacting, or to about 7000 Btu per lb of hydrocarbon produced.

The equilibrium constants were calculated from the standard-state free energies,

$$-\Delta F^\circ = 2.303\, RT \log_{10} k$$

where R is the gas constant and T the absolute temperature in degrees Kelvin. ΔF° becomes less negative with increasing temperature, but is still highly negative up to 350°C. The high values of the equilibrium constants indicate that 250–350°C is a favorable operating range. At 380–420°C the ΔF° for many hydrocarbons becomes zero, which indicates the limiting temperature range for favorable equilibrium.

The kinetics of the Fischer-Tropsch reaction has been studied on both cobalt[1] and iron.[2] These studies supply data for the rational design of reactors and selection of optimum operating conditions; they also provide information on the mechanism of the synthesis, thus aiding development of catalysts and processes.

The synthesis of hydrocarbons on cobalt is quite different from that on iron. Water is virtually the only oxygenated product obtained with cobalt over a wide range of conditions, while both carbon dioxide and water are formed with iron. Whereas the rate of the synthesis is virtually independent of pressure with cobalt, for iron it is almost linear with the pressure (at least up to 675 psi) and approximately proportional to the partial pressures of carbon monoxide and hydrogen. Thus the reaction over iron catalysts is approximately first order.

Most of this discussion is confined to the kinetics of the synthesis on iron catalysts because most of the recent development is concerned with these catalysts. Anderson[3] has derived a relationship between throughput and conversion, based on kinetic studies of iron catalysts. With r the differential reaction rate per unit volume of catalyst, x the fraction of

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[1] ANDERSON, KRIEG, FRIEDEL, and MASON, *Ind. Eng. Chem.*, **41**, 2189 (1949); EROSEJEV, RUNTSO, and VOLKOWA, *Acta Physicochem. U.R.S.S.*, **13**, 111 (1940).

[2] ANDERSON, "Catalysis," vol. 4, Emmett (ed.), Reinhold Publishing Corporation, New York, 1956.

[3] *Ibid.*

$H_2 + CO$ converted, and S the hourly space velocity [volume of $H_2 + CO$/(volume of catalyst space)(hour)],

$$r = \frac{dx}{d(1/S)} \tag{1}$$

For conversions of $H_2 + CO$ up to 80 per cent, the following empirical relationship holds:

$$r = k\,(1 - x) \tag{2}$$

By equating (1) and (2) and integrating, one obtains the following expression:

$$-\log\,(1 - x) = \frac{k}{S} \tag{3}$$

Anderson made further studies on precipitated- and fused-iron catalysts to determine the relationship between rate and operating temperature. Tests were made with varying temperatures and flows at a constant conversion of $1H_2{:}1CO$ synthesis gas. Arrhenius plots of space-time yield [volume of $H_2 + CO$ converted/(volume of catalyst)(hour)] against reciprocal of the absolute temperature were approximately linear. The over-all apparent activation energy was 20.0–20.9 kcal/g mole, and a general expression was established to include temperature

$$-\log\,(1 - x) = \frac{A}{S}e^{-E/RT} \tag{4}$$

where A is a temperature-independent rate constant, E the over-all activation energy, and T the absolute temperature. Equation (4) can be used to correlate data obtained at different flows, temperatures, and pressures. Although based on data obtained with $1H_2{:}1CO$, it is fairly reliable for gases of other ratios.

The rate of reaction on fused or sintered iron increases with decreasing particle size.[1] The increase is approximately linear with increase in external surface area for large particles, but appears to reach a limiting value when the particle size becomes small. The rate dependence on the particle size is one of the reasons supporting the postulation that only the outer shell of the catalyst particle is believed to be utilized and that diffusion into the catalyst pores appears to control the reaction rate.

V. REACTOR DEVELOPMENT

Many types of reactors have been used for the Fischer-Tropsch synthesis. The chief difference between these reactors is the method provided for removing the large quantity of heat generated in the reaction. The

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[1] Hall, Gall, and Smith, *J. Inst. Petroleum*, **38**, 854 (1952); Anderson, Seligman, Shultz, Kelly, and Elliott, *Ind. Eng. Chem.*, **44**, 391 (1952).

reactors described in this section have been used either commercially or in large-scale pilot plants.

German Fixed-bed Type (Early). The first commercial units built in Germany employed a fixed bed of granular or extruded catalyst. In order to provide adequate cooling surface for heat removal, the reactors were of a complex design and of low capacity. Different reactor designs were used for atmospheric- and medium-pressure (7–10 atm) operation.

For operating at atmospheric pressure, rectangular steel boxes were used containing vertical steel sheets of less than 0.1 in. thickness and spaced slightly more than ¼ in. apart. The catalyst was placed between the sheets. Horizontal tubes of 1.34 in. diameter spaced on 3.2-in. centers, through which cooling water was circulated, pierced the sheets throughout their areas [see Fig. 11-7(*a*)]. About five pounds of steam was generated per pound of oil produced. Only about 15–20 barrels of oil per day was produced in a typical reactor which was 15 ft long, 8 ft high, and 6 ft deep. Most of the German plants employed 60 or more reactors in a two-stage operation.

For medium pressure the reactors were constructed similar to boilers, but with double tubes arranged concentrically. Catalyst was placed in the annulus, and cooling water circulated in the inner tube and outside the outer tube. The outside diameter of the inner tube was 0.95 in. and the inside diameter of the outer tube 1.73 in., giving an annulus of 0.39 in., which was considered to be about the maximum for adequate control of temperature. A 15-ft reactor, 8 ft in diameter containing about 2,000 tubes, was required to produce 15–20 bbl of oil per day.

The weight, volume, and cooling surface of the atmospheric- and medium-pressure reactors of about 18 bbl-per-day capacity in the Ruhrchemie plant are shown in Table 11-3.[1] With low output and complex fabrication, the fixed cost per unit of product was quite high. Other types of reactors were developed because of these inherent drawbacks.

TABLE 11-3. FIXED-BED REACTOR CHARACTERISTICS

	Atmospheric pressure	Medium pressure
Weight, tons	45	45
Total reactor volume, cu ft	650	950
Catalyst volume, cu ft	350	350
Finned surface, sq ft	38,700	None
Tube surface, sq ft	4,300	22,600

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[1] HALL and HAENSEL, *C.I.O.S.* File XXVII–69, Item 30; PB 415, 1945 (Combined Intelligence Objectives Sub-committee).

Slurry. Synthesis with a slurried catalyst has been investigated in large pilot plants. The slurry consists of finely pulverized catalyst particles suspended in a high-boiling oil to which the heat of reaction is transferred. Excellent temperature control is attained with this system. Catalyst particles are usually maintained in suspension by the upward flow of synthesis gas through the slurry [see Fig. 11-7(*c*)]. Forced circulation has also been used to aid in maintaining the slurry.

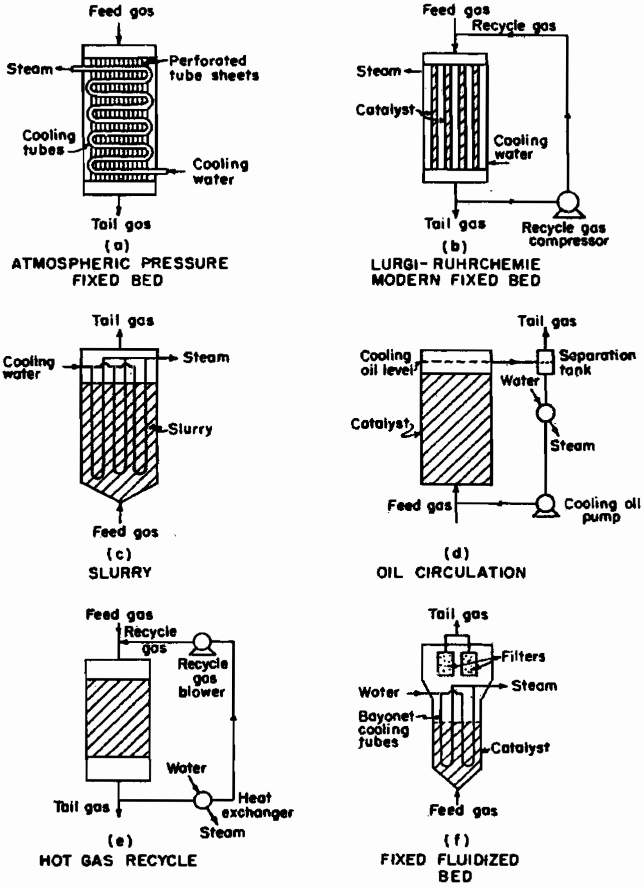

FIG. 11-7. Types of synthesis reactors.

Kölbel of Rheinpreussen in Germany contributed greatly to the development of the slurry technique.[1] His large pilot plant operated with about

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[1] KÖLBEL and ACKERMANN, *Chem.-Ing.-Tech.*, **6**, 381–388 (June, 1956).

350 cu ft of slurry containing approximately 90–100 g of iron per liter. A carbon monoxide–rich synthesis gas, $1H_2:1.5CO$, has been employed at an hourly space velocity of 270 and about 90 per cent conversion obtained in a single reaction stage at 12 atm and 270°C. The yield of $C_1 + C_2$ hydrocarbons was 12 g per cu m of gas converted, and the yield of C_3+ was 166 g per cu m on the same basis.

Kölbel stated that the process is extremely flexible and that the yields of low- and high-boiling hydrocarbons can be varied by modifying the catalyst pretreatment and operating conditions. Extremely low yields of C_1 and C_2 hydrocarbons are probably the principal advantage of the slurry system. About 30–50 sq ft of cooling surface is required per 1,000 cu ft of synthesis gas throughput per hour.

Oil Circulation. The oil-circulation process is similar to the slurry system in that the catalyst is submerged in a high-boiling oil which serves to remove the heat of reaction and permit close control of the temperature [see Fig. 11-7(*d*)]. Larger catalyst particles are used, either granules or massive iron or steel such as shot or lathe turnings. Fixed or expanded beds of catalyst may be used. In the latter, the bed is expanded about 5–20 per cent above its stationary height by the upward flow of cooling oil. Heat is removed in an external heat exchanger through which the cooling oil is circulated.

Initially this type of system was operated by Duftschmid in Germany. During the past ten years it has been developed further at the U.S. Bureau of Mines, with most of the heat being removed as sensible heat rather than by vaporizing the oil. Conversions of synthesis gas of 90 per cent have been achieved at hourly space velocities of 600–900, with feed gases of $H_2:CO$ ratios of 0.7–1.3:1. Carbon dioxide is generally removed from the recycle gas. The catalyst life is about 4–6 months. Yields of $C_1 + C_2$ hydrocarbons are 25–40 g per cu m of $H_2 + CO$ converted, and yields of C_3+ hydrocarbons range from 135–170 g. The yield of gasoline and heavy products can be adjusted by varying the alkali content of the catalyst and changing operating conditions.

Fluid Bed. Synthesis in a fluid bed of catalyst, in a manner similar to that employed for catalytic cracking of hydrocarbons, has been developed chiefly by American companies.[1] The fixed bed of fluidized catalyst is kept within the reactor space [see Fig. 11-7(*f*)] by limiting the linear velocity of the gas to about one foot per second. A dilute-phase fluid bed has been developed by the M. W. Kellogg Company in which the linear velocity of gas is 5–10 fps; catalyst is circulated through the reactor, separated from the gas by cyclones, and returned to the bottom of the reactor to be caught up into the gas stream again. The fixed-bed fluidized process is used by the Hidalgo Chemical Company at Brownsville, Tex., and the dilute-phase

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[1] Latta and Walker, *Chem. Eng. Progr.*, **44**, 173–176 (1948).

process is used in part of the South African Fischer-Tropsch plant. The principal advantages of the fluid-bed technique are high gas throughputs, high yields of gasoline, and use of cheap catalyst such as mill scale.

Considerable pilot-plant work was done between 1945 and 1952 with fixed fluidized beds of iron in reactors of about 2–8 in. in diameter and 10–20 ft in height. Temperature control is maintained by transfer of the heat of reaction through the fluidized bed to bayonet tubes in which steam is generated. The fresh catalyst ordinarily is finer than 100 mesh. Temperatures of 300–325°C and pressures of 300–450 psi are usually employed. Hydrogen-rich feed gas ($1.5\text{–}2.5H_2{:}1CO$) and recycling of end gas serve to maintain a high partial pressure of hydrogen in order to minimize formation of free carbon. Difficulties have been encountered in operation in a large-scale unit, and further development is proceeding.

The yield of C_3+ hydrocarbons is about 140–150 g per cu m of converted gas, most of which can be refined to high-grade gasoline by conventional treating. About 20–25 per cent of the feed gas can be converted to water- and oil-soluble oxygenates, such as alcohols, aldehydes, and acids, at certain operating conditions.

Hot-gas Recycle. Removal of the heat of reaction as sensible heat of fresh feed and recycle gas is utilized in the hot-gas-recycle system [see Fig. 11-7(*e*)]. The process devised by Michael in Germany operates with a 10°C rise of the gas temperature, and about 100 vol of end gas had to be recycled per volume of fresh gas to keep within this range.[1] Gas flows from the reactor to a heat exchanger, where it is cooled slightly to the temperature of the inlet of the reactor. A portion of the end gas, equivalent to the feed, is withdrawn for recovery of products, and the rest is recycled hot. Because of the need for high gas throughputs (superficial linear velocity of 2–10 fps at operating conditions), the shape and size of the catalyst must be designed to avoid excessive pressure drop and high costs for circulating gas.

Temperatures above 300°C are usually employed to favor high yields of low-boiling liquids in the gasoline range. The pressure is 20–30 atm. Uniform distribution of gas across the bed of catalyst is necessary to prevent local overheating and resulting carbon deposition. Michael stated that the gas flow had to be streamlined to maintain uniform distribution through the bed. When turbulence occurred, the gas velocity was uneven, with excessive flows in some parts of the bed and stagnation in others.

The hot-gas-recycle process was tested in a large pilot plant with a reactor having a catalyst volume of 140 cu ft and a bed depth of less than 3 ft to keep the pressure drop reasonable.

Since the operating conditions of the hot-gas-recycle system are about the same as those of the fluid bed, the products are similar. Yields of

[1] Atwell, Powell, and Storch, *Fischer-Tropsch TAC Report* Sn Mcl, PB 2051, 1945.

C_3+ product are 140–150 g per cu m of converted gas for two-stage operation with 92 per cent conversion of gas.

Modern Ruhrchemie Fixed-bed Reactor. A joint development by Ruhrchemie and Lurgi has resulted in an improved fixed-bed reactor having about twenty times the capacity of the early fixed-bed units [see Fig. 11-7(*b*)]. The unit consists of a water-jacketed tube bundle with catalyst inside the tubes. The major improvement in the new units is that larger tubes and higher gas throughputs can be used without danger of overheating. Improved temperature control is accomplished in part by use of catalyst particles of larger size and by recycling at least three volumes of end gas per volume of feed gas. Because the linear velocity of the gas is higher, greater heat-transfer coefficients are obtained. About 60–70 per cent conversion of the synthesis gas is achieved in a single stage.

Comparison of Temperature-control Characteristics of Various Types of Reactors. Several methods of heat removal are used in the various reactors. Heat removal for the most part may be considered to take place either directly, as in the oil- or gas-cooled systems where the catalyst surface is in contact with the cooling medium, or indirectly, as in the fixed or fluid beds where heat must be transferred through the bed to a cooling surface. Admittedly this is an oversimplification, especially in the case of the fixed and fluid beds where some direct heat transfer occurs.

A comparison is shown in Table 11-4 among various types of reactors of heat transfer, estimated heat-transfer coefficients, and calculated average temperature gradients between catalyst and cooling medium or surface. For each reactor, the heat load is based on a feed-gas flow typical for that type of operation. For example, the early fixed-bed units employed space velocities of about 100, while the fluid- and hot-gas-recycle systems are based on a space velocity of 1,000. Conversion of 90 per cent of the gas is assumed in all cases, with a heat evolution of 70 Btu per cu ft of converted gas.

The over-all heat-transfer coefficients for the fixed-bed and hot-gas-recycle systems were calculated from a correlation of heat transfer through packed beds.[1] A relatively high transfer coefficient of 50 Btu/(hr) (sq ft) (°F) is obtained for the hot-gas-recycle system because of the high linear velocity of the gas. A uniform amount of reaction has been assumed through the catalyst bed. When the reaction occurs nonuniformly and a large amount of conversion takes place in a limited area, as is often the case near the point of entry of the fresh gas, the gradients are higher.

The extremely low temperature gradient for the directly cooled processes is due to the fact that the large geometric surface area of the catalyst itself is the area of contact between the cooling medium and the catalyst. In the cases of indirect cooling, the heat-transfer coefficient is based on the area

[1] LEVA, *Ind. Eng. Chem.*, **42** (12), 2498 (1950).

TABLE 11-4. HEAT-TRANSFER CHARACTERISTICS OF SYNTHESIS REACTORS*

Type of reactor	Hourly space velocity	Gas recycle ratio, recycle gas:fresh gas	Type of heat transfer	Estimated over-all heat transfer coefficient, Btu/(hr)(sq ft)(°F)	Calculated avg catalyst temperature gradient, °F
Fixed bed, catalyst in 0.5-in.-diam. tube	100	1:1	Indirect, conduction through bed to cooling surface	6	13.5
Modern fixed bed, catalyst in larger tube	300	3:1	Direct by convection and indirect as above	30	27
Direct oil-cooled, either oil circulation or slurry	600	1–2:1	Direct, convection through oil film	40	1.7
Hot-gas recycle	1,000	40–100:1	Direct, convection through gas film	50	4.8
Fluidized bed	1,000	2:1	Mainly indirect, transfer through bed to cooling surface	100	105†

* Heat load based on 90 per cent conversion in all cases.

† Based on use of 6.02 sq ft of cooling surface per cubic foot of catalyst; this is the ratio of wall surface to volume in an 8-in.-diameter pipe with no internal coolers. Adequate temperature control is accomplished in a fluidized-bed pilot plant with this size of reactor.

of the cooling surface, which is considerably smaller. Accordingly, the calculated temperature gradients are much larger. Lower gradients ensure better temperature control and freedom from overheating.

VI. COMMERCIAL OPERATION

In 1939 there were 14 commercial Fischer-Tropsch plants operating throughout the world. Nine of these were in Germany, one in France, and the others in Japan and Manchukuo. About three-fourths of the total annual output of about a million tons of synthetic fuels came from Germany.

Most of the German plants were destroyed during World War II, and operation has been resumed at only two plants in West Germany. These are Chemische Werke Bergkamen A.G. at Essen,[1] a 50,000-ton-per-year plant, and Krupp Kohlechemie G.m.b.H. at Wanne-Eickel.[2] Since the economics of producing liquid fuels are unfavorable, principally waxes and high-boiling aliphatic alcohols are produced, the latter for use in detergents and fatty acids. A third Fischer-Tropsch plant in operation is that of Courrières-Kuhlmann at Harnes, France; its capacity is about 20,000 tons a year. Other plants probably are operating in Soviet-controlled lands.

Plants have recently been constructed at Brownsville, Tex., and Sasol, South Africa, that have incorporated the newest operating techniques.

Brownsville Plant. The first American synthetic-fuels plant was constructed at Brownsville, Tex., by the Carthage Hydrocol Company in 1951. Reactor design was based on a fixed fluidized bed of iron catalyst to convert hydrogen-rich synthesis gas, produced from natural gas, to liquid hydrocarbons and chemicals. The rated capacity of the plant is 7,000 bbl of products per day, but this production was never reached because of operating difficulties. Appreciable modification of some of the units was started in 1955 by the Stanolind Oil and Gas Company in an effort to surmount earlier operating problems. After two years experimentation, it was concluded that under prevailing domestic conditions the process could not produce gasoline and chemicals as cheaply as competitive processes.

A simplified flow sheet of the original plant is shown in Fig. 11-8.[3] About 64 million cu ft per day of natural gas is required, including that used as fuel for processing the products. An oxygen plant supplies about 1,800 tons per day to the gas generator where the partial combustion of natural gas occurs at a pressure of about 400–450 psi in accordance with the following equation:[4]

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[1] LÖPMANN, *Erdöl u. Kohle*, 7, 622–626 (1954).

[2] WOOD, *Chemical Age* (London), Mar. 10, 1956, p. 587.

[3] ARNOLD and KEITH, Progress in Petroleum Technology, Division of Petroleum Chemistry, American Chemical Society, 1951.

[4] MAYLAND and HAYS, *Chem. Eng. Progr.*, **45**, 452–458 (1949).

$$CH_4 + 0.61O_2 = 0.96CO + 1.82H_2 + 0.04CO_2 + 0.18H_2O$$
$$\Delta H_{291°C} = -21.7 \text{ kcal/g mole}$$

Approximately 180 million cu ft per day of synthesis gas is produced. High-pressure steam is generated by heat recovery from the hot synthesis gas. This steam is utilized in the oxygen plant. Carbon dioxide is scrubbed from the synthesis gas at elevated pressure.

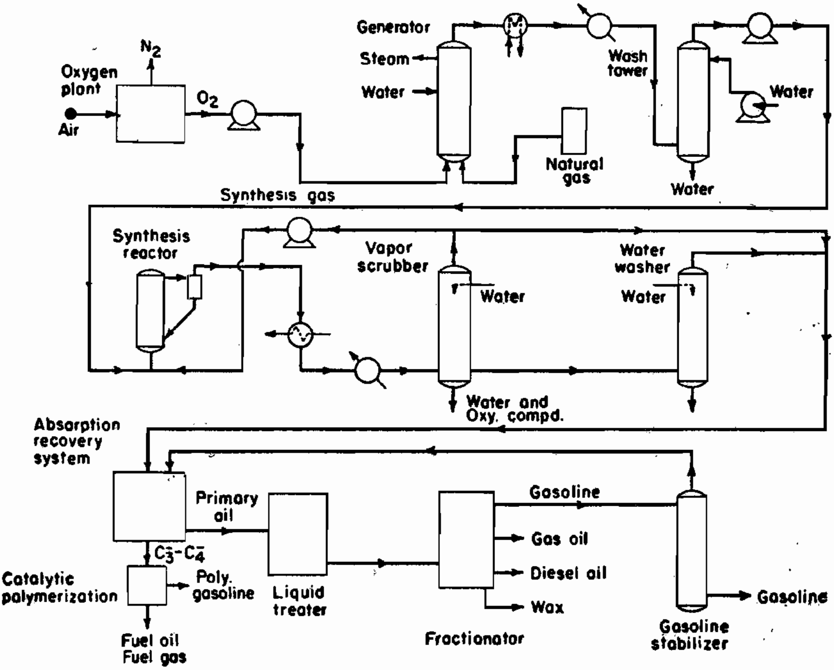

FIG. 11-8. Simplified flow sheet of Hydrocol plant.

Purified synthesis gas and recycled end gas flow to the two synthesis reactors. These vessels have a maximum diameter of 17 ft, are approximately 80 ft high, and contain about 200 tons of catalyst. Bayonet tubes carrying cooling water are located in the catalyst bed, and the heat evolved in the synthesis is used to generate steam. Gas and products leave the top of the reactors, and any fine catalyst entrained in the gases is removed by cyclones, filters, or other devices. Condensable oxygenates and hydrocarbons are removed by cooling and water scrubbing. Lighter hydrocarbons are removed in an absorption-recovery system, and C_3 and C_4 olefins are polymerized catalytically to gasoline. The primary gasoline is treated by conventional refinery techniques, including a bauxite treatment to decompose oil-soluble oxygenates.

The distribution of liquid products from this plant was expected to be about 25 per cent oxygenated compounds and 75 per cent hydrocarbons. Of the hydrocarbon liquids, about 85 per cent is gasoline, 10 per cent distillate fuel, and 5 per cent heavier fuel oil. The finished gasoline is highly olefinic, with a research octane number of about 85 unleaded. The scheduled annual production of water-soluble chemicals is shown in Table 11-5.

TABLE 11-5. SCHEDULED ANNUAL PRODUCTION OF OXYGENATED COMPOUNDS FROM HYDROCOL PLANT*

(Millions of Pounds per Year)

Methanol	0.5	Acetone	17.9
Ethanol	61.2	Methyl ethyl ketone	3.6
Isopropanol	1.3	Acetic acid	25.2
n-Propanol	19.6	Higher ketones	2.0
Acetaldehyde	11.2	Higher acids	11.0
Higher aldehydes	4.4	Higher hydrocarbons	8.5

* ARNOLD and KEITH, Progress in Petroleum Technology, Division of Petroleum Chemistry, American Chemical Society, 1951.

Recovery and sale of these oxygenated chemicals would yield an appreciable part of the plant revenue.

Sasol Plant. A commercial Fischer-Tropsch plant using coal as raw material was put on stream late in 1955 at Sasolburg in South Africa.[1] Large quantities of coal are located in the area, the cost of the mined coal being about $1.00 per ton. This coal is the weakly caking type and contains about 25 per cent ash and 10 per cent water; its heating value is 9000 Btu per lb.

The daily capacity of the plant is about 5,000 bbl of total liquid products. Coal consumption is 5,000 tons per day, of which 1,800 tons is for the power plant and 3,200 tons for gasification. A block diagram of the synthesis plant is shown in Fig. 11-9. Units for producing ammonium sulfate and other materials are not shown.

Raw coal is crushed and classified into three sizes. The finest portion is used in the power plant, which has four boilers, each having a capacity of 160 tons of steam per hour. A total of about 7 million cu ft per hr of raw gas is supplied at 25 atm from nine Lurgi fixed-bed gasifiers. A Linde air-liquefaction plant supplies about 70 tons per hr of oxygen for the gasification. Carbon dioxide and sulfur compounds are removed in a Rectisol plant.

The purified gas at elevated pressure is divided into two streams: one flows to the so-called Arge synthesis section, which consists of the modernized Ruhrchemie-Lurgi fixed-bed tubular reactors, and the other flows to

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[1] TRAMM, *Brennstoff-Chemie*, **37** (7/8), 117–119 (1956).

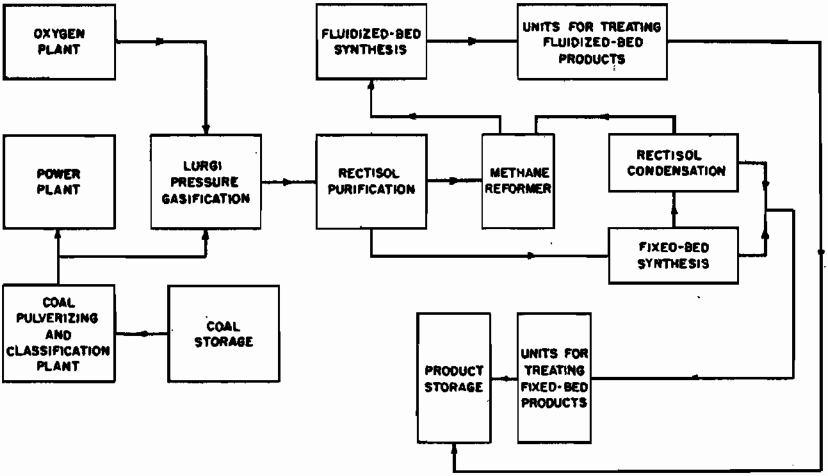

FIG. 11-9. Block diagram of synthetic fuels section of Sasol plant.

Kellogg fluid-bed units, which also use gas obtained from reforming the C_1 and C_2 hydrocarbons produced in the Arge section. There are five fixed-bed reactors, each with a heat exchanger, cooler, and recycle blower. The reactors are almost 10 ft in diameter and approximately 40 ft in height.

TABLE 11-6. PRODUCTS FROM SASOL PLANT*

	Planned production
Refinery products:	
Gasoline, bbl/day	4,300
Diesel oil, bbl/day	335
Fuel oil, bbl/day	180
Paraffin waxes, 105–240°F mp, ton/year	18,000
Liquefied petroleum gas, imp. gal/day	720
Pitch and tar road primers, imp. gal/day	2,685
Chemical products:	
Ethanol, imp. gal/year	4,000,000
Propanol, imp. gal/year	2,000,000
Butanol, imp. gal/year	525,000
Acetone, imp. gal/year	210,000
Methyl ethyl ketone, imp. gal/year	260,000
Mixed solvents, imp. gal/year	60,000
Benzene, imp. gal/year	500,000
Toluene, imp. gal/year	280,000
Xylene and solvent naphtha, imp. gal/year	500,000
Creosote wood preservative, imp. gal/year	1,000,000
Crude phenols, ton/year	6,000
Ammonium sulfate, ton/year	35,000

* SWAMINATHAN, *Petroleum Processing*, 10 (7), 987 (July, 1955).

Synthesis is conducted at about 220°C and about 25 atm. Each reactor is supplied with about 700,000 cu ft per hr of synthesis gas, and about 50 to 60 per cent conversion is achieved. The gas-recycle ratio is 3 vol of end gas per volume of fresh gas. Precipitated iron catalysts are used in this section, and a catalyst life of about one year is expected. Little information has been released on the fluid-bed section, which consists of two reactors with auxiliary equipment. Each synthesis section has its own product-treating units.

Much of the product of the Arge units is high-boiling hydrocarbons, while the product from the fluidized reactors is chiefly gasoline. The production of refinery and chemical products is listed in Table 11-6. The research octane number of the gasoline is about 85, and the diesel oil has a pour point of −5°C, a flame point of 82°C, and a cetane number of 90. The distribution of the products can be shifted to some extent in accordance with market demand.

VII. ECONOMICS OF FISCHER-TROPSCH OPERATIONS

Estimates of investment and operating costs of Fischer-Tropsch plants were made in 1953 by the U.S. Bureau of Mines and the National Petroleum Council. The cost of a 27,000-bbl-per-day synthetic liquid-fuels plant using coal-steam-oxygen pressure gasification was estimated at 290 million dollars, not including the costs for a coal mine, royalties, start-up expense, and working capital. With these items included, the total investment cost amounted to 380–400 million dollars, which is equivalent to about $14,500 per daily barrel of oil.

From information released by the National Petroleum Council, the cost of manufacturing synthetic gasoline has been estimated at slightly more than 17 cents per gal without allowance for return on investment and Federal income taxes. These two items amount to a total of 12 cents per gal for a 6 per cent return on investment. Improvements in technology should result in reduction of the costs. A breakdown of the various manufacturing costs is shown in Table 11-7.

VIII. METHANATION

High-Btu gas consisting principally of methane can be produced by conversion of synthesis gas over nickel or iron catalysts; nickel is more active. Four volumes of synthesis gas is consumed per volume of methane formed. A feed gas of $3H_2$:1CO ratio is desirable in accordance with the reaction

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

TABLE 11-7. SUMMARY OF MANUFACTURING COSTS OF SYNTHETIC LIQUID FUELS BY SYNTHESIS OF HYDROGEN AND CARBON MONOXIDE*

	Cost, cents/gal of gasoline
Raw materials and supplies:	
Coal	5.56
Catalyst replacement	0.10
Chemicals	0.40
Tetraethyllead	0.13
Utilities:	
Steam and electricity†	1.16
Cooling water	0.10
Labor:	
Direct labor	0.89
Indirect labor and overhead	2.01
Catalyst preparation	0.01
Fixed charges:‡	
Taxes and insurance	1.16
Maintenance	3.09
Amortization	3.86
	18.47
Credit for sulfur	0.83
Net manufactured cost	17.64

* Based on Supplementary Report of Subcommittee on Synthetic Fuels—Production Costs to National Petroleum Council, 1953; 27,000 barrel-per-day capacity. Based on 1951 investment costs and labor rates.

† Coal cost only; rest is included in other items as steam and power facilities are part of the total plant.

‡ No capital charges included.

A lower H_2:CO consumption ratio may occur, in which case carbon dioxide is formed by a secondary water-gas shift

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Methanation is highly exothermic, there being an evolution of 49.27 kcal per mole (298.2°K) of methane.

Methane was first synthesized by Sabatier and Senderens more than fifty years ago. For many years little work was done on developing methanation. Within the past fifteen years considerable amount of catalyst research and development has been done by the British Gas Research Board,[1] which is interested in ways of producing or enriching town gas to a heating value of 400–600 Btu per cu ft. One of their principal contribu-

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[1] DENT, MOIGNARD, EASTWOOD, BLACKBURN, and HEBDEN, *Brit. Gas Research Board, Commun. G.R.B.* 20, 1945.

DENT and HEBDEN, *ibid.*, 51, 1950.

tions has been the development of active and stable catalysts such as thoria-promoted nickel on kieselguhr of weight ratio 100NiO : 13.6ThO_2 : 78.4 kieselguhr. Catalysts of nickel alumina and nickel manganese have also been developed. Pilot-plant tests for as long as 3,500 hr showed that high activity could be maintained, provided that the sulfur content of the synthesis gas was extremely low (less than 0.01 grain sulfur per 100 cu ft). The heat of the reaction was removed from the fixed bed by a high flow of recycle gas, the ratio of recycle to fresh gas being at least 10:1.

Because of the large supplies of natural gas in this country, the synthesis of methane was of little interest. Recently, however, because of the tremendous increase in consumption of natural gas, attention has been given to the possible synthesis of high-Btu gas from coal to augment our natural supply.[1] A cooperative experimental program by the U.S. Bureau of Mines and the Southern Natural Gas Company dealt with the gasification of American coals by the German Lurgi process,[2] purification of the synthesis gas for methanation,[3] and the methanation step itself. Lurgi gasification was chosen as a well-developed pressure process that normally produces a gas containing considerable methane. Thus, a smaller amount of subsequent methanation is required, and temperature control in the methanation step is simplified because less heat is evolved. Difficulty was encountered in gasifying caking coals, but not noncaking fuels. The heating value of the carbon dioxide–free Lurgi gas was 410 Btu per cu ft, the methane content being about 10–15 per cent on a carbon dioxide–free basis. After purification to remove carbon dioxide and sulfur compounds, the gas was methanated over a nickel catalyst (British Gas Board type) so that the product had a heating value of 950 Btu per cu ft and was suitable as a pipeline gas. Another series of experiments, made with feed gases having different concentrations of carbonyl sulfide to determine the sensitivity of the nickel catalyst, indicated that sulfur was absorbed cumulatively by the catalyst, and activity decreased when about 0.58 g of sulfur had been absorbed per 100 g of nickel.

Recently the synthesis of methane has been investigated with a fluid bed of nickel catalyst.[4] The advantage of this technique is that only small amounts of end gas need be recycled to remove the heat of reaction because of the relatively high heat transfer obtained in the fluid bed. Bench-scale experiments made with catalysts of 80–250 mesh size in ¾- and 1-in.-diameter reactors indicated the need for multiple-entry points for feed

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[1] Breck, paper at American Institute of Mining Engineers, New York, February, 1952.

[2] Cooperman, Davis, Seymour, and Ruckes, *U.S. Bur. Mines Bull.* 498, 1951.

[3] Wainwright, Egleson, Brock, Fisher, and Sands, *U.S. Bur. Mines Rept. Invest.* 4891, 1952.

[4] Greyson, Demeter, Schlesinger, Johnson, Jonakin, and Myers, *U.S. Bur. Mines Rept. Invest.* 5137, July, 1955.

gas to avoid overheating in the bottom of the bed. However, almost complete conversion of synthesis gas was effected at fresh-gas hourly space velocities of 7,000–14,000. During the maximum catalyst life of 550 hr, 6,500 lb of methane was produced per pound of nickel. Raney nickel also was found to be an extremely durable and active catalyst for operation in the fluidized bed.[1] The fluid-bed technique must be tried in much larger beds before any conclusion can be reached as to the adequacy of the rate of heat transfer.

Concerning the economics of a synthetic high-Btu gas, the manner of processing, whether fluid or fixed bed, will have little effect on the cost of the final gas. The cost of producing purified synthesis gas is thought to amount to about 80–85 per cent of the total cost of high-Btu gas, while methanation itself accounts for only 1–2 per cent. Estimates of the cost of a synthetic high-Btu gas have varied from $0.55 to $1.25 per thousand cubic feet.[2]

IX. PROCESSES RELATED TO THE FISCHER-TROPSCH SYNTHESIS

General Introduction. Three processes, the *Oxo*, *Synol*, and *Isosynthesis*, are related to the Fischer-Tropsch process in that hydrocarbons or oxygenated chemicals are produced from mixtures of hydrogen and carbon monoxide. The principal catalysts, operating conditions, and products of these syntheses and similar data on the Fischer-Tropsch process and some of its variations are compared in Table 11-8.

Under Fischer-Tropsch synthesis there are listed two variations from the usual synthesis with iron and cobalt catalysts. By use of an iron nitride catalyst or an iron catalyst at special conditions (Oxyl process), considerably higher yields of oxygenated chemicals are produced than in the normal synthesis. Aliphatic oxygenated compounds, mainly alcohols, also are the chief products of the Oxo and Synol processes. The Oxo process, which exemplifies the *hydroformylation* reaction, differs from the others in that the feed contains an olefin in addition to hydrogen and carbon monoxide; also, its end products are specific alcohols containing one more carbon than the olefin in the feed, while a wide range of materials is synthesized in the other processes. A mixture of straight-chain alcohols and olefins is produced in the Synol process. The isosynthesis is especially adapted for the formation of a high yield of branched hydrocarbons; more recently, it has been modified to produce considerable amounts of aromatics.[3]

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[1] SCHLESINGER, DEMETER, and GREYSON, *Ind. Eng. Chem.*, **48**, 68 (January, 1956).

[2] ALBERTS, BARDIN, BEEBY, JONES, and VIDT, *Chem. Eng. Progr.*, **48**, 486–493 (1952). FOSTER and LUND (eds.), "Economics of Fuel Gas from Coal," McGraw-Hill Book Company, Inc., New York, 1950.

[3] U.S. 2,727,055 (1955); 2,768,961 (1956).

TABLE 11-8. FISCHER-TROPSCH AND RELATED SYNTHESIS PROCESSES

Synthesis process	Usual catalyst	Feed gas	Temp, °C	Press., atm	Principal products
Fischer-Tropsch......	a* Iron	0.7–2H_2:1CO	240–320	1–30	CH_4 hydrocarbons to waxes; appreciable olefins; some oxygenated compounds
	a* Cobalt	2H_2:1CO	180–240	1–20	CH_4 hydrocarbons to waxes; little olefins; small quantities of oxygenated compounds
	b† Iron nitride	0.7–2H_2:1CO	200–250	10–30	30–40% C_1–C_{14} alcohols; C_1 and higher hydrocarbons mainly boiling below 200°C
	b† Iron (Oxyl)	0.8–1.3H_2:1CO	180–210	20–30	80% C_1 alcohols and higher homologues; claims greater yield of high-boiling alcohols than by nitrided catalyst
Oxo................	Cobalt	1H_2:1CO plus 1 part C_n olefin	150–200	150–300	Chiefly C_{n+1} aldehydes which are subsequently hydrogenated to C_{n+1} alcohols
Synol..............	Iron	1–1.3H_2:1CO	185–225	15–30	C_1 to 450°C straight-chain alcohols plus hydrocarbons; also minor quantities of other oxygenated compounds
Isosynthesis..........	Thoria with alumina promoter	0.8–1H_2:CO	400–450	100–300	Chiefly C_1–C_6 hydrocarbons; extremely high percentage of isopropane and isobutene

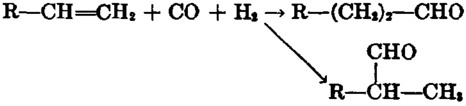
* Usual Fischer-Tropsch synthesis.

† Variations to produce higher oxygenate yields.

In the past five years considerable interest has developed in this country in the Oxo process as a source of specific petrochemicals, and several commercial plants have been placed in operation. Up to this time, none of the other processes has been of commercial importance.

The Oxo Process: Hydroformylation

Most of this section will be concerned with the Oxo process because of its commercial importance. This reaction of an olefin with hydrogen and carbon monoxide in the presence of a cobalt catalyst to produce aldehydes, containing one carbon atom more than that of the hydrocarbon in the feed, may be written as



$$\mathrm{R{-}CH{=}CH_2 + CO + H_2 \rightarrow R{-}(CH_2)_3{-}CHO}$$
$$\searrow \quad \mathrm{R{-}\overset{\overset{CHO}{|}}{C}H{-}CH_3}$$

Because the reaction results in the addition of a hydrogen atom and the formyl group (CHO) to the double bond, it would more properly be called hydroformylation.[1] However, the name Oxo has been generally accepted. The commercial process involves a second step in which aldehydes are reduced with hydrogen to primary alcohols.

Background. Otto Roelen of Ruhrchemie, Germany, was chiefly responsible for development of the Oxo process.[2] Some early work by Smith and his coworkers at the U.S. Bureau of Mines in 1930 had indicated that an increased yield of oxygenated compounds, as compared with conventional Fischer-Tropsch practice, was obtained when ethylene was added to water gas in the presence of cobalt catalyst at 200–225°C and atmospheric pressure.[3] Roelen modified the operating conditions significantly and found that, at temperatures below 200°C and pressures of 100–200 atm, all liquid products from the reaction of ethylene and water gas were oxygenated. He showed that the reaction could be applied generally to the formation of aldehydes from olefins and filed patents on the process as early as 1938.

Development of the process in Germany was expedited when Ruhrchemie and I.G. Farbenindustrie pooled their facilities about 1940. Results of laboratory- and bench-scale operations led to the construction of a demonstration unit at Leuna employing a catalyst slurry in a continuous two-stage process with an output of 1¼ metric tons of alcohols per day. The olefin feed was obtained by mild thermal cracking of soft paraffin wax from the Fischer-Tropsch synthesis. The product, a mixture of alcohols, was readily sulfonated to detergents, which were in great demand in

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[1] ADKINS and KRSEK, *J. Am. Chem. Soc.*, **71**, 3051 (1949).

[2] Roelen, U.S. 2,327,066 (1943).

[3] SMITH, HAWK, and GOLDEN, *J. Am. Chem. Soc.*, **52**, 3221 (1930).

Germany. Further expansion of the Oxo process was interrupted by World War II.

American companies became interested in the process during the war and initiated a substantial research program. Since production of specific alcohols was desired, more attention was focused on the use of narrow cuts of individual olefins in contrast to the mixed feeds employed by the Germans. The first commercial plant in the United States was constructed by the Standard Oil Company at Baton Rouge, La., in 1949. The main product from this plant is isooctyl alcohol produced from a heptene feed. As shown in Table 11-9, additional plants have been constructed by other large petrochemical companies, and the combined annual capacity at the end of 1956 exceeded 100 million lb of alcohols. In addition to isooctyl alcohol, the American plants produce normal and isobutyl aldehydes and alcohols, decyl and tridecyl alcohol.[1]

Raw Materials. *Synthesis gas* and an olefin are the reactants of the Oxo process. The ratio of H_2:CO is usually 1:1. Although equal molar quantities of synthesis gas and olefin are consumed, normally an excess of synthesis gas is used.

Hydrogen, which is required in the second step of the process to reduce the aldehydes, can be obtained from synthesis gas by the water-gas shift with steam, followed by removal of carbon dioxide:

$$CO + H_2O \rightarrow CO_2 + H_2$$

In some installations in this country, by-product hydrogen from a refinery operation has been used.

Carbon dioxide and sulfur compounds, such as hydrogen sulfide or carbonyl sulfide, must be removed from the gas. The latter, although they do not adversely affect the Oxo reaction, interfere with hydrogenation of the aldehydes. Carbon monoxide also is undesirable in that step and must be removed prior to it.

Olefins of many types, ranging from ethylene to hexadecene, have been found reactive. Many substituted ethylenes, in which groups other than alkyl are attached to the double bond, have also been treated. Compounds like divinyl ether, ethyl oleate, allyl alcohol, and cyclopentadiene have been used. Mixtures of olefins react as readily as pure compounds, and the presence of saturated hydrocarbons does not interfere with the reaction. Commercial installations in the United States employ principally a heptene fraction from polymerization of C_3 and C_4 unsaturated hydrocarbons. Propylene, butylene, and nonene are also being used.

Catalysts. Cobalt catalysts are universally used for the Oxo reaction. Roelen believed that cobalt hydrocarbonyl, $HCo(CO)_4$, was the active

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[1] Kiddoo, *Chem. Eng.*, **59** (9), (1952).

TABLE 11-9. COMMERCIAL OXO PLANTS IN THE UNITED STATES IN 1956

Company and location	Feed	Principal products	Reported annual capacity, lb
Tennessee Eastman Company,* Longview, Tex.	Propylene	Normal and isobutyraldehyde and butyl alcohols	
Union Carbide Corporation (Carbide and Carbon Chemicals Company),† Texas City, Tex.	Heptene Dodecene Nonene Butene	Isooctyl alcohols Primary tridecyl alcohols Primary decyl alcohols Primary amyl alcohols	60,000,000
Gulf Oil Company,‡ Port Arthur, Tex.	Heptene Nonene	Isooctyl alcohols Primary decyl alcohols	9,000,000
Standard Oil Company of Indiana,‡ Wood River, Ill.	Heptene Nonene	Isooctyl alcohols Primary decyl alcohols	10,000,000
Esso Standard Oil Company,§ Baton Rouge, La.	Heptene Nonene Dodecene	Isooctyl alcohols Primary decyl alcohols Primary tridecyl alcohols	Several million

* ANON., *Chem. Eng.*, **60** (3), 206 (March, 1953).

† SHERWOOD, *Petroleum Eng.*, **28** (5), C11–C14 (May, 1956).

‡ 1955 Chemical Engineer Inventory Plants and Facilities, *Chem. Eng.*, **62** (13), (October, 1955).

§ ANON., *Chem. Week*, **76** (11), 66 (Mar. 12, 1955).

form of the catalyst.[1] Recent investigators have indicated that dicobalt octacarbonyl, $[Co(CO)_4]_2$, or the hydrocarbonyl is the active catalyst.[2] Both dicobalt octacarbonyl and cobalt hydrocarbonyl are formed by nearly all cobalt salts and freshly reduced cobalt metal at 125–160°C in the presence of sufficient carbon monoxide and hydrogen.

For operation above 150°C and at about 3,000 psi, almost any salt of cobalt can be used. For operations below this temperature, dicobalt octacarbonyl or reactive cobalt metal such as Raney cobalt must be used. A laboratory method of preparing dicobalt octacarbonyl from cobalt carbonate and synthesis gas has been described by Wender.[3] Dicobalt octacarbonyl is formed according to the equation

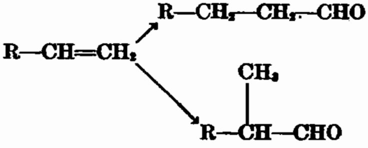
$$2CoCO_3 + 2H_2 + 8CO \rightarrow Co_2(CO)_8 + 2H_2O + 2CO_2$$

In this method cobalt carbonate, $CoCO_3$, and petroleum ether (35–50°C boiling range) are charged to a high-pressure stainless-steel autoclave, which is filled with $1H_2:1CO$ gas to 3,500 psi. The autoclave, while being agitated, is heated to 150–160°C and maintained at this temperature for about three hours. The clear dark solution formed is filtered and cooled below 32°F for 10–20 hr to promote the growth of large well-formed crystals of dicobalt octacarbonyl.

Commercially, either cobalt powder or soluble cobalt salts of fatty acids or naphthenates are used, depending upon the process. Usually a quantity of catalyst equivalent to about 0.5–5 mole per cent of cobalt is used.

Chemistry of the Oxo Reaction

Effect of Structure of the Olefins. One may regard the Oxo reaction as consisting of the addition of H and CHO to the carbon atoms joined by the double bond of the olefin. With a straight-chain unsymmetrical olefin, addition can lead to one or the other of two compounds or to a mixture of both, depending on where the formyl group is added:



Most of the straight-chain olefins studied in the Oxo reaction have been those in which the double bond is in the terminal position. The product

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[1] *B.I.O.S. Final Rept.* 447, Item 22, p. 40 (British Intelligence Objectives Sub-committee).

[2] Wender, Metlin, Ergun, Sternberg, and Greenfield, *J. Am. Chem. Soc.*, **78,** (October, 1956); Natta, Ercoli, Castellano, and Barbieri, *ibid.*, **76,** 4049 (1954); Martin, *Chemistry & Industry*, **1954,** p. 1536.

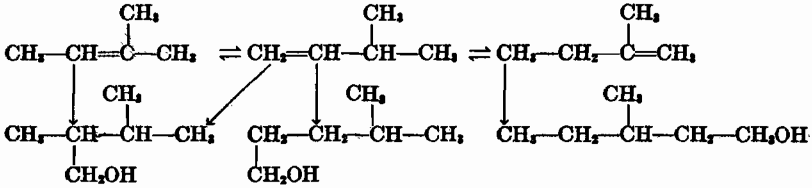
[3] Moeller, "Inorganic Synthesis," vol. V, McGraw-Hill Book Company, Inc., New York, 1957.

from such olefins is usually a mixture of aldehydes in which the straight- and branched-chain isomers occur in about equal proportions.

When straight or branched olefins, with the double bond in other than the terminal position, are subjected to the Oxo reaction, the products are almost identical with those obtained from the isomeric olefin in which the double bond is in the terminal position. For example, almost the same distribution of products was obtained from pentene-2 as from pentene-1.[1] In these tests the aldehydes (which are sensitive to heat and light) were reduced to the corresponding alcohols, and these were separated and identified. The alcohols from pentene-2 contained 10 per cent 2-ethylbutanol-1, 46 per cent 2-methylpentanol-1, and 44 per cent 1-hexanol; those from pentene-1 contained 6 per cent 2-ethylbutanol-1, 46 per cent 2-methylpentanol-1, and 48 per cent 1-hexanol. However, the rates of hydroformylation were quite different, that of pentene-1 being approximately 3.5 times that of pentene-2.[2] This is a general rate relationship for isomeric olefins with the double bond in the terminal and internal positions.

A general rule about the nature of the products is that, starting with a straight-chain olefin, about 60–40 per cent normal alcohol and 40–60 per cent alpha-branched alcohol are obtained, no matter where the double bond is located.

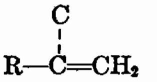
An example illustrating that the same products are formed from isomeric branched-chain olefins of different double-bond location is shown by hydroformylation of 2-methylbutene-2, 3-methylbutene-1, or 2-methylbutene-1:



2,3-Dimethylbutanol-1 5%

4-Methylpentanol-1 53%

3-Methylpentanol-1 42%

Olefins possessing the structure  $R{-}\overset{\overset{\textstyle C}{|}}{C}{=}CH_2$ add H and CHO predominantly one way; the formyl group goes almost entirely to the terminal

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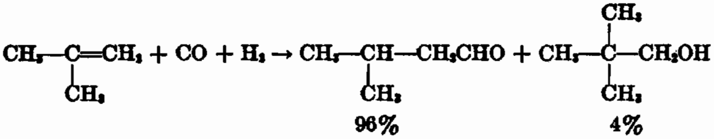
[1] Keulemans, Kwantes, and van Bavel, *Rec. trav. chim.*, 67, 298 (1948); Naragon, Hillendorf, and Larson, paper presented before the Petroleum Division, American Chemical Society meeting in Houston, Tex., March, 1956.

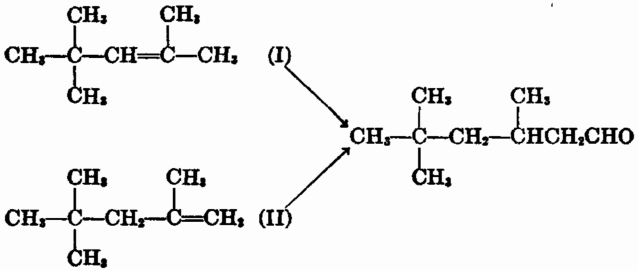
[2] Wender, Metlin, Ergun, Sternberg, and Greenfield, *J. Am. Chem. Soc.*, 78 (October, 1956).

carbon atom.[1] With isobutene, for example, distribution of products is as follows:



$$CH_3{-}\underset{CH_3}{C}{=}CH_2 + CO + H_2 \rightarrow \underset{96\%}{CH_3{-}\underset{CH_3}{CH}{-}CH_2CHO} + \underset{4\%}{CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2OH}$$

Of particular commercial interest, in connection with the effect of the olefin structure on the nature of the products of the Oxo reaction, is the behavior of diisobutylene. Diisobutylene is a mixture of 2,4,4-trimethylpentene-2 (I) and 2,4,4-trimethylpentene-1 (II). Only one product results from treatment of the mixture of isomers:



Effect of Temperature and Pressure. Temperatures of hydroformylation range from 110–190°C, depending upon the catalyst activity and the nature of the olefins. Usually low-molecular-weight olefins react at lower temperatures and more rapidly than do the higher-molecular-weight olefins. For maximum yield of aldehydes, the reaction should be operated at as low a temperature as is compatible with a reasonable reaction rate. Natta and Ercoli found that the specific reaction rate doubled for every 7°C increase in temperature at a constant concentration of dicobalt octacarbonyl catalyst.[2]

Operating pressures in commercial plants are in the range of 100–250 atm.

Kinetics and Mechanism of the Oxo Reaction. Kinetic data from batch autoclave experiments indicate that the rate of the hydroformylation reaction when using $1H_2{:}1CO$ synthesis gas is independent of the total pressure between 100 and 400 atm.[3] A plot of the log of the change in

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[1] WENDER, FELDMAN, METLIN, GWYNN, and ORCHIN, *J. Am. Chem. Soc.*, **77**, 5760 (1955).

[2] NATTA and ERCOLI, *Chimica industria* (*Milan*), **34**, 503–510 (1952).

[3] NATTA, *Brennstoff-Chemie*, **36** (11–12), 176 (1955).

concentration of the olefin with time at several pressures (Fig. 11-10) shows the independence of the rate and the total pressure.

From studies of the kinetics of the hydroformylation reaction made by Natta and Ercoli,[1] Martin,[2] and Wender, Greenfield, and coworkers,[3] the mechanism of the reaction has been postulated. These investigators have shown that the rate of hydroformylation

1. Is first order with respect to olefin concentration.
2. Is approximately proportional to the amount of cobalt present.
3. Increases with increasing hydrogen pressure at constant carbon monoxide pressure.

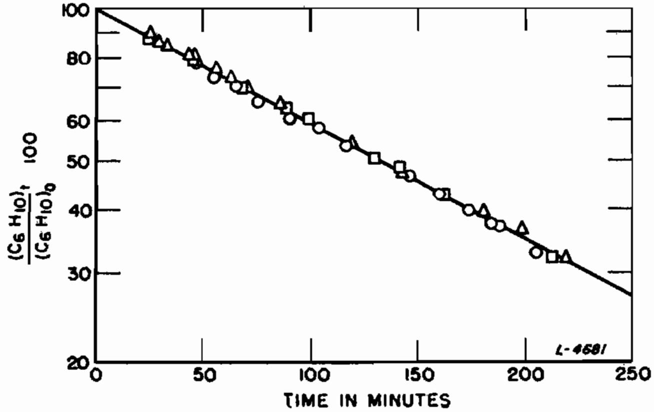

FIG. 11-10. The rate of hydroformylation of cyclohexene at varying total pressures of equimolar amounts of CO and H_2.

4. Decreases with increasing carbon monoxide pressure at constant hydrogen pressure.

Item 4 is the basis for the postulate that the first step involves formation of an olefin-carbonyl complex and carbon monoxide by reaction of dicobalt octacarbonyl with the olefin:

$$Co_2(CO)_8 + RCH{=}CH_2 \rightarrow Co_2(CO)_7{\cdot}RCH{=}CH_2 + CO$$

Decomposition of the complex by reaction with hydrogen or cobalt hydrocarbonyl, $HCo(CO)_4$, which also may be present, is then suggested to yield the aldehyde and a precursor of dicobalt octacarbonyl. Dicobalt octacarbonyl is formed again by reaction of this precursor with carbon monoxide.

Wender and coworkers showed that the rates of reaction of various

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[1] NATTA, ERCOLI, CASTELLANO, and BARBIERI, *J. Am. Chem. Soc.*, **76**, 4049 (1954).

[2] MARTIN, *Chemistry & Industry*, **1954**, 1536.

[3] WENDER, METLIN, ERGUN, STERNBERG, and GREENFIELD, *J. Am. Chem. Soc.*, **78** (October, 1956).

olefins were influenced by the structure of the olefin.[1] They postulated that the rate of formation of the olefin-carbonyl complex depended upon the magnitude of the steric effect caused by the olefin structure and that this was a rate-determining factor.

Thermodynamics. The heat liberated in the Oxo reaction is about 30 kcal per mole and does not vary greatly with the structure of the olefin. In view of the magnitude of this exotherm, heat removal is an important factor in the design of a reactor.

Some interesting thermodynamic calculations regarding the Oxo synthesis have been made by Wenner.[2] He considered the two equations:

$$C_2H_4 + CO + H_2 \rightarrow C_2H_5CHO\ (g) \qquad \Delta H = -34{,}787 \text{ cal} \qquad (1)$$

$$C_3H_6 + CO + H_2 \rightarrow (CH_3)_2CHCHO\ (g) \qquad \Delta H = -31{,}140 \text{ cal} \qquad (2)$$

For heats of reaction and entropy values, he calculated the free energies for reactions (1) and (2) by the equation $\Delta F = \Delta H - T\Delta S$,

$$\Delta F_1 = -34{,}787 + 58.1T \qquad (3)$$

$$\Delta F_2 = -31{,}140 + 61.4T \qquad (4)$$

From the free-energy equations for (1) and (2), the equilibrium constants (K) were calculated from the usual relationship $\Delta F = -RT \ln K$. For temperatures of 25 and 227°C, the equilibrium constants are as follows:

Temp, °C	C_2H_5CHO	$(CH_3)_2CH—CHO$
25	6×10^{12}	2.5×10^{9}
227	324	1.6

Accordingly, conversion of ethylene and propylene to the aldehydes is thermodynamically possible at 1 atm of synthesis gas and at moderate temperatures. Commercially the reaction pressures are above 100 atm.

Technical Operation

Commercial Processes. The Oxo reaction is carried out in the liquid phase. With gaseous olefins, a suspension medium such as an inert hydrocarbon is used of a boiling range sufficiently different from the aldehyde product to allow easy separation. No additional medium is required for hydroformylation of liquid olefins. Two liquid-phase processes have been developed. In the earlier one the catalyst is slurried in the feedstock or added liquid medium. Less operating difficulty is claimed for the newer fixed-bed system because the need for filtration and solids handling is eliminated.

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[1] *Ibid.*

[2] WENNER, *Chem. Eng. Progr.*, **45**, 194 (1949).

The slurry system (Fig. 11-11) was originally developed by I.G. Farbenindustrie and employed at the Leuna plant. Two reactors are used in both the Oxo and hydrogenation steps. A suspension of about 3–5 per cent by weight of cobalt catalyst in olefin is pumped to the bottom of the first reactor after being preheated to about 150°C. The hourly space velocity of slurry through the reactor ranges from about 1.3–3, depending upon the olefin in the feed. Fresh synthesis gas, containing equal volumes of hydrogen and carbon monoxide, and recycle gas are preheated to about 150°C and fed to the bottom of the reactor at an hourly space velocity of 250 and a pressure of 220–240 atm. About 20–30 per cent of the total gas feed is fresh gas. About 70 per cent of the olefins are converted in the first reactor, and the products are passed to the bottom of the second reactor, where about 20 per cent more of the original olefins are converted with an additional equal amount of gas of the same composition.

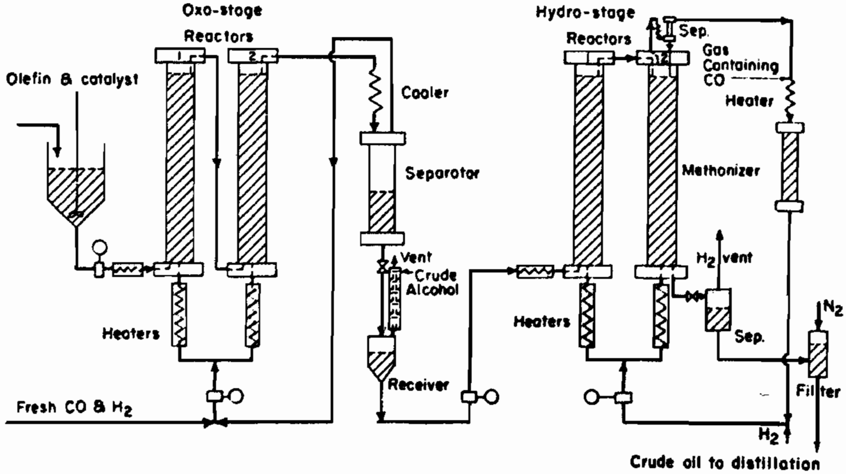

FIG. 11-11. Oxo process with slurried catalyst.

The carbon-steel reactors in the Leuna plant had an internal diameter of 220 mm (7.86 in.) and were 8 m (26.2 ft) high. The first reactor contained six vertical steel cooling tubes, 21 mm (0.825 in.) outside diameter and 17 mm (0.668 in.) inside diameter, which were connected to a water jacket surrounding the reactor. No cooling tubes were used in the second reactor because only a small part of the heat of reaction was liberated there. The second reactor contained baffles to increase contact between reactants.

Materials leaving the top of the second Oxo reactor are cooled and flow to a separator from which unreacted gas is recycled to the preheater. The liquid products are depressurized in a receiver, and dissolved gases are released and scrubbed countercurrently with crude alcohol to prevent entrainment of product in the off-gas. Simultaneously, cobalt carbonyl decomposes to metallic cobalt and carbon monoxide. The crude product containing metallic cobalt is pumped at 200–250 atm through a preheater to the bottom of the first hydrogenation reactor. Fresh and recycle hydrogen is preheated and fed at an hourly space velocity of 250 to the bottom of this reactor. Cocurrent flow is used in the first hydrogenation reactor and countercurrent flow in the second. Exit material from the top of the first hydrogenation reactor is fed to the top of the second reactor and hydrogen is fed to the bottom. A temperature of about 180°C is used in the first reactor and about 200°C in the second. Liquid product withdrawn from the bottom of the reactor is let down to an intermediate pressure and filtered to separate the catalyst, which, suspended in wash olefin, is pumped to the mixing tank for reuse. Crude alcohols are purified by distillation to remove materials such as polymers which may form in the Oxo reactors. Gases leaving the top of the hydrogenation reactor are recycled after removal of carbon monoxide by methanation over an iron catalyst.

An alternative method of hydrogenation uses a copper chromite catalyst. In this case, metallic cobalt is removed from the crude product before hydrogenation.

In the fixed-bed process, shown schematically in Fig. 11-12, soluble cobalt salts of fatty acids or naphthenates are pumped with the olefin to the top of the first reactor and flow countercurrent to the synthesis gas. One type of fixed-bed catalyst consists of 2 per cent metallic cobalt on a pumice carrier.[1] Part of the cobalt is converted to carbonyl, leaves the reactor with the overhead product, and is replaced by the cobalt salts in the feed. A high recycle of cooled crude product to the converter aids in controlling the reaction temperature. Unreacted synthesis gas leaving the top of the reactor is cooled, passed through a packed tower countercurrent to the olefin feed to remove cobalt carbonyl, and recycled to the reactor.

The second vessel is a decobalting converter in which cobalt carbonyl, dissolved in the product from the first reactor, is decomposed by hydrogen treatment at about 200–220 atm and 120–150°C. The liquid enters at the top, flows countercurrent to the hydrogen, and metallic cobalt is deposited on the packing. Gas flows from the top of the decobalting unit to the carbonyl scrubber, while the liquid leaving the bottom is sent to the hydrogenation reactor. This is operated at a higher temperature than the decobalting unit. Copper chromite is generally used as the catalyst. Crude alcohols are withdrawn from the bottom of the reactor and purified by fractionation.

Conditions are shown in Table 11-10 for operating a fixed-bed unit with

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[1] SHERWOOD, *Petroleum Engr.*, **28** (5), C11–C14 (May, 1956).

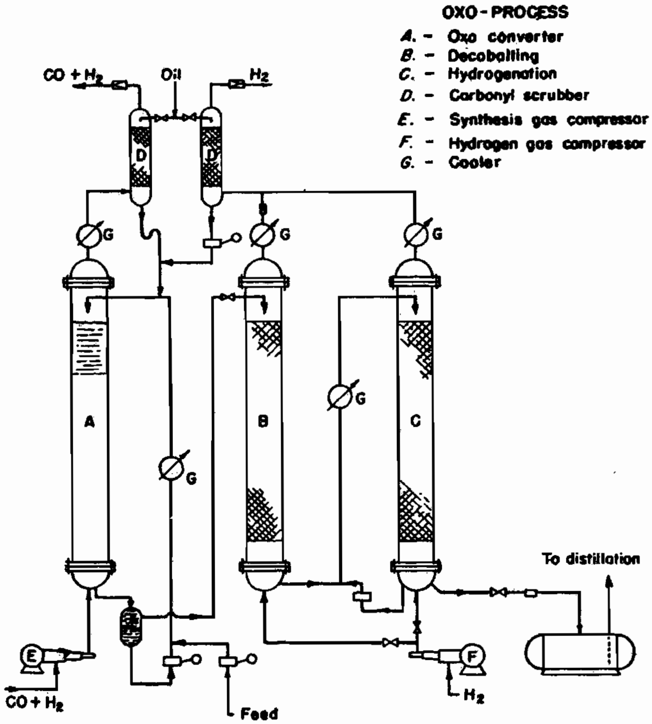

FIG. 11-12. Oxo process with fixed catalyst bed.

a heptene feed of 170–210°F ASTM distillation range and 5 and 90 per cent points of 185 and 200°F, respectively.

Products and Uses. The Oxo process has provided a new source of high-boiling aliphatic alcohols. Isooctyl alcohol has been the principal product thus far. Isooctyl alcohol from the Oxo synthesis sold at about 21 cents per lb in 1955.[1] Chief use of this alcohol is as raw material for plasticizers such as diisooctyl phthalate. Derivatives of isooctyl alcohol such as isooctanoic acid and isooctylamine are used in manufacturing paint driers and as surface-active agents. Esters of decyl alcohol are used as plasticizers and are superior to esters of lower-boiling alcohols because of their low volatility. Tridecyl alcohol is another Oxo product which is being used in commercial quantities. A derivative, tridecyl mercaptan, is an ingredient of GR-S rubber.

In general, high-molecular-weight alcohols are used as intermediates for preparing surface-active agents and plasticizers. Provided that proper

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[1] ANON., *Chem. Week*, p. 66, Mar. 12, 1955.

TABLE 11-10. FIXED-BED OPERATING CONDITIONS

Oxo stage:	
Catalyst, wt % cobalt naphthenate	2.5
Temperature, °F	349
Pressure, psig	3,000
Fresh feed, vol./vol. hr	0.4
Recycle product, vol. % of fresh feed	500
Recycle gas rate, cu ft/bbl fresh feed	6,100
H_2:CO ratio:	
Fresh synthesis gas	1.1
Fresh + recycle gas to reactor	1.1
Synthesis gas consumption, cu ft/bbl fresh feed	2,400
Olefin conversion, %	81
Decobalting stage, pancake-type steam oil heater:	
Pressure, psig	95
Temperature, °F	308
Feed rate, vol./vol. hr	0.35
Stripping gas rate, cu ft/bbl fresh feed	150
Soluble cobalt, wt %:	
Before decobalter	0.081
After decobalter	0.001
Hydrogenation stage:	
Temperature, °F	393
Pressure, psig	2,900
Feed rate, vol./vol. hr	0.6
Gas rate, cu ft/bbl	5,000
Product, carbonyl number	11
Product yields, wt % output of feed:	
Octyl alcohols	74.6
Bottoms	26.8

feedstocks are available, alcohols containing up to 15 or more carbon atoms can be produced by the Oxo process. Production of such materials depends upon the development of uses and markets for them.

n-Butyraldehyde and *n*-butanol are the principal relatively low-molecular-weight oxygenates produced commercially from the Oxo process in this country. The aldehyde is readily converted to butyric acid and anhydride which are used in large quantities for esterification of cellulose.[1] Polyvinyl butyral, used in safety-glass manufacture, is produced from *n*-butyraldehyde and polyvinyl alcohol. *n*-Butanol is a solvent for urea-formaldehyde resins and an important esterification reactant.

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[1] SHERWOOD, *loc. cit.*

Synol and Isosynthesis Processes

The *Synol* and *isosynthesis* processes, as well as the Oxyl and iron nitride variations of the Fischer-Tropsch synthesis, were developed to produce special products from synthesis gas. All but the isosynthesis are designed to produce high yields of oxygenated materials. The isosynthesis yields highly branched aliphatic hydrocarbons and aromatics. While none of these processes has been used commercially, they could be of interest at some future time.

A tabulation of operating conditions and yields for the Synol process, iron nitride synthesis, and original isosynthesis is given in Table 11-11. Detailed data have not been released on the Oxyl process. Operating temperatures and pressures of the Synol,[1] Oxyl, and iron nitride syntheses[2] are not significantly different. The Synol process utilizes a high ratio of gas recycle, and because the products are carried out of the reactor rapidly,

TABLE 11-11. OPERATING CONDITIONS AND YIELDS OF SYNTHESIS PROCESSES RELATED TO FISCHER-TROPSCH

	Synol	Fischer-Tropsch	Isosynthesis
Catalyst	Fused iron	Iron nitride	Thoria with Al promoter
Synthesis gas, H_2:CO ratio	1–1.3	0.7–2	0.8–1
Temperature, °C	185–225	200–250	400–450
Pressure, atm	15–30	10–30	100–300
Hourly fresh gas space velocity	250	100–500	150–300
Recycle ratio, end gas to fresh gas	10–100	0–2	0–6
Synthesis stages	2	1–2	2
Over-all synthesis gas conversion, %	90	90	75
Yield, g/cu m converted gas:			
$C_1 + C_2$	20	40–50	30
C_3+	170	150	150–160
Products, wt % of C_3+:			
$C_3 - C_4$	8.4 (0)*	29.1 (0)	57.0 (80% of C_4 is iso)†
40–100°C	19.2 (5–10)	27.0 (50–60)	43.0
100–200°C	21.9 (42.0)	21.5 (75–85)	
200–300°C	17.7 (66.0)	11.6 (30–40)	
300–400°C	13.4 (65.0)	6.0 (2–5)	
>400°C	19.4 (35.0)	4.8 (0–5)	

* Values in parentheses show weight percentage of alcohol in fraction.

† Two per cent yield of methanol, only oxygenate.

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[1] REICHL, *U.S. Naval Technical Mission in Europe, Rept.* 248–45, PB 22,841, 1945.

[2] ANDERSON, SHULTZ, SELIGMAN, HALL, and STORCH, *J. Am. Chem. Soc.*, **72**, 3502 (1950).

the high-molecular-weight alcohols are not dehydrated. The products from the synthesis over iron nitride are predominantly of low molecular weight. The percentage of C_1—C_4 hydrocarbons is high, and comparatively little material boiling above 300°C is produced. The fraction boiling between 100 and 200°C has the highest concentration of alcohols, and the alcohol content drops sharply in the higher-boiling cuts. By contrast, the highest alcohol concentrations in products from the Synol process are in the fractions boiling between 200 and 400°C. The high-boiling alcohols are considerably more valuable. Few data are available on the products from the Oxyl process, but a high yield of high-boiling alcohols is claimed.

A common difficulty of all these processes is the complexity of separating the mixtures of oxygenates and paraffinic and olefinic hydrocarbons. Fractionation alone may not be sufficient, because of overlapping boiling points and formation of azeotropes between oxygenates and hydrocarbons. Costly treatments, such as boric acid esterification, may be necessary to recover marketable products from certain fractions. Another hindrance to commercial development is the difficulty of developing markets for the wide range of materials that are produced.

The conventional isosynthesis for producing branched hydrocarbons appears to be mainly of academic interest, especially in this country. It was developed on a laboratory scale in Germany when there was an extreme need for isobutene and isobutane, as a starting material for the production of aviation fuels.[1] As shown in Table 11-11, about 57 per cent of the C_3+ product is C_3 and C_4 hydrocarbons, and 80 per cent of the C_4 is branched. Rather severe operating conditions include a temperature of 400–450°C and pressure of 100–300 atm. The common Fischer-Tropsch catalysts are not satisfactory for the isosynthesis. The more recent development to yield aromatics may be of commercial value at some time.

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[1] Pichler and Ziesecke, *U.S. Bur. Mines Bull.* 488, 1950.

CHAPTER 12

ESTERIFICATION

By E. Emmet Reid, Marvin L. Peterson, and John W. Way

In this chapter, esterification will be considered in the broadest sense as including all processes by which esters are produced. The importance of esters has increased enormously in recent years. The references cited in this chapter are only a small fraction of those which might have been given. More detailed information may be found in several reviews.[1]

The processes are given in this chapter in broad outline. The principles that underlie them are emphasized. The principles are matters of general knowledge and do not change; the details of their application vary from time to time and from plant to plant and are usually kept secret as long as they are of private advantage. In fact, there is no absolutely best way to make any one ester, such as ethyl acetate; an experienced and skillful operator can determine the most economical method for a certain scale of operation to produce a specified grade of ester with acetic acid, alcohol, and steam at certain prices, but for another scale or with materials at other prices, an entirely different process may have the advantage. Anyone with a thorough understanding of the principles can apply them to special cases as they arise. Manufacturing processes are described for several esters, but these are presented as examples of how the principles may be applied, rather than as recipes.

To give an idea of the quantities of esters now being produced and consumed, a few figures are given for United States production, in millions of pounds for 1954.[2]

Ethyl acetate	72	Cellulose acetate	364
Butyl acetate	78	Cellulose xanthate	700
Dibutyl and dioctyl phthalate	108	Rosin esters	57
Alkyd resins	417	Plasticizers	301
Polyester resins	49	Vinyl acetate	106

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[1] Goldsmith, *Chem. Revs.*, **33**, 257–349 (1943); Reid, *Ind. Eng. Chem.*, **29**, 1344 (1937); **40**, 1552 (1948); **41**, 1821 (1949); **42**, 1667 (1950); **43**, 1942 (1951); **44**, 1988 (1952); **45**, 1936 (1953); **46**, 1801 (1954); Peterson and Way, *ibid.*, **47**, 1849 (1955).

[2] *U.S. Tariff Commission Rept.* 196, Synthetic Organic Chemicals, U.S. Production and Sales, 1954.

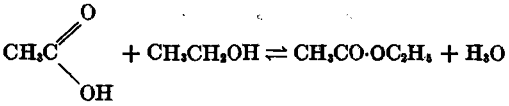
Cellulose nitrate, glyceryl trinitrate, ethylidene diacetate, methyl methacrylate, and phosphate esters are also produced in large quantities.

I. ESTERIFICATION BY ORGANIC ACIDS

This is esterification in its narrow sense and is what is usually meant when the term esterification is used. It has been extensively studied by both organic and physical chemists. It has been one of the most useful reactions in preparative organic chemistry, one of the best examples of the application of the mass-action law, and has involved one of the most baffling problems in homogeneous catalysis.

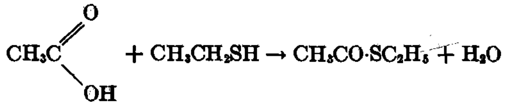
An ester is usually defined as a compound formed by substituting an organic radical for an ionizable hydrogen of an acid.

The mechanisms by which this replacement occurs have been well established. If the direct esterification of an acid, such as acetic, by an alcohol, such as ethanol, is considered, the possibility of breaking either



$$CH_3C(=O)OH + CH_3CH_2OH \rightleftharpoons CH_3CO{\cdot}OC_2H_5 + H_2O$$

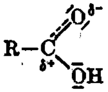
the carbonyl-oxygen bond or the alkyl-oxygen bond is evident. Evidence for the breaking of the carbonyl-oxygen bond was found in the study of the following reaction,



$$CH_3C(=O)OH + CH_3CH_2SH \rightarrow CH_3CO{\cdot}SC_2H_5 + H_2O$$

in which water was formed.[1] If the alkyl-sulfur bond had broken, hydrogen sulfide would have been formed. That the carbonyl-oxygen bond is the one broken was confirmed by the finding that esterification of benzoic acid containing the normal oxygen isotope distribution by methanol enriched with 0^{18} produced methyl benzoate containing the heavy oxygen isotope, while the water formed had only the normal isotope distribution.[2]

A generalized explanation for the selectivity of the bond-breaking process is found in the electronic structure of the reactants and products. Since oxygen is more electronegative than carbon, the carbonyl carbon is more positive than the carbonyl oxygen. This may be represented as:



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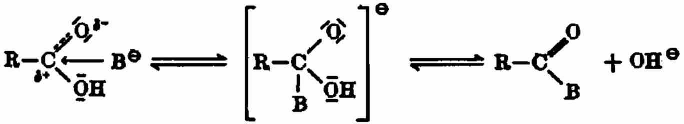
[1] Reid, *Am. Chem. J.*, **43**, 489 (1910).

[2] Roberts and Urey, *J. Am. Chem. Soc.*, **60**, 2391 (1938); Mumm, *Ber. deut. chem. Ges.*, **72**, 1874 (1939).

Any compound (B) containing a free pair of electrons, whether due to ionization or not, can attack this positive center. Thus,



I II III

the transition state can lose the negative charge by loss either of a hydroxyl ion or of the species which originally attacked the positive center. An equilibrium will be established between the starting materials and the final products since the hydroxyl ion produced can attack III to form the same transition state as that from I and II.

Berthelot and Pean de St. Gilles[1] made the first exact measurements on the ethanol–acetic acid–ethyl acetate equilibrium and determined the equilibrium point. Their results showed that the reaction was reversible and that the extent of reaction depended on the relative amounts of each compound present. The equilibrium constant for the reaction is

$$\frac{\text{Ester} \times \text{water}}{\text{Acid} \times \text{alcohol}} = K$$

Unless activities are used in this expression, the value of K changes with the presence of salts.[2]

Menschutkin[3] made a comparative study of the relative rates of esterification and the equilibrium constants of a large number of acids and alcohols. He found striking differences among primary, secondary, and tertiary alcohols, both as to the rates and as to the limits of esterification. Table 12-1 gives some of his results for acetic acid heated to 155°C with equivalent amounts of various alcohols.

It will be observed that, of all the alcohols studied, methyl shows the greatest initial rate of esterification and the highest limit. The primary alcohols, ethyl, propyl, and butyl, have approximately the same initial rates and limits but are inferior to methyl alcohol in both of these respects. Allyl alcohol is much slower than propyl, the saturated alcohol with the

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[1] BERTHELOT, *Ann. chim.* (3), **66**, 110 (1862); **68**, 274 (1863); (5), **14**, 437 (1878); **15**, 220, 238 (1878); *Bull. soc. chim. France* (2), **31**, 341 (1879); BERTHELOT and PEAN DE ST. GILLES, *Ann. chim.* (3), **65**, 385 (1862); **66**, 5 (1862); **68**, 225 (1863).

[2] KNOBLAUCH, *Z. physik. Chem.*, **22**, 268 (1897); SWIETOSLAWSKI, *J. Phys. Chem.*, **37**, 701 (1933); CANTELO and BILLINGER, *J. Am. Chem. Soc.*, **50**, 3212 (1928); SCHLESINGER, *Ber. deut. chem. Ges.*, **59**, 1965 (1926); SCHLESINGER and MALKINA-OKUN, *ibid.*, **60**, 1479 (1927).

[3] MENSCHUTKIN, *Ann. Chem., Justus Liebigs*, **195**, 334 (1879); **197**, 193 (1879); *Ber. deut. chem. Ges.*, **13**, 162 (1880); *Ann. chim.* (5), **23**, 14 (1881); **30**, 81 (1883); *Z. physik. Chem.*, **1**, 611 (1887); **9**, 237 (1892); *Ber. deut. chem. Ges.*, **42**, 4020 (1909).

TABLE 12-1. RATES AND LIMITS OF ESTERIFICATION, ACETIC ACID AT 155°C WITH VARIOUS ALCOHOLS

	Alcohol	Per cent conversion		K
		1 hr	Limit	
1	Methyl	55.59	69.59	5.24
2	Ethyl	46.95	66.57	3.96
3	Propyl	46.92	66.85	4.07
4	Butyl	46.85	67.30	4.24
5	Allyl	35.72	59.41	2.18
6	Benzyl	38.64	60.75	2.39
7	Dimethylcarbinol	26.53	60.52	2.35
8	Methylethylcarbinol	22.59	59.28	2.12
9	Diethylcarbinol	16.93	58.66	2.01
10	Methylhexylcarbinol	21.19	62.03	2.67
11	Diallylcarbinol	10.31	50.12	1.01
12	Menthol	15.29	61.49	2.55
13	Trimethylcarbinol	1.43	6.59	0.0049
14	Dimethylpropylcarbinol	2.15	0.83	
15	Phenol	1.45	8.64	0.0089
16	Thymol	0.55	9.46	0.0192

same number of carbon atoms. The presence of the phenyl group in benzyl alcohol has a retarding influence.

The secondary alcohols (7 to 12, Table 12-1) are markedly lower than the primary in both initial velocity and limit but vary considerably among themselves. The tertiary alcohols (13 and 14) show little esterification in 1 hr and hardly any more in 100. In the case of the tertiary alcohols, the limit is seldom if ever reliable, since these alcohols are dehydrated easily to the unsaturated hydrocarbons. Also the esters can decompose to form an unsaturated hydrocarbon and the acid. It is not unusual, with esters of tertiary alcohols, to find less ester present after a long heating period than after a short one. Phenol and thymol, which may be regarded as tertiary alcohols but from which water cannot be split off, show low initial rates but comparatively high limits.

As was pointed out by Michael,[1] the three classes of alcohols are not always sharply separated as in the above examples; i.e., some tertiary alcohols may be esterified as rapidly and to the same extent as certain secondaries, and primary alcohols have been found that do not esterify so readily or so completely as some secondary ones. It may be stated generally that the more branched the carbon chain of the alcohol and the nearer the branches are to the hydroxyl group, the slower will be its esteri-

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[1] MICHAEL, *Ber. deut. chem. Ges.*, **42**, 310 (1909); **43**, 464 (1910); MICHAEL and OECHSLIN, *ibid.*, **42**, 317 (1909); MICHAEL and WOLGAST, *ibid.*, **42**, 3157 (1909).

TABLE 12-2. RATES AND LIMITS OF ESTERIFICATION OF ISOBUTYL ALCOHOL WITH VARIOUS ACIDS AT 155°C

	Acid	Per cent conversion		K
		1 hr	Limit	
1	Formic	61.69	64.23	3.22
2	Acetic	44.36	67.38	4.27
3	Propionic	41.18	68.70	4.82
4	Butyric	33.25	69.52	5.20
5	Isobutyric	29.03	69.51	5.20
6	Methylethylacetic	21.50	73.73	7.88
7	Trimethylacetic	8.28	72.65	7.06
8	Dimethylethylacetic	3.45	74.15	8.23
9	Phenylacetic	48.82	73.87	7.99
10	Phenylpropionic	40.26	72.02	7.60
11	Cinnamic	11.55	74.61	8.63
12	Benzoic	8.62	72.57	7.00
13	*p*-Toluic	6.64	76.52	10.62

fication and the lower the limit. These effects are due to steric hindrance to the approach of the alcohol to the acid molecule.

Similar experiments were made by Menschutkin, who used isobutyl alcohol with a variety of acids. Some of the results are given in Table 12-2. By examining the data for the per cent conversion for the first hour, the similarity of the extents of conversion to those observed in Table 12-1 may be noted. Formic acid reacts much more rapidly than do the other straight-chain acids, and the branched-chain acids, trimethylacetic and dimethylethylacetic, are particularly slow. The introduction of a phenyl group (as in 9 and 10, Table 12-2) does not retard esterification, but the purely aromatic acids, benzoic and *p*-toluic, are esterified very slowly. By contrasting cinnamic acid with phenylpropionic, it may be seen that the double bond in conjugation with a phenyl group has a marked retarding effect on the rate of esterification. Maleic acid is esterified 14 times as rapidly as is fumaric.[1] An alcohol dissolved in excess of formic acid is esterified several thousand times as rapidly as in acetic.[2]

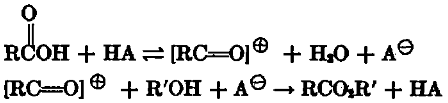
Although, with the alcohols, low rate of esterification and a low limit of reaction go together, it is quite otherwise with the acids. Thus, dimethylethylacetic acid gives only 3.4 per cent of ester in 1 hr but finally, after 500 or 600 hr, reaches a limit that is even higher than the limit for acetic acid. The esterification of the unsaturated acids, cinnamic and sorbic, starts off much more slowly than that of the corresponding saturated acids but goes

[1] SCHWAB, *Rec. trav. chim.*, 2, 46 (1883).

[2] KAILAN et al., *Monatsh. Chem.*, 62, 284 (1933); 63, 155 (1933); 68, 109 (1936).

somewhat farther. Formic acid, which has an extremely high initial rate, has a relatively low limit.

A special case which has received much attention is that of the 2,6-disubstituted benzoic acids (*hindered acids*), which, as shown by Victor Meyer and others,[1] are esterified extremely slowly by the usual method. Even one ortho group has a marked effect; a methyl group ortho to the carboxyl group reduces the rate of esterification of benzoic acid by 68 per cent, an ethyl group by 80 per cent, and a propyl group by 83 per cent.[2] However, Newman[3] has found that highly hindered acids can be esterified rapidly by dissolving the acid in concentrated sulfuric acid and then pouring the resulting solution into the alcohol. The mechanism of the reaction involves the formation of a carbonium ion from the acid, which reacts with the alcohol.



$$R\overset{O}{\overset{\|}{C}}OH + HA \rightleftharpoons [RC{=}O]^{\oplus} + H_2O + A^{\ominus}$$

$$[RC{=}O]^{\oplus} + R'OH + A^{\ominus} \rightarrow RCO_2R' + HA$$

Catalytic Esterification

If samples are taken at intervals from a mixture of acetic acid and ethyl alcohol at room temperature and titrated, a slow decrease in acidity can be observed, but days and even months will elapse before the minimum value, or limit, is reached. Like most other reactions, the speed of esterification approximately doubles with a 10°C rise in temperature. Hence, heat is used to speed up esterification reactions. However, in most instances, heating alone does not speed up esterification to a practical rate. Except in the case of a high-boiling alcohol, such as glycerol, with a high-boiling acid such as stearic, esterification cannot be effected at atmospheric pressure in a reasonable time without the use of a catalyst.

It has long been known that the process of esterification may be enormously hastened by the addition of a strong acid, such as sulfuric or hydrochloric acid. The equilibrium point of the reaction is not altered by the catalyst; only the rate of esterification is increased.[4]

As was discussed earlier, esterification proceeds by attack of an alcohol molecule on the slightly positive carbonyl carbon of an acid. The larger this positive charge, the more rapid the reaction will be. While the nature of the R group attached to the carboxyl group will influence this charge,

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[1] MEYER, *Ber. deut. chem. Ges.*, **27**, 510 (1894); HUFFERD and NOYES, *J. Am. Chem. Soc.*, **43**, 925 (1921).

[2] ZWECKER, *Ber. deut. chem. Ges.*, **68**, 1289 (1935).

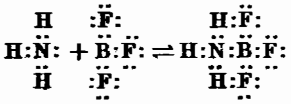
[3] NEWMAN, *J. Am. Chem. Soc.*, **63**, 2431 (1941).

[4] BERTHELOT and PEAN DE ST. GILLES, *Ann. chim. et phys.* (3), **65**, 385 (1862); **66**, 5 (1862); **68**, 225 (1863).

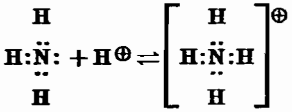
other methods, or catalysts, can be used to increase the positive charge so that a given acid will esterify more rapidly.

Ostwald[1] found a close relationship between the activity of an acid in the hydrolysis of methyl acetate and in the inversion of sugar with the conductivity of the acid and concluded that the acceleration is due to the presence of the hydrogen ion. Some of his figures are given in Table 12-3.

Esterification catalysts are compounds which are acidic in nature. Acidic compounds, in this case, are those in which the central atom has an incomplete external electron shell, so that besides the hydrogen ion, compounds such as boron trifluoride, aluminum chloride, or zinc chloride can be considered to be acids. The neutralization reaction of such an acid is written as the donation of an electron pair by a base to the acid.

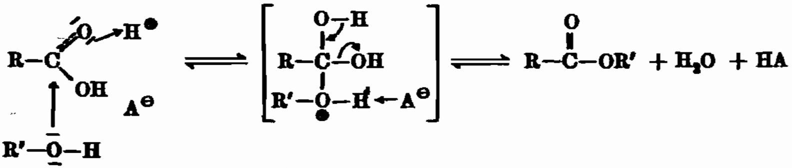


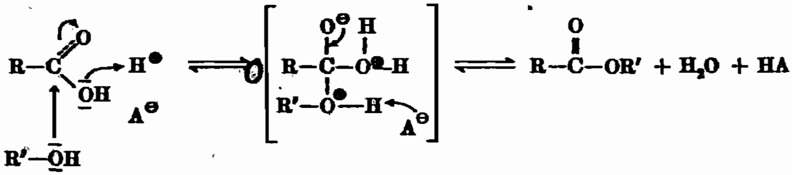
$$\begin{array}{c}\mathrm{H}\\ \mathrm{H:\ddot{N}:}\\ \mathrm{\ddot{H}}\end{array} + \begin{array}{c}\mathrm{:\ddot{F}:}\\ \mathrm{\ddot{B}:\ddot{F}:}\\ \mathrm{:\underset{..}{F}:}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{H:\ddot{F}:}\\ \mathrm{H:\ddot{N}:\ddot{B}:\ddot{F}:}\\ \mathrm{\ddot{H}:\underset{..}{F}:}\end{array}$$



$$\begin{array}{c}\mathrm{H}\\ \mathrm{H:\ddot{N}:}\\ \mathrm{H}\end{array} + \mathrm{H}^{\oplus} \rightleftharpoons \left[\begin{array}{c}\mathrm{H}\\ \mathrm{H:\ddot{N}:H}\\ \mathrm{H}\end{array}\right]^{\oplus}$$

When an acid (HA) is added to an esterification mixture, the oxygens present will act as bases and coordinate with the acid. The mechanism may be written two ways, depending on which oxygen of the carboxyl group acts as the base.





Attention should be called to the fact that the alcohol oxygen also can act as a base toward the acid. However, this reaction hinders esterification

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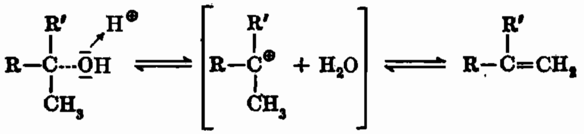
[1] OSTWALD, *J. prakt. Chem.* (2), **28**, 449 (1883); **30**, 93 (1884); **35**, 122 (1887).

and, in addition, may lead to dehydration of the alcohol. Dehydration is an especially important side reaction with tertiary alcohols.



In certain cases when the acid is sufficiently strong, the esterification is self-catalyzed. Quite often the speed of the reaction is increased by working under increased pressure so that higher temperatures can be used.

The figures in Table 12-3 may be considered to represent the relative efficiencies of mineral acids as catalysts in the reverse reaction of esterification. It will be noted that the very strong acids have nearly equal effects, whereas the organic acids, with the exception of oxalic, are poor catalysts. Substitution of chlorine in acetic acid gives an acid, chloroacetic, of much greater strength. Sulfuric acid appears to be only slightly more than half as effective as hydrochloric, i.e., if sulfuric is considered to be dibasic, whereas ethylsulfuric and ethanesulfonic acids are among the strongest catalysts.

TABLE 12-3. RELATIVE RATES OF HYDROLYSIS OF METHYL ACETATE WITH VARIOUS ACIDS AS CATALYSTS

Acid	Rate of hydrolysis, %	Acid	Rate of hydrolysis, %
Hydrochloric	100	Malonic	2.87
Hydrobromic	89.3	Succinic	0.496
Nitric	91.5	Tartaric	2.30
Sulfuric	54.7	Formic	1.31
Ethylsulfuric	98.7	Acetic	0.345
Ethanesulfonic	97.9	Chloroacetic	4.3
Benzenesulfonic	99.0	Dichloroacetic	23.0
Oxalic	17.46	Trichloroacetic	68.2

In general practice, hydrochloric and sulfuric acids are the catalysts most commonly used, the former being in favor in the laboratory because of its efficiency and the latter in the plant because of its cheapness and lower corrosive effect on metals. Sulfuric acid may cause the dehydration of an alcohol if used in too great an amount or at too high a temperature. Thus, cyclohexanol when boiled 30 min with 2 moles of acetic acid and 3 per cent by volume of sulfuric acid gives 30 per cent cyclohexene. The use of any strong acid as a catalyst may cause isomerization or destruction of a tertiary alcohol, such as linalool.

Perchloric and phosphoric acids have been recommended as catalysts. Phosphoric acid is less efficient but also less destructive. The sulfonic acids, particularly those containing a considerable number of carbon atoms, are desirable catalysts on account of their high efficiency, solubility in the higher alcohols and acids, and less destructive action. The most commonly used is *p*-toluenesulfonic acid. Twitchell's reagent, a complex formed from naphthalene, oleic acid, and sulfuric acid, is a good catalyst; a wetting agent such as dodecanesulfonic acid is recommended.[1] Ion-exchange resins are excellent catalysts and offer the advantage of being easily removed by simple filtration.[2] Boron and silicon fluorides also are excellent catalysts.[3]

Acid salts, such as potassium bisulfate, and salts of strong acids with weak bases have been tried as catalysts, but any activity they have may be attributed to the hydrogen ions present in their solutions. The presence of zinc chloride seems to enhance the catalytic effect of acids. The addition of a large amount of calcium chloride aids in the separation of water as a layer. Zinc and tin chlorides are said to be active catalysts.[4]

Various patents claim the use of aluminum, cobalt, lead, magnesium, tin, and zinc soaps as esterification catalysts. Catalysts comprising metals, such as tin, manganese, bismuth, lead, silver, and copper, in the finely divided state are disclosed to be suitable, zinc being especially favored. Oxides of aluminum, lead, and magnesium also are said to be esterification catalysts. A trace of pyridine was found by one investigator[5] to retard esterification, while others[6] report large amounts of it to be a more effective catalyst than sulfuric acid.[7]

Completing Esterification

Because esterification is an equilibrium reaction and because obtaining the highest possible yield from a reaction is always desirable, various esterification methods in which the equilibrium is displaced by removal of one of the reaction products have been designed so that the ester is obtained in high yield and conversion.

One way of completing an esterification is to remove the water as it is formed. When the acid, alcohol, and ester are nonvolatile, the mixture is heated, usually to around 200°C or higher, without a catalyst to drive out the water. The removal of the water is aided by bubbling an inert gas through the mixture or by the application of a vacuum. Glycerides of nonvolatile acids are made in this way. To ensure the complete esterification of the trivalent glycerol, an excess of the acid is used. This is later

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[1] BUN-ITI TOI, *J. Chem. Soc. Japan*, **61**, 1279 (1940).

[2] LEVESQUE and CRAIG, *Ind. Eng. Chem.*, **40**, 96 (1948).

[3] NIEUWLAND et al., *J. Am. Chem. Soc.*, **57**, 1549 (1935); **58**, 271, 786 (1936); TOOLE and SOWA, *ibid.*, **59**, 1971 (1937); KASTNER, *Angew. Chem.*, **54**, 273 (1941).

[4] FEUGE, KRAEMER, and BAILEY, *Oil & Soap*, **22**, 202 (1945).

[5] BAILEY, *J. Chem. Soc.*, **1928**, 1204, 3256.

[6] SCHLESINGER and MALKINA-OKUN, *Ber. deut. chem. Ges.*, **60**, 1479 (1927).

[7] SMITH and ORTON, *J. Chem. Soc.*, **95**, 1060 (1906).

removed by an alkaline wash. Glycols, polyglycols, and pentaerythritol are similarly esterified.[1]

Ester gum, a widely used resin, is esterified completely by heating glycerol with rosin so as to drive out the water. Other rosin esters are obtained similarly from rosin and nonvolatile alcohols or glycols. As abietic acid is a hindered acid, a high esterification temperature (275–300°C) is required to speed up the reaction.

Another method of removing the water is to pass superheated steam through the mixture; the steam both agitates the mixture and carries off the water as it is formed.[2]

When either or both the acid and the alcohol are volatile, the reaction may be carried to completion by distilling out the water produced in the reaction, usually as an azeotrope. The azeotrope can be water with one of the components of the reaction mixture or with an inert solvent which is insoluble in water. Generally, an azeotrope is selected which has a boiling point below 100°C and which condenses into two phases. The butyl alcohols and their higher homologues form azeotropes with water which behave in this manner, as do the inert solvents benzene, toluene, chloroform, ethylene dichloride, and carbon tetrachloride. When methyl, ethyl, or propyl alcohol is used in an azeotropic esterification, one of the inert solvents can be used to produce a two-phase distillate.

In some cases the azeotropes obtained will consist of more than two components. The composition of azeotropes is easily obtained from a compilation of azeotropic data.[3]

The operating conditions must be adapted to the particular acid and alcohol. Not only must the boiling point of the azeotropes be considered but also the solubilities of the esters and alcohols in water.

The apparatus used for azeotropic esterification includes a receiver in which the phases separate. The nonaqueous phase automatically returns to the esterification vessel by an overflow, while the aqueous phase is withdrawn from the bottom of the receiver.

When both ester and alcohol are volatile and form an azeotrope with the water, additional refinements are necessary. A careful study[4] of the continuous esterification of acetic acid by ethanol laid the foundation for modern esterification methods. Ethyl acetate can be made continuously by starting with a mixture of ethanol and acetic acid, with some sulfuric acid. This mixture is heated until the ester begins to distill out, and then the mixture of alcohol and acetic acid is added at a rate such that the volume

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[1] BARREL, *Oil & Soap*, **21**, 206 (1944).

[2] Jordan, U.S. 2,307,794 (1943).

[3] HORSLEY et al., Advances in Chemistry Series No. 6, Azeotropic Data, American Chemical Society, Washington, D.C., 1952.

[4] WADE, *J. Chem. Soc.*, **87**, 1656 (1905); *J. Soc. Chem. Ind.*, **24**, 1322 (1905).

remains constant. The distillate is a ternary mixture of ethyl acetate, 83.2 per cent; alcohol, 9.0 per cent; and water, 7.8 per cent. The boiling point of this ternary azeotrope is 70.3°C, whereas pure ethyl acetate boils at 77.15°C. Two binary azeotropes also are formed: (1) one which contains 69.4 per cent of the ester and 30.6 per cent of the alcohol and boils at 71.8°C and (2) the other which contains 8.6 per cent of water and 91.4 per cent of the ester and boils at 70.45°C. The important fact is that the ternary azeotrope boils lower than any of the individual constituents of the system or either of the binary azeotropes and is the distillate from an efficient column as long as all three of the constituents are present in the still. Because this ternary azeotrope cannot be separated by distillation, most of the alcohol is extracted from the mixture by washing with water. When the washed ethyl acetate is redistilled, the forerun of distillate again is the ternary azeotrope, ester, water, and alcohol, which boils at 70.3°C, although owing to the washing out of most of the alcohol, only a limited amount of the ternary azeotrope can be present. The forerun is followed by a binary azeotrope of the ester with either the water or the alcohol, depending on which remains after formation of the ternary azeotrope; then the boiling point rises to 77.15°C, and pure dry ethyl acetate is obtained.

It is evident that this procedure gives a satisfactory method of converting a given amount of acetic acid completely to ethyl acetate. It also can be seen that, if the ester is removed as rapidly as it is formed, esterification must go on even in the presence of a considerable proportion of water. To form the ternary azeotrope, a small excess of alcohol must be added.

As can be readily seen from the above, the manufacture of ethyl acetate becomes a matter of distillation. With proper adjustments of rates of addition and distillation, the esterification can be carried out as a continuous process. Actually, the liquor containing acetic acid and the proper amount of sulfuric acid is fed into the column at the proper plate where it meets the alcohol. Esterification takes place on the plates in the column, and the ternary azeotrope of ester, alcohol, and water comes out at the top continuously. The distillate is washed with water and the ester passed to another column. The dilute alcohol obtained by washing the ternary azeotrope goes to a still for the recovery of the alcohol, which is returned to make more ester.

For other volatile esters, there are corresponding ternary and binary azeotropes. In general, the ternary azeotrope of an alcohol, its ester, and water boils slightly lower than the binary of the ester and water. The percentage of water in the ternary increases and that of the ester decreases with an increase in molecular weight of the alcohol, as can be seen from the data in Table 12-4, most of which are from Hannotte.[1]

Graphical methods have been developed and experimentally verified by

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[1] Hannotte, *Bull. soc. chim. Belges.*, **35**, 86 (1926).

TABLE 12-4. BOILING POINTS OF ESTERS, ALCOHOLS, THEIR BINARIES AND TERNARIES WITH WATER
(E = Ester, A = Alcohol, W = Water)

	A, bp, °C	E, bp, °C	Binary, EW		Binary, EA		Ternary			
			Bp, °C	H_2O, %	Bp, °C	A, %	Bp, °C	E, %	A, %	W, %
Propyl formate	97.2	81	71.6	2.3	80.6	9.8	70.8	82	5	13
Butyl formate	117.7	106.9	83.8	16.5	105.8	23.7	83.6	68.7	10	21.3
Isobutyl formate	107.9	98.5	80.4	7.8	97.8	20.6	80.2	76	6.7	17.3
Isoamyl formate	131.6	123.3	90.2	21	123.6	26	89.8	48	19.6	32.4
Methyl acetate	64.6	54.0	.....	....	54	18.5	....	....	....	
Ethyl acetate	78.3	77.1	70.45	8.6	71.8	30.6	70.3	83.2	9	7.8
Propyl acetate	97.2	101.6	82.4	14	94.2	40	82.2	59.5	19.5	21
Butyl acetate	117.7	125.1	90.2	28.7	117.2	47	89.4	35.3	27.4	37.3
Isobutyl acetate	107.9	116.3	87.4	16.6	87.4	16.6	86.8	46.5	23.1	30.4
Amyl acetate	137.8	148	95.2	41	.....	....	94.8	10.5	33.3	56.2
Isoamyl acetate	131.6	139	93.8	36.2	.....	....	93.6	24	31.2	44.8

Gay, Mion, and Aumeras for determining the conditions required for complete esterification for various mixtures.[1]

Design of a Continuous Esterification Column

The design of a continuous esterification column, at one time accomplished by empirical methods, can be carried out by calculation, provided that sufficient data are available. Commonly, the apparatus used is a bubble-cap column. In the case of high-boiling esters, such as the phthalates, the water produced in the reaction is removed overhead and the product is withdrawn from the bottom plate. A mixture of the alcohol, acid, and acid catalyst is fed to the top plate of the column, and the esterification is carried out as the mixture flows through the column. The problem of calculating the number of plates necessary is complicated by the laws of mass action, kinetics, and distillation, which all operate simultaneously. The variables, mole ratio of reactants, catalyst concentration, and temperature, control the kinetics of the reaction. The distillation laws must take into account the fact that moles of reactants are replaced by moles of products on each plate.

Othmer and his coworkers[2] have studied esterification reactions to develop a theoretical basis for the design of continuous reactors. For a given system of acid and alcohol, the kinetics are studied and an equation is developed which relates the rate constant to the mole ratio of reactants, catalyst concentration, and reaction temperature. Vapor-liquid equilibrium data are obtained by operation of a small continuous reactor.

As an illustration of the method, the design of a column for the con-

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[1] GAY, MION, and AUMERAS, *Bull. soc. chim. France* (4), **39**, 1329 (1926); **41**, 1027 (1927).

[2] LEYES and OTHMER, *Trans. Am. Inst. Chem. Engrs.*, **41**, 157 (1945); BERMAN, ISBENJIAN, SEDOFF, and OTHMER, *Ind. Eng. Chem.*, **40**, 2139 (1948).

tinuous esterification of monobutyl phthalate by *n*-butyl alcohol (as described by Othmer) will be given. The apparatus is represented schematically in Fig. 12-1.

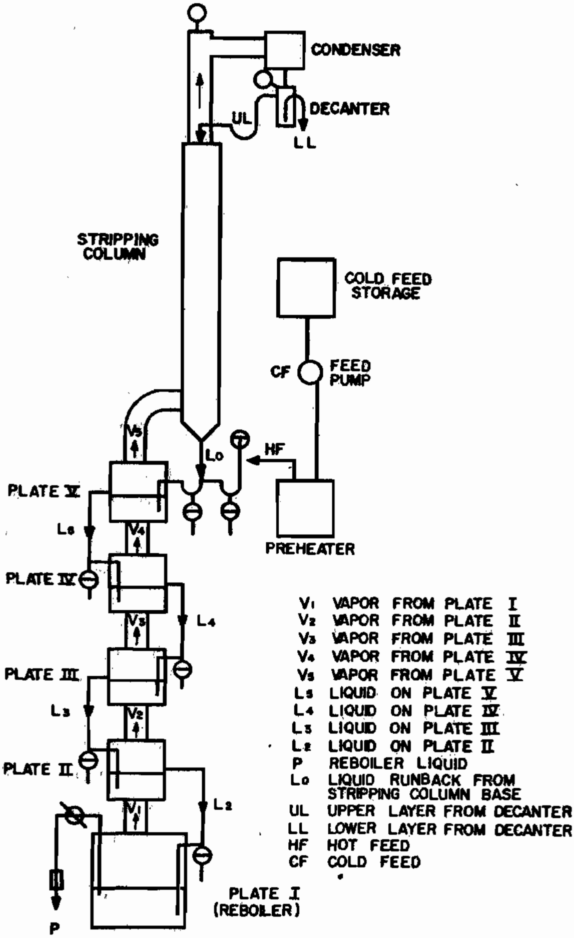

FIG. 12-1. Schematic diagram of a continuous esterification column. [*Berman, Isbenjian, Sedoff, and Othmer, Ind. Eng. Chem.*, 40, 2139 (1948). *Copyright* 1948 *by the American Chemical Society and reprinted by permission of the copyright owner.*]

The assumptions and specifications used in the calculations are:

1. Feed stream: 0.010 mole per min of monobutyl phthalate (*M*); 0.010 mole per min of *n*-butyl alcohol (*B*); 2.00 weight per cent of sulfuric acid catalyst (*C*).

2. Conversion: 99 per cent of monobutyl phthalate in feed stream.

3. An adiabatic column, equal molar heats of vaporization, no heats of reaction or dilution.

4. Overhead vapors: *n*-butyl alcohol-water azeotrope, 79 mole per cent water.

5. Plate holdup volume: 1.00 liter.

The composition of the product streams and a suitable reflux ratio are established first. The amount of water in the product stream is determined by the mass-action law at a 99 per cent conversion. The composition, omitting water, of the product stream is:

n-Butyl alcohol (*B*)	0.0901 mole/min
Dibutyl phthalate (*D*)	0.0099
Monobutyl phthalate (*M*)	0.0001
Sulfuric acid catalyst (*C*)	0.0020

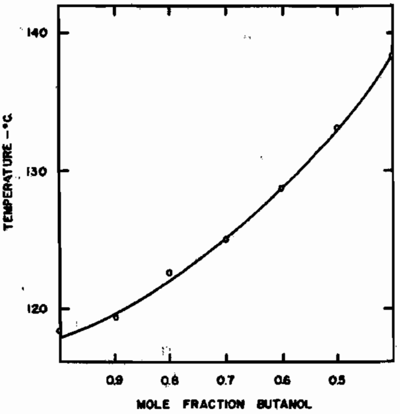

FIG. 12-2. Boiling-point diagram for butanol–dibutyl phthalate mixtures. [*Berman, Isbenjian, Sedoff, and Othmer, Ind. Eng. Chem.*, 40, 2139 (1948). *Copyright 1948 by the American Chemical Society and reprinted by permission of the copyright owner.*]

The temperature of the reboiler (Plate I) is established to be 120.5°C from Fig. 12-2 by using the mole fraction of *n*-butyl alcohol, 0.88. The equilibrium constant next is found from experimental data to be 0.802. The amount of water in the product stream then is calculated to be 0.000730 mole per min. The overhead vapor must contain 0.00917 mole per min of water (moles produced in reaction less moles present in product stream). If the decanter temperature is 20°C, from the mutual solubility of water and *n*-butyl alcohol, the water layer contains 0.9811 mole fraction of water and the *n*-butyl alcohol layer contains 0.0181 mole fraction of water. The amount of overhead product required is

$$\frac{0.00917}{0.9811} = 0.00935 \text{ mole/min}$$

From mole balances around the decanter, the water layer is 0.599 mole per mole of overhead vapor, and the *n*-butyl alcohol layer is 0.401 mole per mole of overhead vapor. The minimum reflux ratio then is

$$\frac{0.401}{0.599} = 0.669$$

The minimum reflux is

$$0.669 \times 0.00935 = 0.00626 \text{ mole/min}$$

In order to maintain water on all the plates, as determined by preliminary mole balances, a constant vapor rate of 0.125 mole per min finally is chosen.

The over-all mole balance for the reactor now can be obtained:

	mole/min			
	Feed	Reaction	*P*	*LL*
M	0.010	−0.0099	0.00010	
D	.....	+0.0099	0.00990	
B	0.100	−0.0099	0.08992	0.00018
W	.....	+0.0099	0.00073	0.00917
C	0.002	....	0.00200	
Total	0.112	....	0.10265	0.00935

The number of plates necessary for 99 per cent conversion now can be determined, starting with the reboiler (Plate I):

	P, mole/min	*P*, mole fraction	V_1, mole/min
M	0.00010	0.000972	
D	0.00990	0.09628	
B	0.08992	0.8762	0.121038
W	0.00073	0.00710	0.003962
C	0.00200	0.01945	
Total	0.10265	1.000	

T = 120.5°C, from Fig. 12-2

C = 2.030 wt %

Average density = 8.396 moles/liter

Holdup = 1.000 liter or 8.396 moles

$$\text{Contact time} = \frac{8.396}{0.10265} = 81.65 \text{ min}$$

Moles on plate:

$M = 0.00010 \times 81.65 = 0.008165$ mole

$B = 0.08992 \times 81.65 = 7.357$ moles

$B/M = 901.0$

$$M_o = \frac{0.008165}{1.000} = 0.008165 \text{ mole/liter}$$

The mole fractions of the components of V_1 in equilibrium with *P* are obtained from Figs. 12-3 and 12-4 and are used with the vapor rate, 0.125 mole per min, to calculate the vapor composition. The rate constant (k_T) now is determined from Eq. (1), obtained from experimental data:

$$k_T = 2.1 \times 10^{-5} - 8.896 \times 10^{-4}C + 1.228 \times 10^{-3}C\left[\frac{B}{M}\right]\left[\frac{10^{(15.185 - 4515.9/T)}}{1205.8}\right] \quad (1)$$

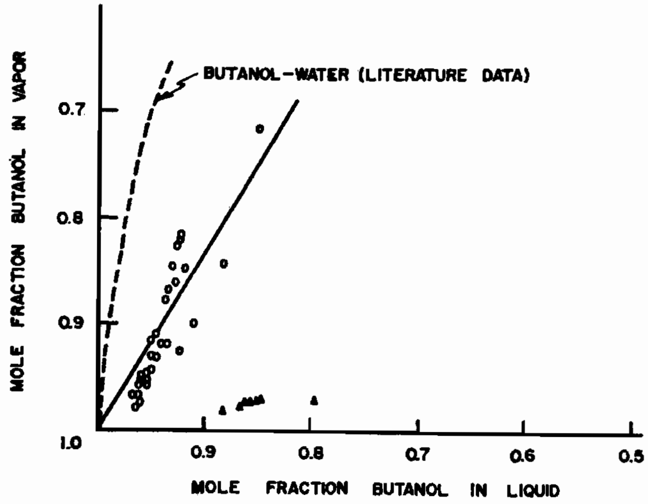

Fig. 12-3. Vapor-liquid equilibria data for butanol. [*Berman, Isbenjian, Sedoff, and Othmer, Ind. Eng. Chem.*, 40, 2139 (1948). *Copyright* 1948 *by the American Chemical Society and reprinted by permission of the copyright owner.*]

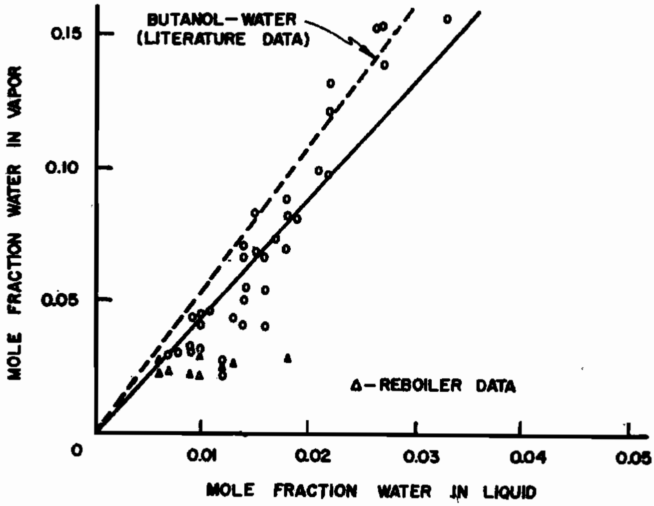

Fig. 12-4. Vapor-liquid equilibria data for water. [*Berman, Isbenjian, Sedoff, and Othmer, Ind. Eng. Chem.*, 40, 2139 (1948). *Copyright* 1948 *by the American Chemical Society and reprinted by permission of the copyright owner.*]

The rate of reaction in a continuous system is constant on a given plate, since the average liquid composition is constant. Applying this condition to the integrated second-order rate equation [Eq. (2)]

$$x = \frac{(k_T M_o t)M}{k_T M_o t + 1} \tag{2}$$

the limiting rate ($t \rightarrow 0$), or extent of reaction, corresponding to a constant monoester concentration is [Eq. (3)]

$$X = \lim_{t \rightarrow 0} \frac{x}{t} = k_T M_o M \tag{3}$$

The composition of the liquid overflow from Plate II now can be obtained by a mole balance around the reboiler.

	mole/min			
	P	V_1	Reaction (X)	L_1
M..........	0.000100	....	−0.000639	0.000739
D...........	0.00990	....	+0.000639	0.009261
B............	0.089920	0.121038	−0.000639	0.211597
W...........	0.000730	0.003962	+0.000639	0.004053
C...........	0.00200	....	....	0.002000
Total......	0.102650	0.125000	....	0.227650

The procedure is continued, plate by plate, until a plate is reached at which a liquid of feed composition is being introduced; a total of four plates is required. The results just obtained can be applied to any size unit, as long as direct multiples of the feed and product rates and holdup volumes are used.

In addition to the practical significance of being able to calculate the number of plates required for a continuous reactor, other important information can be obtained from the method. (1) Attainment of mass-action equilibrium is not necessary; in addition, long contact times, obtained by large holdup volumes and numerous plates, are not necessary to obtain high over-all conversions. (2) Similar calculations show that, for a given plate and composition, the rate of reaction increases with the reflux ratio. (3) The effects of catalyst concentration, whether alcohol and acid should be added separately, or mixed, the temperature of the feed, etc., may be evaluated.

II. ESTERIFICATION OF CARBOXYLIC ACID DERIVATIVES

Alcoholysis

$$CH_3COOC_2H_5 + HOCH_3 \rightarrow CH_3COOCH_3 + HOC_2H_5 \tag{4}$$

In the alcoholysis or ester-interchange reaction (4), an alcohol reacts with an ester to give a new ester.

If a mixture of amyl nitrite and ethyl alcohol containing an acid catalyst is warmed, ethyl nitrite distills out. Friedel and Crafts[1] heated ethyl acetate with amyl alcohol and amyl acetate with ethyl alcohol and observed alcoholysis in both cases. They also heated ethyl benzoate and amyl acetate together and obtained ethyl acetate and amyl benzoate, although this reaction was slow below 300°C.

Thermodynamics of Alcoholysis. Alcoholysis may be regarded as a special case of esterification. Equilibrium expressions which are similar to those for the esterification of acids by alcohols may be written for alcoholysis reactions.

$$C_6H_5COOC_2H_5 + CH_3OH \rightarrow C_6H_5COOCH_3 + C_2H_5OH$$

$$\frac{(C_6H_5COOCH_3)(C_2H_5OH)}{(C_6H_5COOC_2H_5)(CH_3OH)} = K$$

The alcoholysis equilibrium (K) can be calculated from the respective esterification constants (K_1 and K_2) of methanol and ethanol with benzoic acid. If benzoic acid is heated with a mixture of methyl and ethyl alcohols, the following equilibriums occur [Eqs. (5) and (6)]:

$$K_1(C_6H_5COOH)(CH_3OH) = (C_6H_5COOCH_3)(H_2O) \qquad (5)$$

$$K_2(C_6H_5COOH)(C_2H_5OH) = (C_6H_5COOC_2H_5)(H_2O) \qquad (6)$$

By dividing Eq. (5) by Eq. (6), we have

$$K = \frac{(C_6H_5COOCH_3)(C_2H_5OH)}{(C_6H_5COOC_2H_5)(CH_3OH)} = \frac{K_1}{K_2} = \frac{5.237}{3.968} = 1.32$$

This relationship between the esterification constants is as true in the absence of water and free acid as it is in their presence.[2] Thus, if 1 mole of methanol is added to 1 mole of ethyl benzoate, 0.53 mole of the methyl ester will be formed and a like amount of ethyl alcohol set free.

Since the alcoholysis equilibrium is related to the esterification constants of the alcohols with the acid, a tertiary alcohol will not replace a primary alcohol in alcoholysis, and a secondary alcohol will replace a primary alcohol to a small extent only.[3]

At room temperature in the absence of a catalyst, equilibrium is established extremely slowly. The strong acids that are used as catalysts in ordinary esterification serve equally well for alcoholysis. The most commonly used catalysts for alcoholysis, however, are the sodium alkoxides. They must be used in anhydrous systems since they are hydrolyzed by water and the resulting hydroxides hydrolyze the esters. The usual practice is to dissolve a small amount of sodium in the alcohol to be used

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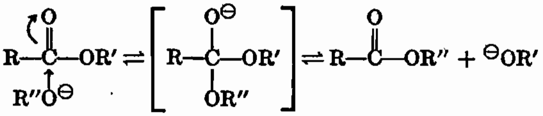
[1] FRIEDEL and CRAFTS, *Ann. Chem., Justus Liebigs*, **130**, 198 (1864); **133**, 207 (1865).

[2] REID, *Am. Chem. J.*, **45**, 479 (1911).

[3] REIMER and DOWNES, *J. Am. Chem. Soc.*, **43**, 945 (1921).

and then to add the ester. Low concentrations of these catalysts cause the transformation to take place rapidly even at room temperature. Sodium ethoxide is about one thousand times as active as an equivalent amount of hydrochloric acid.

An explanation for this increase in rate is that the basicity of the alcohol oxygen is increased and that this increase in basicity facilitates attack on the positive carbonyl carbon.



$$\underset{R''O^{\ominus}}{R\text{—}\overset{O}{\overset{\|}{C}}\text{—}OR'} \rightleftharpoons \left[R\text{—}\underset{OR''}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}}\text{—}OR' \right] \rightleftharpoons R\text{—}\overset{O}{\overset{\|}{C}}\text{—}OR'' + {}^{\ominus}OR'$$

$$R'O^{\ominus} + R''OH \rightleftharpoons R''O^{\ominus} + R'OH$$

The sodium methoxide–catalyzed methanolysis of 1-menthyl benzoate is first order with respect to both ester and methoxide ion and does not involve fission of the alkyl-to-oxygen bond.[1] The evidence indicates that the mechanisms of basic ester interchange and basic ester hydrolysis are similar. The mechanism of acid-catalyzed alcoholysis is similar to that of acid-catalyzed esterification.[2]

The remarkable quality of alcoholysis in the presence of sodium ethoxide as catalyst is the rapidity of the reaction as compared with esterification and saponification. The saponification of phenyl benzoate in aqueous alcohol ordinarily would be represented by Eq. (7):

$$C_6H_5COOC_6H_5 + NaOH \rightarrow C_6H_5COONa + C_6H_5OH \qquad (7)$$

$$C_2H_5OH + NaOH \rightleftharpoons C_2H_5ONa + H_2O \qquad (8)$$

$$C_6H_5COOC_6H_5 + NaOC_2H_5 \rightleftharpoons C_6H_5COOC_2H_5 + C_6H_5ONa \qquad (9)$$

What actually takes place is the alcoholysis [represented in Eqs. (8) and (9)], which was estimated by Gibby and Waters[3] to be one thousand times as rapid as the saponification according to Eq. (7). Then the ethyl benzoate is saponified slowly. The greater rapidity of alcoholysis compared with hydrolysis may be shown qualitatively by a simple experiment with triacetin. Some triacetin, $C_3H_5(OCOCH_3)_3$ which is odorless, is added to a solution of sodium hydroxide in 50 per cent alcohol; the odor of ethyl acetate is apparent at once and shows that the immediate reaction is the formation of ethyl acetate. On this account, it is necessary to use an efficient reflux condenser when determining saponification numbers of even high-boiling acetates.[4]

Besides the sodium alkoxides, various other catalysts for this reaction have been recommended: ammonia, pyridine, tetramethylammonium

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[1] Taft, Newman, and Verhoek, *J. Am. Chem. Soc.*, **72**, 4511 (1950).

[2] Carroll, *J. Chem. Soc.*, **1949**, 557.

[3] Gibby and Waters, *J. Chem. Soc.*, **1932**, 2643.

[4] Hasche, Pardee, and Reid, *Ind. Eng. Chem.*, **12**, 129, 481 (1920).

hydroxide, aluminum alkoxides,[1] lithium methoxide, sodium hydroxide, and sodium carbonate. In the alcoholysis of ethyl esters of α-halogenated acids by allyl and methallyl alcohols, zinc is used as the catalyst. An acid might polymerize the unsaturated alcohol, while sodium methoxide would react with the halogen of the acid.[2] Titanium esters are excellent ester-exchange catalysts. They are effective in catalyzing interchange between two esters as well as between an alcohol and an ester. They usually do not catalyze side reactions, and they are especially useful with polymerizable materials such as methacrylates which are attacked or polymerized by standard ester-exchange catalysts. Table 12-5 gives comparative rates with titanium esters and other catalysts in the reaction represented by Eq. (10):

$$C_6H_5CO_2C_2H_5 + C_4H_9OH \rightleftharpoons C_6H_5CO_2C_4H_9 + C_2H_5OH \tag{10}$$

TABLE 12-5

Catalyst used	Conc., %	Rate of C_2H_5OH removal, ml/hr
Isopropyl titanate	5	>84
Aluminum isopropoxide	5	70
Sodium ethoxide	5	50
Tetraethyl silicate	5	10
Butyl zirconate	5	0
Tributyl borate	5	0

Completing Alcoholysis. Since alcoholysis is an equilibrium reaction, the reaction must be forced to completion in a manner similar to that discussed above in esterification; the removal of one of the reaction products permits the reaction to go to completion. Thus, when a higher alcohol such as butyl, amyl, or benzyl alcohol is heated under a fractionating column with methyl or ethyl acetate and a catalyst, the most volatile constituent, methyl or ethyl alcohol, distills out and the ester of the other alcohol is left. Or the new ester may be distilled off, as when ethyl alcohol reacts with glycol acetate. When a glyceride is alcoholized by an alcohol, such as ethyl, the glycerol separates out on account of its low solubility in esters, and the reaction goes far toward completion. Glycerol is washed out with water, and the alcoholysis is repeated if necessary. This is a practicable way of obtaining glycerol.[3]

Glycerol 2-monopalmitin can be converted to glycerol 1-monopalmitin

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[1] CALINGAERT, SOROOS, HNIZDA, and SHAPIRO, *J. Am. Chem. Soc.*, **62**, 1545 (1940); REHBERG and FISHER, *J. Org. Chem.*, **12**, 226 (1947).

[2] Strassburg, U.S. 2,446,114 (1948).

[3] Colgate-Palmolive-Peet Co., Brit. 578,751 (1946); 587,523, 587,524 (1947).

by shaking an ether solution of the monoglycerides with urea. The 1-monopalmitin forms a urea inclusion compound, but the 2 isomer does not. Precipitation of glycerol 1-monopalmitin as a urea complex disturbs the equilibrium between the 1- and 2-monopalmitins, and consequently, the 2-monopalmitin is converted to the 1 isomer. Formation of a urea inclusion compound also results in considerable methanolysis of glycerol monostearate in 90 per cent methanol solution in spite of the absence of catalysts normally required to effect alcoholysis. The slow crystallization of the urea inclusion compound of methyl stearate in preference to the inclusion compound of glycerol monostearate results in the removal of methyl stearate from solution as an insoluble urea adduct.

Utilization of Alcoholysis. An interesting use of alcoholysis is the preparation of the monomeric cyclic polymethylene carbonates which can be obtained in no other way. A higher polymethylene glycol and sodium are heated with butyl carbonate to obtain the polymeric polymethylene carbonate. The crude product, which still contains the catalyst, is heated in a high vacuum; the trace of monomeric cyclic ester that is present distills out, and more is formed by rearrangement until nearly all the material is obtained in the desired form.[1]

Recently, much attention has been given to the alcoholysis of glycerides. When mixtures of glycerides are heated with a catalyst, they are interesterified and approach the composition expected from random distribution.[2] In some cases the drying properties of a mixture of oils are much improved by this treatment.[3] If the alcoholysis of a glyceride containing both saturated and unsaturated acids is effected below the melting points of the more saturated, less soluble glycerides so that they separate out, the equilibrium will be destroyed and additional amounts of the saturated glycerides will be formed. Thus, a natural glyceride can be split into more and less saturated portions.[4] An example of an industrial process for stabilizing lard by interesterification is discussed in Sec. V. Esters of acetylenic alcohols, such as methylbutynol, can be prepared by the reaction of the alcohol with the isopropenyl ester. Alcoholysis takes place with the enol esters derived from aldehydes and ketones,[5] and also with silicates,[6] phosphates,[7] and titanates.[8]

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[1] CAROTHERS et al., *J. Am. Chem. Soc.*, **55**, 5031 (1933); **57**, 929 (1935).

[2] NAUDET and DESNUELLE, *Bull. soc. chim. France*, **1946**, 595; NORRIS and MATTIL, *Oil & Soap*, **23**, 289 (1946).

[3] REUTENAUER and SISLEY, *Oleagineux*, **3**, 305 (1948).

[4] Procter and Gamble Co., Brit. 574,807 (1946).

[5] Quattlebaum and Noffsinger, U.S. 2,466,737; 2,467,095 (1949).

[6] PEPPARD, BROWN, and JOHNSON, *J. Am. Chem. Soc.*, **68**, 73, 77 (1946).

[7] RUEGGERBERG and CHERNACK, *J. Am. Chem. Soc.*, **70**, 1802 (1948).

[8] KRAITZER, MCTAGGERT, and WINTER, *Paint Notes*, **2**, 304, 348 (1947).

Equipment and Operation for Alcoholysis. Since anhydrous esters, alcohols, and alkaline catalysts, none of which causes corrosion, are used primarily in alcoholysis reactions, the equipment need not be made of especially corrosion-resistant materials. For a batch process, the equipment may be quite simple and consist of a kettle and column with suitable attachments. Usually, the alcohol is put in the kettle first, and the sodium metal (0.1–1 per cent of the weight of the ester) then is introduced. After the ester has been run in, the kettle is heated and distillation of the volatile component is begun.

The alcoholysis process also is readily adaptable to continuous operation. Procedures in general are similar to those used for continuous esterification processes.

Acidolysis

$$CH_3COOC_2H_5 + C_{15}H_{31}COOH \rightleftharpoons C_{15}H_{31}COOC_2H_5 + CH_3COOH \quad (11)$$

The counterpart of alcoholysis, acidolysis, in which one acid displaces another from an ester [Eq. (11)] is so similar to alcoholysis that little need be said about it. Since the alkaline catalysts which are so efficient in alcoholysis cannot be used, the slower acid catalysts or heat alone must be used. Boron trifluoride is effective.[1] Mercury salts[2] are recommended as catalysts for the acidolysis of vinyl esters. Quantitative studies show that one acid displaces another to about the extent that would be expected from the esterification constants.[3] The reaction goes to completion if the displaced acid can be eliminated. Volatile acids can be distilled out, either alone or as an azeotrope.

Esterification by Acid Anhydrides

Reactions (12) to (14) go to completion, since the products which are formed do not interact to produce the starting material. Esterification of an alcohol by an anhydride is more rapid than by the corresponding acid.

$$(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH \quad (12)$$

$$(CH_3CO)_2O + (CH_3)_3COH \rightarrow CH_3COOC(CH_3)_3 + CH_3COOH \quad (13)$$

$$(CH_3CO)_2O + C_6H_5ONa \rightarrow CH_3COOC_6H_5 + CH_3COONa \quad (14)$$

However, the relative velocities of the reaction of acetic anhydride with different alcohols are much the same as the relative velocities of the reaction of acetic acid with the alcohols.[4] The relative rates for the reactions of a series of alcohols with acetic anhydride are given in Table 12-6.

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[1] Sowa, *J. Am. Chem. Soc.*, **60**, 654 (1938).

[2] Toussaint and MacDowell, U.S. 2,299,862 (1942).

[3] Gault and Chablay, *Compt. rend.*, **207**, 283 (1938); Barkenbus, *J. Am. Chem. Soc.*, **62**, 1251 (1940).

[4] Menschutkin, *Z. physik. Chem.*. **1**, 611 (1887); **9**, 237 (1892).

TABLE 12-6. RATE OF REACTION OF ALCOHOLS WITH ACETIC ANHYDRIDE

Alcohol	Rate constant, min^{-1}	Relative rate (CH_3OH = 100)
Methyl	0.1053	100
Ethyl	0.0505	47.9
Propyl	0.0480	45.6
n-Heptyl	0.0393	37.3
n-Octadecyl	0.0245	23.2
Allyl	0.0287	27.2
Benzyl	0.0280	26.6
Isopropyl	0.0148	14.1
t-Butyl	0.00091	0.8

This discussion will be limited to acetic anhydride, the cheapest and most commonly used anhydride of a monobasic acid.

The simpler primary and secondary alcohols can be esterified satisfactorily by the methods already described, but certain tertiary alcohols, mercaptans, and phenols require the use of acetic anhydride. It is frequently used for esterifying small lots of expensive alcohols in cases where speed and completeness of esterification are of more importance than the added cost of the anhydride.

Reactions of an alcohol with acetic anhydride are greatly accelerated by acid catalysts, such as sulfuric acid, zinc chloride, phosphorus pentoxide, ferric chloride, etc. However, such catalysts cannot be used with sensitive alcohols, such as linalool, which are isomerized or otherwise affected by them. The effective acid strength of a catalyst in an anhydrous medium is the predominant factor in determining its activity. The acidities of mineral acids in glacial acetic acid correspond remarkably well with their activities as acetylation catalysts. Sulfuric and perchloric acids in acetic acid solution have been termed superacid solutions because of their exceptional strength as compared with the strength of other acids. Most anhydrides react more rapidly with an alcohol in the presence of a base. The base can be sodium hydroxide, the sodium salt of the acid, or a tertiary amine, which can also be the solvent for the reaction.[1]

Many thousands of tons of cellulose esters are made by the action of the anhydrides of acetic and other acids on cellulose in the presence of acid catalysts, such as sulfuric acid. A more detailed description of the acetylation is given in Sec. V.

Esters from Anhydrides of Dibasic Acids. Monoalkyl phthalates are obtained with great ease by heating phthalic anhydride with an alcohol:

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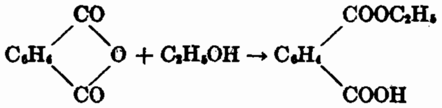
[1] BYER and DULL, *J. Am. Chem. Soc.*, **69**, 973 (1947); BADGETT and WOODWARD, *ibid.*, **69**, 2907 (1947).



The speed of this reaction is also dependent on the nature of the alcohol. Advantage is taken of this fact to separate alcohols of the various classes; primary alcohols react readily, even when diluted with benzene, secondary alcohols have to be heated several hours at 130–140°C, and tertiary alcohols are dehydrated instead of being converted to esters.

There are great differences in the rates at which monoesters are formed; maleic anhydride[1] reacts rapidly with an alcohol, whereas tetrachlorophthalic anhydride[2] reacts slowly.

Esterification of the second carboxyl group of an anhydride requires much the same conditions, high temperature or a catalyst, as esterification of a simple carboxylic acid.

Large quantities of phthalic anhydride are used in the preparation of diesters for use as plasticizers (175,600,000 lb of esters in 1954) and in the preparation of alkyd resins (382,367,000 lb of phthalic alkyds in 1954).

Use of Acid Chlorides

Acid chlorides are widely used in esterifications, particularly on a laboratory scale. The remarks that were made about acid anhydrides might be repeated with little change about acid chlorides. The latter are much more reactive and are, in general, easier to prepare, and the inorganic by-products are readily removed from the esters produced. Hence, they are widely used, particularly in the laboratory. The disadvantages are that the hydrogen chloride evolved may cause changes in the organic compounds or serious corrosion of metal equipment.

$$C_2H_5OH + ClCOCl \rightarrow C_2H_5OCOCl + HCl \qquad (15)$$

$$C_2H_5OH + C_2H_5OCOCl \rightarrow (C_2H_5O)_2CO + HCl \qquad (16)$$

$$C_6H_5ONa + CH_3COCl \rightarrow C_6H_5OCOCH_3 + NaCl \qquad (17)$$

For making alkyl carbonates, phosgene, the acid chloride of carbonic acid, must be used. The first-stage reaction (15) goes rapidly at room temperature or below; the second reaction (16) is slow. When an ester chloride, ROCOCl, is desired, an alcohol is added to an excess of cold liquid phosgene. To obtain the neutral ester, phosgene is passed into an excess of an alcohol, and the reaction is complete after long standing or warming. Mixed dialkyl carbonates, ROCOOR′, are prepared by the reaction of the alkyl chlorocarbonate with an alcohol, R′OH. The reaction is accelerated by the addition of a tertiary amine or by agitation with cold aqueous alkali.

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[1] SIEGEL and MORAN, *J. Am. Chem. Soc.*, **69**, 1457 (1947).

[2] NORDLANDER and CASS, *J. Am. Chem. Soc.*, **69**, 2679 (1947).

There is a great deal of difference in the reactivity of different acid chlorides; those derived from aromatic acids react much more slowly than those from aliphatic acids, and aryl sulfonyl chlorides react even more slowly. Thus, when benzoyl chloride is dissolved in an excess of ethyl alcohol and kept at 0°C, 4 hr is required for complete reaction, but acetyl chloride reacts practically instantly. To speed up the reaction of a sluggish acid chloride, the mixture may be heated, or the Schotten-Baumann method may be used [Reaction (17)], i.e., the alcohol or phenol is mixed with 10 or even 25 per cent sodium hydroxide solution, and the acid chloride is added slowly with vigorous agitation, while the temperature of the mixture is kept at or below 0°C.[1] Instead of aqueous alkali, anhydrous tertiary amines may be used. The cold reactants are mixed, but the mixture may be heated later.

The reaction of an acid chloride with a phenol is facilitated by aluminum chloride.[2] The yields of esters from phenols and tertiary alcohols are high when magnesium is present.[3]

Esterification of Amides

An excellent way to make an acid amide is to treat an ester with ammonia:

$$CH_3COOC_2H_5 + NH_3 \rightleftharpoons CH_3CONH_2 + HOC_2H_5 \tag{18}$$

Although reaction (18) is reversible, the yield of the amide is almost quantitative, since the equilibrium is far over on that side. However, it is easy to convert an amide completely into the ester by the addition of an excess of an acid, such as sulfuric or hydrochloric, which combines with the ammonia. When a high-boiling alcohol is used, the ammonia can be driven off by heating. Since the reaction to the left in Eq. (18) is endothermic, high temperatures thermodynamically favor alcoholysis of the amide. The mechanism of the esterification probably is very similar to that discussed for the esterification of acids.

Esters from Metal Salts and Alkyl Halides

When the metal salt of an acid is heated with an alkyl halide, the corresponding alkyl ester is formed [reactions (19) and (20)].

$$CH_3COONa + BrC_2H_5 \rightarrow CH_3COOC_2H_5 + NaBr \tag{19}$$

$$CH_3COONa + ClCH_2C_6H_5 \rightarrow CH_3COOCH_2C_6H_5 + NaCl \tag{20}$$

This type of reaction is frequently used for preparing esters, especially those which may be used for identification of the acids.[4] For this purpose, an alkyl halide which is likely to give a crystalline ester is chosen. Silver salts, which are readily prepared from acids, are frequently employed for

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[1] Baumann, *Ber. deut. chem. Ges.*, **19**, 3218 (1886); Schotten, *ibid.*, **17**, 2545 (1884); **23**, 3430 (1890).

[2] Ross, U.S. 2,345,006 (1944).

[3] Spassov, *Ber. deut. chem. Ges.*, **70**, 1926 (1937); **75**, 779 (1942).

[4] Moses and Reid, *J. Am. Chem. Soc.*, **54**, 2101 (1932).

this purpose, since no solvent is required and the resulting esters need little purification. Thallium salts are reported to give particularly good yields of esters. For manufacturing purposes, this reaction is useful in a few cases only—those in which the alkyl halide is cheaper than the corresponding alcohol or in which the ester is difficult to obtain by direct esterification. The best-known case is that of the manufacture of benzyl acetate from sodium acetate and benzyl chloride. Since benzyl chloride is made by chlorinating toluene, it is the most readily available benzyl compound. The two reactants are brought together in a mutual solvent, which may be acetic acid or aqueous alcohol, and the mixture is heated until the benzyl chloride is used up, which is apparent by the disappearance of the sharp odor. The *p*-nitrobenzyl ester is made similarly.[1] Amyl chloride, from the chlorination of pentane, is used for the large-scale manufacture of amyl acetate.

Dialkyl phthalates, in which the two alkyl groups may be the same or different, can be prepared by heating a sodium monoalkyl phthalate with an alkyl halide[2] or a polymethylene halohydrin.[3]

Various compounds, particularly amines, are claimed as catalysts. An excellent yield of benzyl benzoate can be obtained by heating dry sodium benzoate with benzyl chloride and 1 per cent of a tertiary amine.[4]

Since reactions of this type are slow, except at temperatures above 100°C, they usually are carried out in autoclaves to avoid loss of volatile materials. When the reaction is complete, the autoclave is cooled and the charge drowned in water. The ester is separated, washed free of salts, dried, and rectified.

The reaction may be reversed. Thus, when triethyl phosphate or an ester of an aliphatic acid is heated with lithium, calcium, zinc, or ferric chloride, an alkyl halide and a salt of the acid are obtained.[5]

Esters from Nitriles

$$CH_3CN + H_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + NH_3$$

If the ester of an acid corresponding to an available nitrile is desired, it may be prepared by saponifying the nitrile and then esterifying the acid in the usual way. However, one operation is saved if the ester is prepared directly from the nitrile. The nitriles of hydroxy acids, in particular, are readily obtained by the addition of hydrocyanic acid to an aldehyde:

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

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[1] Hartman and Rahrs, *Org. Syntheses*, **24**, 81 (1944).

[2] Pollack and Chenicek, U.S. 2,275,467 (1942).

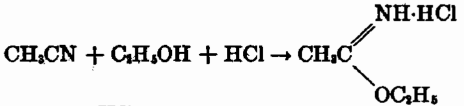
[3] Vereinigte Glanzstoff-Fabriken A. G., Ger. Appln. V 5,269, Class 12o, 14 (Apr. 5, 1956).

[4] Rueggeberg, Ginsburg, and Frantz, *Ind. Eng. Chem.*, **38**, 207 (1946).

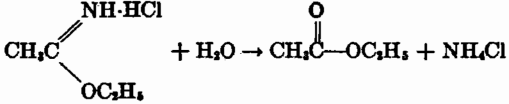
[5] Chesfuliez, Leber, and Bonvier, *Helv. Chim. Acta*, **36**, 1203 (1953).

The hydroxy nitrile is readily dehydrated to acrylonitrile, from which acrylic esters generally are manufactured by alcoholysis.

The esterification of the nitrile presents no great difficulty. An amount of acid catalyst greater than that required to combine with the ammonia that is formed must be used. Higher reaction temperatures and longer reaction times are required than for simple esterification. A common procedure is to dissolve the nitrile in the appropriate alcohol and to saturate the resulting solution with hydrogen chloride. Under these conditions imino ether hydrochlorides are formed [reaction (21)]. When the imino ethers are caused to react with water, esters are formed [reaction (22)].

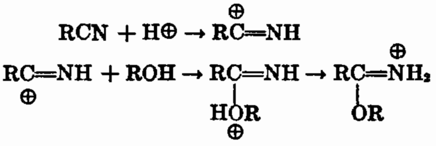


$$CH_3CN + C_2H_5OH + HCl \rightarrow CH_3C(=NH\cdot HCl)OC_2H_5 \qquad (21)$$



$$CH_3C(=NH\cdot HCl)OC_2H_5 + H_2O \rightarrow CH_3C(=O)\text{—}OC_2H_5 + NH_4Cl \qquad (22)$$

Sulfuric acid is the most commonly used commercial catalyst, but at high acid strengths, hydrochloric acid is much more effective. It is possible that a reactive intermediate, such as R—C(Cl)=NH, is formed by the reaction of the nitrile with hydrogen chloride. At low acid concentrations, the reaction probably proceeds via the addition of a proton:[1]

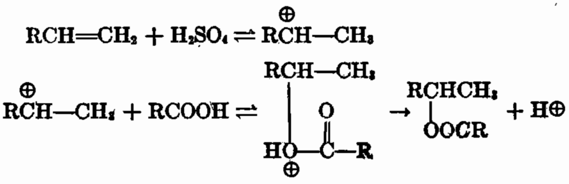


$$RCN + H^{\oplus} \rightarrow R\overset{\oplus}{C}{=}NH$$
$$R\underset{\oplus}{C}{=}NH + ROH \rightarrow RC(=NH)\text{—}\underset{\oplus}{HOR} \rightarrow RC(OR){=}\overset{\oplus}{NH_2}$$

III. ESTERS BY ADDITIONS TO UNSATURATED SYSTEMS

Addition of an Acid to an Olefin

The addition of an organic acid to an unsaturated hydrocarbon in the presence of a strong-acid catalyst probably occurs through an intermediate carbonium ion:



$$RCH{=}CH_2 + H_2SO_4 \rightleftharpoons R\overset{\oplus}{C}H\text{—}CH_3$$
$$R\overset{\oplus}{C}H\text{—}CH_3 + RCOOH \rightleftharpoons RCH(CH_3)\text{—}\underset{\oplus}{HO}\text{—}C(=O)\text{—}R \rightarrow RCH(CH_3)OOCR + H^{\oplus}$$

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[1] Kirkpatrick, *J. Am. Chem. Soc.*, **69**, 42 (1947).

The addition takes place according to Markownikoff's rule. The addition of carboxylic acids to the double bonds of isobutylene and trimethylethylene gives tertiary esters. A true equilibrium independent of sulfuric acid concentrations is established in the exothermic reaction.[1] The addition does not go well with ethylene, but goes well with many of the higher alkenes, particularly with some of the terpenes. To avoid the polymerizing effects of sulfuric acid, various other catalysts, such as sulfonic acids, triethylamine, hydrofluoric acid, boron trifluoride, and cuprous chloride have been used. The addition may take place at room temperature or higher and is aided by pressure. The vapors of the acid and hydrocarbon may be passed over catalysts, such as activated carbon,[2] heteropoly acids,[3] or metal phosphates.[4]

The addition of formic acid to olefins is easily controlled and gives high yields of esters.[5] Since the formates are easily hydrolyzed, the method provides a convenient way of introducing hydroxyl groups into hydrocarbons.

The optimum conditions for the esterification of olefins by carboxylic acids require low reaction temperatures, high concentrations of reactants, relatively large quantities of catalyst, and anhydrous conditions.

Esters from Acetylene

When acetylene and acetic acid are brought together with a suitable catalyst, a vinyl ester or an ester of ethylidene glycol is formed according to reaction (23) or (24):

$$CH{\equiv}CH + CH_3COOH \xrightarrow{Hg(OOCCH_3)_2} CH_3COOCH{=}CH_2 \qquad (23)$$

$$CH{\equiv}CH + 2CH_3COOH \xrightarrow{Hg(OOCCH_3)_2} CH_3CH(OCOCH_3)_2 \qquad (24)$$

By altering the reaction conditions, a preponderance of either product may be produced as desired.[6] Vinyl acetate, which is used for making polymers, and ethylidene diacetate, which is an intermediate for the manufacture of acetic anhydride, are produced on a large scale. The reaction may be applied to other carboxylic acids and acetylene derivatives. Strong acids, such as sulfuric, methane di- and trisulfonic, and phosphoric acids, are catalysts. They may be used in conjunction with mercury salts. Other catalysts which have been disclosed for the reaction include boron trifluoride and the salts of various metals, such as zinc silicate, zinc acetate, and mercuric phosphate. The addition may be effected in the vapor phase

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[1] ALTSCHUL, *J. Am. Chem. Soc.*, **68**, 2605 (1946).

[2] Larson, U.S. 2,093,695 (1937).

[3] Lazier, U.S. 2,174,985 (1939).

[4] The Distillers Co., Brit. 541,056 (1941).

[5] KNIGHT, KOAS, and SWERN, *J. Am. Chem. Soc.*, **75**, 6212 (1953).

[6] MORRISON and SHAW, *Trans. Electrochem. Soc.*, **63**, 23 (1933).

over a solid catalyst at 200°C or above.[1] Zinc salts of aliphatic acids on carbon carriers are excellent catalysts for the vapor-phase reaction. Zinc acetate is widely used in the manufacture of vinyl acetate. Zinc salts may be used also as catalysts for the preparation of vinyl esters of higher carboxylic acids in the liquid phase.

Esterification by Ketene

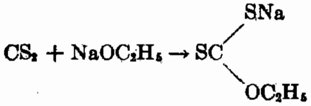
The reaction of ketene with alcohols to produce esters is attractive, since all the ketene goes into the product and there are no by-products. Ketene

$$CH_2{=}CO + C_2H_5OH \rightarrow CH_3COOC_2H_5$$

is as effective an acetylating agent as is acetic anhydride. Salicylic acid is acetylated by ketene. Esters are produced by the reaction of ketene with an acetal or ortho ester.[2] Boron trifluoride is an excellent catalyst for the addition. A catalyst is often necessary to complete the reaction. Even *t*-butyl alcohol reacts readily with ketene in the presence of sulfuric acid.[3]

Xanthates

Carbon disulfide combines readily with a sodium alkoxide to yield the corresponding sodium xanthate. The procedure for the preparation is



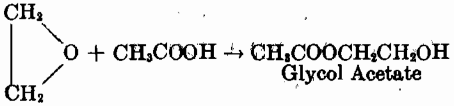
$$CS_2 + NaOC_2H_5 \rightarrow SC\begin{cases} SNa \\ OC_2H_5 \end{cases}$$

very simple. Metallic sodium is dissolved in the anhydrous alcohol, or sodium hydroxide is mixed with the alcohol, which may contain some water, and carbon disulfide is added. The union takes place at room temperature. The sodium or potassium xanthate may be purified by recrystallization.

The preparation of cellulose xanthate, which is made in large quantities as an intermediate in the manufacture of rayon and cellophane, is discussed in more detail in Sec. V.

Esterification by Ethylene Oxide

Ethylene oxide reacts with water to form glycol, with an alcohol to form a glycol ether, and with acetic acid to form glycol acetates:



$$CH_3COOH + CH_3COOCH_2CH_2OH \rightarrow \underset{\text{Glycol Diacetate}}{CH_3COOCH_2CH_2OCOCH_3}$$

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[1] Fischer and Freytag, U.S. 2,339,066; 2,342,463 (1944).

[2] Brooks, U.S. 2,449,447 (1948); Gresham, U.S. 2,449,471 (1948).

[3] Morey, *Ind. Eng. Chem.*, **31**, 1129 (1939).

The esterification is carried out by passing the ethylene oxide into the heated acid containing sulfuric acid or a similar catalyst. Under these conditions, a second molecule of the acid, if available, will esterify the free alcohol group of the monoester to produce the diester of the glycol.[1] Alkaline catalysts also have been recommended for this reaction. When benzoyl chloride is caused to react with ethylene oxide, the product is β-chloroethyl benzoate. Above 150°C, under pressure, and in the presence of catalysts, ethylene oxide and carbon dioxide combine to give ethylene carbonate.[2]

Esters from Carbon Monoxide

Carbon monoxide unites with an alcohol at an elevated temperature and under high pressure, in the presence of a metal alkoxide, to give an alkyl formate.

$$CH_3OH + CO \rightarrow HCOOCH_3$$

In the presence of acids or of boron trifluoride at somewhat higher temperatures under high pressure, the product is an acid. The acid so

$$CH_3OH + CO \rightarrow CH_3COOH$$

formed may react with a second molecule of the alcohol so that the final product is an ester.

A single molecule of an ether may react with carbon monoxide.

$$CH_3OCH_3 + CO \rightarrow CH_3COOCH_3$$

An olefin, an alcohol, and carbon monoxide may be made to unite.[3] As shown in Chap. 11, processes involving carbon monoxide are of increasing importance.

IV. ESTERS OF INORGANIC ACIDS

Among the commercially important esters of inorganic acids are those of nitric, sulfuric, phosphoric, and silicic acids. The nitrates of glycerol and cellulose are among the oldest of synthetic chemical products. They are prepared by the direct esterification of the alcohol by nitric acid.

$$C_2H_5OH + HNO_3 \rightarrow C_2H_5ONO_2 + H_2O$$

$$\underset{\text{Glycerol}}{C_3H_5(OH)_3} + 3HNO_3 \rightarrow \underset{\text{Glyceryl Trinitrate}}{C_3H_5(ONO_2)_3} + 3H_2O$$

$$\underset{\text{Cellulose Unit}}{[C_6H_7O_2(OH)_3]} + 3HNO_3 \rightarrow \underset{\text{Nitrocellulose Unit}}{[C_6H_7O_2(ONO_2)_3]} + 3H_2O$$

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[1] Fraenkel-Conrat and Olcott, *J. Am. Chem. Soc.*, **66**, 1420 (1944); Stein, U.S. 2,224,026 (1940).

[2] Vierling, Ger. 740,366 (1943).

[3] Hanford, U.S. 2,378,000 (1941); Ford, U.S. 2,424,653 (1947).

The nitration may be carried out in either a homogeneous or a heterogeneous reaction system. In both cases, the operations are simple, although the working out of the exact details for obtaining the desired products in high purity and good yields must be carefully chosen and controlled. So-called *mixed acid,* which is employed in nitrations, is a mixture of nitric and sulfuric acids and may contain water or sulfur trioxide, the concentrations of these being accurately adjusted to give the desired degree of nitration.

In the nitration of cellulose, the reaction is carried out under accurately controlled conditions, so that a product having the desired properties is obtained. These properties differ according to the use for which the material is destined. The product, nitrocotton, is always classified by the percentage of nitrogen that it contains. In carrying out the reaction, care must be taken to achieve uniformity of nitration, since the value of the product is largely dependent on its approach to homogeneity.

A monosulfate is formed when sulfuric [reaction (25)] or chlorosulfonic acid [reaction (26)] reacts with an alcohol:

$$C_2H_5OH + HO{\cdot}SO_2{\cdot}OH \rightleftarrows C_2H_5O{\cdot}SO_2OH + H_2O \qquad (25)$$

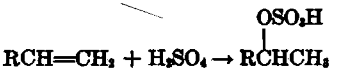
$$C_2H_5OH + Cl{\cdot}SO_2{\cdot}OH \rightarrow C_2H_5O{\cdot}SO_2OH + HCl \qquad (26)$$

Reaction (25) is used for converting the higher alcohols into their monosulfates, which have wide use as detergents and wetting agents.

$$C_{12}H_{25}OH + H_2SO_4 \rightarrow C_{12}H_{25}OSO_2OH + H_2O$$

The reactions of alcohols with nitric and sulfuric acids slow down and come to a standstill when the water formed in the reaction accumulates. The reactions are aided by an excess of sulfuric acid or sulfur trioxide.

An alkyl monosulfate may be made in quite a different manner by the addition of an unsaturated hydrocarbon to sulfuric acid, as is represented by reaction (27):



$$RCH{=}CH_2 + H_2SO_4 \rightarrow R\overset{OSO_3H}{\overset{|}{C}}HCH_3 \qquad (27)$$

The addition takes place on simple contact of the hydrocarbon with the acid, but the speed of the reaction depends on the strength of the acid and the nature of the hydrocarbon. To avoid polymerization and isomerization of the hydrocarbons, the temperature is kept relatively low, usually from 0–40°C. Sulfuric acid solutions of 10–100 per cent sulfuric acid or containing some excess sulfur trioxide may be used; the strength to be used will depend on the hydrocarbon. Some of the terpenes react with the 10 per cent acid, while ethylene reacts extremely slowly with less than 90 per cent acid. When a reactive hydrocarbon is shaken with the 10 per cent acid, the alkyl sulfuric acid may be formed and hydrolyzed immediately, so that apparently the hydrocarbon simply takes up a molecule of water. By adjusting the strength of the sulfuric acid solution, the absorption may be made selective, so that certain unsaturated hydrocarbons may be removed from a mixture of olefins. Thus, if a mixture of ethylene and propylene is brought into contact with 85 per cent sulfuric acid, the propylene is completely absorbed and the ethylene is practically untouched. The normal butylenes are absorbed by somewhat weaker sulfuric acid than is propylene, but the difference in reactivity is not sufficient for a sharp separation. Isobutylene reacts particularly readily and, when treated with 65 per cent sulfuric acid with cooling, is absorbed selectively by the acid.

The best-known case of the selective absorption by sulfuric acid is in the manufacture of isopropyl alcohol from cracking still gases. The more easily condensable constituents of the still gas, the butylenes and higher-molecular-weight materials, are removed by condensation or absorption; the residue, consisting of ethylene and propylene (with some hydrogen, methane, and ethane), is cooled and passed up through towers, over the packing of which 85 per cent sulfuric acid flows. The acid which is drawn off at the bottom of the tower is largely isopropylsulfuric acid. When it is diluted with water and boiled, the isopropylsulfuric acid is hydrolyzed, and the isopropyl alcohol distills over. Under 100 lb pressure, a second molecule of propylene is taken up to form isopropyl sulfate, which separates on the addition of water.

Other inorganic esters are generally prepared by the reaction of an acid chloride with a hydroxy compound or its sodium salt. Phosphates are prepared by the reaction of phosphorus pentachloride or phosphorus oxychloride with the appropriate alcohol or phenol. If the sulfur analogue of phosphorus oxychloride, $PSCl_3$, is caused to react with an alcohol, or its sulfur analogue, a mercaptan, the corresponding thioester is obtained.

$$3ROH + PSCl_3 \rightarrow (RO)_3PS + 3HCl$$
$$3RSH + PSCl_3 \rightarrow (RS)_3PS + 3HCl$$

The reactants are mixed at room temperature, or below, but may be heated in a later stage. The hydrogen chloride formed can be removed by a current of air or neutralized by the addition of alkali. The replacement of the chlorine atoms is rather rapid but can be carried out in a stepwise fashion so that mixed esters, such as alkyl diaryl phosphates, can be produced. The first chlorine is replaced most rapidly; the second and third are replaced more slowly unless a base is present.[1] Intermediate ester chlorides, such as $C_2H_5OSiCl_3$, can be obtained from silicon tetrachloride and an alcohol in a similar manner.[2] A useful method for preparing tita-

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[1] MARTIN, NORMAN, and WEILMUENSTER, *J. Am. Chem. Soc.*, **67**, 1662 (1945).

[2] SCHUMB and STEVENS, *J. Am. Chem. Soc.*, **69**, 726 (1947).

nium and other inorganic esters of alcohols, such as allyl or benzyl alcohols, consists in treating the inorganic halide with ammonia and then causing the ammoniated compound to react with the alcohol.[1]

V. ESTERIFICATION PRACTICE

Design and Operation of Esterification Plants

By Theodore Baker[2]

A plant for making esters from organic acids and alcohols on a large scale may be of three general types, depending on whether (1) the product is low boiling and is to be fractionated from an accumulated excess of water, as in the manufacture of methyl and ethyl acetates; (2) the ester is somewhat higher boiling and carries over with it considerable water that readily separates, after condensation, as a lower layer that can be decanted, as is the case with butyl and amyl acetates; or (3) the ester is of such low volatility that it is more practical to accumulate it in the still and merely volatilize the water and/or the excess of acid or alcohol, if these cannot be made to react completely. Examples of this type are the ethyl and butyl phthalates.

The first of these types of processes may be operated either in batches or continuously. Both methods require efficient distilling columns, which may be of perforated-plate or bell-cap design or even of the packed type. In every case, it is now customary to employ a catalyst, which is usually sulfuric acid, in admixture with the alcohol and acid that are to react. In making ethyl acetate industrially, ethyl alcohol of 95 per cent by volume and acetic acid of 80 per cent or less concentration are generally used. There being no definite lower limit of acid concentration, it is merely a matter of economic balance as to how far the exhaustion of the acetic acid may be carried. In a continuous process such as that of Backhaus, the concentration of the acetic acid may be reduced to 1 per cent.

Apparatus of special grades of stainless steel is generally used for commercial-scale esterification units. The materials of construction must be fairly resistant to the corrosive effects of organic acids and of sulfuric acid at relatively high temperatures. Lower-grade stainless steels can be used in installations in which a low concentration of catalyst or no catalyst is used, but higher temperatures and longer reaction times will be required. As temperatures and concentrations of corrodents are increased, the choice of stainless steels is narrowed to the ferritic chromium alloys and the austenitic chromium-nickel alloys. Strong, hot, weakly oxidizing solutions, such as sulfuric and acetic acid solutions, normally limit the selection to

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[1] Haslam, U.S. 2,684,972 (1954).

[2] E. I. du Pont de Nemours & Company, Inc.

the high-chromium or to the molybdenum-containing types. Type 347 stainless steel is the best all-around metal for some applications, such as the construction of kettles for the manufacture of alkyd resins. This steel is an 18-8 chromium-nickel alloy which has been alloyed with columbium.

Class 1. Low-boiling Esters: Fractionated from Accumulation of Water. Figure 12-5 illustrates a batch-still layout for making crude ethyl acetate and the like. The organic acid and alcohol are employed in about molecular proportions. At the start, the still can be filled to about four-fifths of its capacity. The catalyst, sulfuric acid, may be added directly to the still charge or previously blended with the organic acid. The charge is brought up to the boil, and the whole distillate is refluxed for a time by closing the take-off valve (A). The steam supply must be limited so that the condenser does not run hot or the pressure bottle show more than the normal back pressure of the column, this being about 1–1¼ in. per plate according to the design. After about an hour, the thermometer at the top

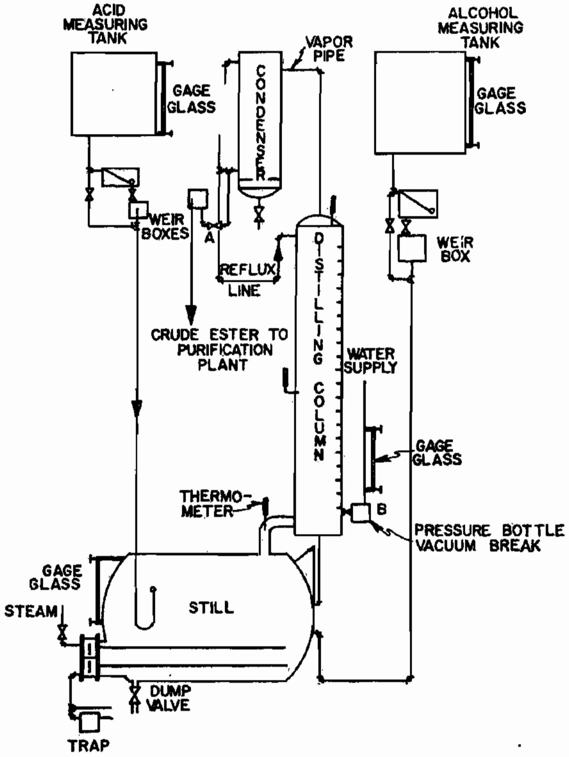

FIG. 12-5. Layout: batch process for manufacturing ethyl acetate.

of the column should read about 70°C for ethyl acetate and remain steady, while the mid-column thermometer will gradually show a drop in temperature. When the latter indicates that several plates are charged with liquor boiling about 70°C, the take-off valve may be opened to bleed off the ethyl acetate as fast as it is formed and so hold the temperature in the mid-column practically constant. As the still charge diminishes owing to the formation and removal of ester, more acid and alcohol can be added gradually through the feed weir boxes to keep the still contents nearly constant in volume. The distillate is approximately the constant-boiling ternary mixture whose composition is 82.6 per cent ethyl acetate, 8.4 per cent ethyl alcohol, and 9 per cent water. Commonly, a slight excess of alcohol is present to prevent any separation into two layers, and a trace of free acid is also present. This distillate is stored, to be purified in a separate apparatus later on. The exact boiling point of the ternary mixture is reported to be 70.23°C, but, under manufacturing conditions, a variation of even 1° up or down is often noted due to the presence of small amounts of other materials.

As less water is carried over than is formed in the reaction and as the acid

$$\begin{array}{ccccccc} \text{Acetic acid} & + & \text{alcohol} & = & \text{ester} & + & \text{water} \\ 60 & + & 46 & = & 88 & + & 18 \end{array}$$

used will generally contain at least 20 parts of additional water and the alcohol about 4 parts, a fairly rapid accumulation of water is taking place in the still. This causes a slowing-up of the reaction and requires a higher rate of reflux. After a while, the accumulation of water is so great that a cleanup is necessary. At this stage, an excess of alcohol is fed to the still and the acid feed discontinued. The distillate is then diverted to another tank and reused in a following charge. When the acid and alcohol are sufficiently exhausted, the residual water is dumped, and the still recharged.

The refining of the ester distillate comprises neutralizing with sodium carbonate or lime under agitation, followed by a water washing, which removes the excess of alcohol. The washing is often done countercurrent in a packed tube, the water flowing downward and the ester upward, the same apparatus acting as a decanter. The ester layer, holding about 4 per cent of water in solution, has to be redistilled through a column. The first distillate, which contains most of the water, is reseparated or rewashed, and the washings are separately redistilled to recover their contents of ester and alcohol, these being returned to the process.

A continuous process for making ethyl acetate, which is especially adapted to the utilization of dilute acetic acid, is illustrated in Fig. 12-6. In this process, the residual acid water, exhausted of its acid and alcohol to as low a point as is economical, is promptly and continuously discharged from the apparatus. The regulation of the still is thus practically fixed.

Another advantage is that the final purification and working up of the wash waters can be tied in with the production of the crude ester. Figure 12-6 illustrates the essentials of this process. The raw materials are first blended in the correct proportions and fed from the feed tank in a steady stream through a preheater into the esterifying column. From the top of the column is taken off a mixture of about 20 per cent ester, 10 per cent water, and 70 per cent alcohol, while a suitable amount of the same distillate is refluxed back to the column at (*A*). The ternary mixture taken off passes to the separating column at point (*B*). Here it is rectified by closed steam in the calandria (*C*). Part of the condensate is returned as reflux to the top of the column, and the take-off goes to a proportional mixing device, where it is blended with about an equal volume of water, which causes a separation into two layers. These are settled out in the separator tank, the watery portion overflowing back to the lower part of the separating column, whence, blended with the alcohol and water accumulating in the base of the column, the watery portion is passed by pipe (*D*) to a point in the esterification column. On the lower plates of the column, the alcohol is exhausted and distills upward as vapor, while the slop water goes to waste at (*E*). The washed ester, containing a little dissolved water and alcohol, overflows

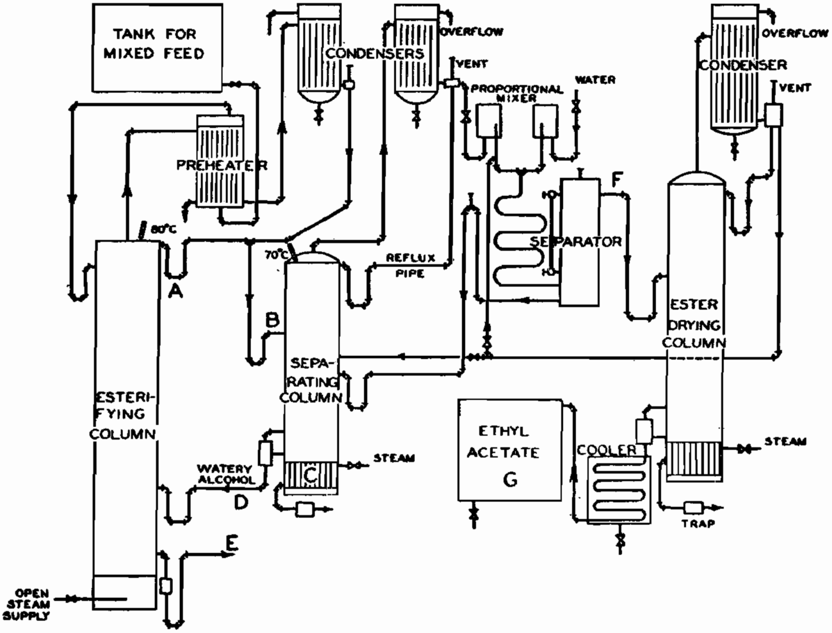

FIG. 12-6. Layout: continuous process for manufacturing ethyl acetate.

from the separator at (*F*) and enters the drying column in which a sufficient amount is distilled off to carry with it the water and alcohol, which may go either to the separating column or back to the mixer, washer, and separator. The dry ethyl acetate that accumulates in the calandria of the drying column is taken off through a cooler to the receiving tank (*G*). In general, this ester, although dry and holding very little alcohol and free acid, needs to be redistilled before it can be placed on the market, because it may contain salts of copper and higher-boiling esters formed from other acids present as impurities in the crude acetic acid employed.

The working up of crude ester made by the batch process is very similar to that employed in the continuous process, but, in the former, a special still must be provided for working up the weak wash waters unless this is done in the main batch still between esterification charges.

Class 2. Esters Such as Butyl and Amyl Acetates. This process differs from the first in that much more water is carried over with the ester when it distills from the esterification column or still. As this, in general, can exceed the total water formed during the reaction plus the free water in the raw materials, there is a general tendency for the still charge to go "dry." In any case, there is no building up of a watery still charge that has to be discharged as with ethyl and methyl acetates. Consequently, apparatus nearly as simple as that shown in Fig. 12-5 can be operated continuously over long periods. Condensate from the condenser is passed to a separator from which part of the oil layer can be refluxed if necessary. Part of the reflux can be taken directly from the condenser without separation, depending on the amount of water to be eliminated. The distillate is always a ternary one, containing ester and alcohol as well as water. This is not, in general, objectionable, as a product is often required that contains a certain proportion (10–15 per cent) of uncombined alcohol. The richness of the distillate in ester may be improved, if desired, by keeping the still charge stronger on the acid side. If a 100 per cent pure ester is required, this may be obtained by rectification of the ester-alcohol mixture after drying. The foreshots in such a distillation contain a mixture richer in alcohol, whereas the tailings can be practically pure ester. The alcohol-rich fraction can be reworked in the esterification process.

By employing an adequate reflux and avoiding too dry a column and still charge, the acetic acid can be substantially kept out of the distillate as it is carried down the column by the reflux, while the lower-boiling ternary mixture accumulates in the heads. The lower temperature and the wetness of the charge also tend to check the formation of sulfur dioxide resulting from reduction of the sulfuric acid.

In the preparation of butyl acetate, it is important that the acetic acid used should be free from other acids; its water content is not so important. The butyl alcohol must be free from other alcohols and is used in about 10 per cent excess. The catalyst is about 0.1 per cent sulfuric acid.

The still is heated under total reflux until the temperature at the top of the distilling column becomes constant at approximately 89°C. Then the distillate is withdrawn from the condenser as rapidly as can be done without permitting the temperature to rise above 90°C (89.4°C is the boiling point of the ternary of ester, alcohol, and water). The percentage composition of the distillate after separation into two layers is given in Table 12-7.

These layers are separated continuously in an automatic separator; the upper layer is returned to the still, while the lower is taken off and measured. As the reaction nears completion, the amount of water that separates diminishes until there is none; the temperature in the still, after rising steadily, flattens out at the refluxing temperature of the butyl acetate. The crude ester is cooled and neutralized with aqueous sodium hydroxide. After separation of the water layer, the ester is ready for refining by distillation. The first fraction is the ester-water binary azeotrope which is caught in an automatic separator, from which the ester layer is returned to the still. The next is a small fraction that contains some water, as shown by turbidity when it is mixed with 10 vol. of benzene. This is added to the next batch. The rest of the distillate is finished ester and goes to storage.

TABLE 12-7

Layer	%	Ester, %	Butyl alcohol, %	Water, %
Upper..............	75	80.5	13.4	6.1
Lower..............	25	1.92	1.69	97.39

A kettle of 2,000-gal capacity with a 30-plate 30-in. column can produce 1,000 gal of finished ester in 48 hr, provided that anhydrous acetic acid and butanol are used. The presence of any considerable amount of water decreases the capacity of the apparatus and lengthens the distillation time.

Class 3. Esters of Very Low Volatility. In this case, the ester does not appreciably volatilize with the water that forms or was originally present but stays behind in the still, while the free acid and alcohol gradually diminish. In general, the arrangement used for Class 2 esters may be used: merely the method of operation is changed. In the case of ethyl alcohol derivatives, by adding benzene to the charge, the water can be eliminated by taking it off from the separator as a lower layer containing some alcohol, which can be rectified elsewhere and its alcohol recovered. In the case of butyl and amyl compounds, the use of benzene is unnecessary, as the employment of an excess of the alcohol serves the same purpose, the water going over as a binary with the alcohol and separating out in the same way. In the case of an easily volatilized acid, as acetic, the water may be eliminated as formed by adding to the charge a compound such as dichloroethylene or ethyl acetate. Such substances form with water binaries of low boiling points; these concentrate at the top of the column and separate after condensation, the water layer being taken off, in one case at the top and in the other at the bottom.

When the reaction is practically complete, the sulfuric and excess of organic acid are neutralized, and the charge is distilled to dryness, being finally heated in a high vacuum to eliminate low-boiling residues.

Other purification treatment, such as filtration, may be required finally to yield a first-class product.

Interesterification of Lard

A good example of a commercial interesterification is the process developed by The Procter & Gamble Company[1] for improving the properties, particularly the plastic range, of natural lard. In the directed interesterification of the process, the transesterification reaction between the mixed glycerides of saturated and unsaturated acids is carried on just below the melting point of the fat so that the highest melting fractions, the trisaturated glycerides, are made to precipitate. This forces the equilibrium in the liquid phase, where transesterification takes place, in the direction of formation of more trisaturated glycerides, which, in turn, precipitate. The changes in lard glyceride composition as interesterification proceeds are shown in Fig. 12-7.

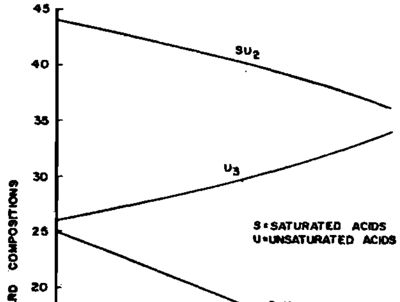

FIG. 12-7. Calculated change in lard glyceride composition with directed interesterification. [*Hawley and Holman, J. Oil Chemists' Soc.*, **33**, 29 (1956).]

The interesterification is run as a continuous process. The rate of interesterification is important since the trisaturated glycerides can precipitate only as fast as they are formed in the liquid phase. When the very active catalyst, sodium-potassium alloy, is used, the rate of interesterification is relatively rapid. Since the alloy is a liquid at room temperature, it is well suited for continuous metering.

In the process, lard is pumped through a vacuum drier, and then cooled to a temperature just above its melting point by passage through a

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[1] HAWLEY and HOLMAN, *J. Oil Chemists' Soc.*, **33**, 29 (1956).

heat exchanger. A stream of sodium-potassium alloy metered through a variable-speed positive-displacement pump is then pumped with the lard into a continuous mixer. The lard with the catalyst dispersed in it is passed on through an ammonia-cooled scraped-wall heat exchanger (a commercial Votator unit), in which the temperature is quickly lowered to the point desired for initiating crystallization of trisaturated glycerides. As the lard leaves the cooler, it goes to a crystallization vessel, in which agitation is carefully controlled and where interesterification proceeds. In the crystallizers, where the precipitation of the trisaturated glycerides takes place, the most critical part of the process occurs. End-for-end mixing as the stock moves through the crystallizer is eliminated by the use of four stages of crystallization, each stage being a separately agitated vessel designed to permit smooth flow through the vessel.

The heat of fusion of the trisaturated glycerides raises the temperature of the stock beyond the desired range for crystallization, and a second cooling step is required. After the second cooling, the lard passes to a second crystallizer, where the precipitation of trisaturated glycerides continues to the desired level. The degree of formation of trisaturated glyceride can be varied by changing the time in the crystallizer or by varying the temperature at which crystallization is taking place.

After interesterification has proceeded to the desired point, the catalyst is destroyed by adding water and carbon dioxide. Carbon dioxide buffers the caustic to a lower pH and minimizes saponification of the lard. The neutralized lard is heated to melt the trisaturated glyceride crystals. Soaps are removed by conventional water washing and centrifuging, and the lard is dried in a continuous-vacuum drier. A basic flow chart for the process is shown in Fig. 12-8.

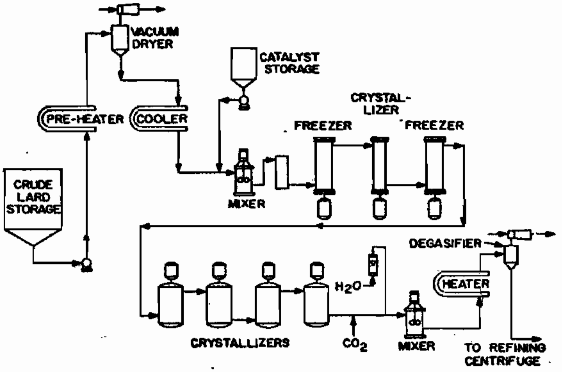

FIG. 12-8. Basic flow chart for directed interesterification of lard. [*Hawley and Holman, J. Oil Chemists' Soc.*, **33**, 29 (1956).]

Production of Polyethylene Terephthalate

BY E. F. IZARD[1]

Polyethylene terephthalate is used in the manufacture of Dacron polyester fiber, Mylar polyester film, and Cronar photographic film base in the United States. In Canada, England, and some European countries, the commercial articles are called Terylene. In Germany, the film is called Hostaphan. Total capacity for producing polymer and its products in this country is in excess of 50 million lb per year.

Polyethylene terephthalate is prepared by a transesterification reaction between dimethyl terephthalate and the dihydric alcohol, ethylene glycol.

$$2n\mathrm{HOCH_2CH_2OH} + n\mathrm{CH_3OOC{-}C_6H_4{-}COOCH_3} \xrightarrow[\text{catalyst}]{\text{heat}} n\mathrm{HOCH_2CH_2OOC{-}C_6H_4{-}COOCH_2CH_2OH} + 2n\mathrm{CH_3OH}$$

$$n\mathrm{HOCH_2CH_2OOC{-}C_6H_4{-}COOCH_2CH_2OH} \xrightarrow[\text{catalyst}]{\text{heat, vacuum}} \mathrm{HOCH_2CH_2{-}O{-}[OC{-}C_6H_4{-}COOCH_2CH_2{-}O{-}]_nH} + (n-1)\mathrm{HOCH_2CH_2OH}$$

Dimethyl terephthalate is obtained by the esterification of terephthalic acid by methanol. Terephthalic acid is a high-melting (above 300°C), insoluble material and requires special conditions for esterification. Two parts of methyl alcohol, 1 part of terephthalic acid, and 0.01 part of sulfuric acid are placed in a closed, agitated pressure vessel and heated to 150°C for 2–3 hr. During the last hour, 5–6 parts of additional methyl alcohol is added slowly to the liquid reactants and distilled to remove the water of reaction. By cooling, the dimethyl terephthalate is completely separated from the solution. Yields run as high as 95 per cent. The dimethyl terephthalate can be purified by crystallization from high-boiling solvents, such as xylene, or it may be distilled.

In the Imhausen process, *p*-xylene is oxidized by air at elevated temperature to *p*-toluic acid. *p*-Toluic acid is soluble and easily esterified. It is converted to methyl *p*-toluate in the usual way. The methyl *p*-toluate is then oxidized by air to monomethyl terephthalate. This product is soluble in organic solvents and is esterified by methanol to give dimethyl terephthalate. The purified dimethyl terephthalate from either of these processes is suitable for use in the manufacture of polyethylene terephthalate.

In the first stage of the manufacture of polyethylene terephthalate, dimethyl terephthalate (1 mole) is caused to react with ethylene glycol (2 moles) in the presence of a catalyst. Suitable catalysts are litharge, zinc salts, calcium salts, magnesium salts, alkali metals or their alkoxides, etc. The catalyst concentration may vary from 0.005–0.1 per cent. The reaction begins at 150–160°C, and the methyl alcohol is distilled out through

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[1] E. I. du Pont de Nemours & Company, Inc.

a good fractionating column until the reaction is complete. In the end, the reaction temperature will have risen to about 230°C. The reaction product is statistically bis(β-hydroxyethyl)terephthalate, but actually it is a mixture of free glycol, bis(β-hydroxyethyl)terephthalate, and low polymer. Pure bis(β-hydroxyethyl)terephthalate melts at 109°C, but the usual commercial product melts somewhat higher because of the presence of low-molecular-weight polymers.

In the second stage of the manufacture of polymer, the temperature is raised further, and reaction takes place between the hydroxyethyl end groups to produce polymer and glycol. Vacuum is applied slowly and the temperature raised to remove the glycol and to continue the reaction. The final polymerization is usually accomplished at 260–300°C under a vacuum of 0.1–10 mm of mercury.

If an attempt is made to prepare the polymeric ester from 1 mole of glycol and 1 mole of dimethyl terephthalate, low-molecular-weight polymers are obtained because of the occurrence of competing reactions. As soon as an ester linkage is formed to fix one end of a glycol molecule, the ester group can enter into a transesterification with the hydroxyl group at the end of a previously formed polymeric molecule. The ethylene glycol which is set free can escape with water or alcohol and is lost at the high temperatures which are required for the reaction. However, when the bis(β-hydroxyethyl)terephthalate is heated and vacuum is applied, excess glycol is removed as transesterification occurs, and an exact balance of glycol and terephthalate constituents is approached.

The duration of the polymerization depends on the catalyst concentration, reaction temperature, size of the batch of polymer being produced, and the amount of surface area generated in the polymerization autoclave. In commercial operation, it is desirable not to have too long a polymerization cycle for economic reasons. In a cycle that is too long, the competing and irreversible thermal degradation reaction will have sufficient time to lower the viscosity and to cause discoloration.

The removal of ethylene glycol from the polymerization reaction mixture should be as continuous and as rapid as possible to assure rapid polymerization. To provide for efficient removal of ethylene glycol, it is desirable to conduct the polymerization in a vessel which provides for maximum surface-area generation. Agitation of the polymerizing mass should provide for the maximum exposure of the batch to the effects of the vacuum. Efficient operation may be carried out in rapidly agitated vessels having relatively large exposed surface areas or in continuous units. The reaction is stopped when the product has attained the desired viscosity. The molecular weight of the polymer is not known accurately, but reproducibility is obtained by control of the viscosity of the polymer. This is usually done by determining the viscosity of a series of dilute solutions of the polymer in a solvent, such as 60:40 phenol:tetrachloroethane, compared with that of the pure solvent. By plotting

$$\frac{\ln \eta_r}{C} \text{ vs. } C$$

in which η_r is the viscosity of the dilute solution and C is the concentration in grams of polyester per 100 ml of solution, and extrapolating to zero concentration, the intrinsic viscosity $[\eta_0]$ is determined. Commercially desirable polymer should have an intrinsic viscosity above 0.45. Polyethylene terephthalate can be water-white. The pure polymer has a melting point of 265°C, although most commercial varieties melt somewhat lower.

Other glycols can be used to make the polymer. The accompanying table gives the melting points of a homologous series of α,ω-glycol esters of terephthalic acid.

Glycols	*Melting point, °C*
Ethylene	265
Tetramethylene	226
Hexamethylene	152
Octamethylene	132
Decamethylene	129
Octadecamethylene	116

Diethylene glycol gives an amorphous, rubbery polymer. Pentaglycol (neopentyl glycol) gives an amorphous, glassy polymer.

Manufacture of Alkyd Resins

Alkyd resins are polymeric esters which are obtained when polyhydric alcohols are heated with dibasic acids. Glyptal, which was the first alkyd to be prepared, is made from phthalic anhydride and glycerol. The alkyds are usually modified with a quantity of a monobasic acid. Alkyds which are modified with oils, such as soybean, linseed, and coconut oils, constitute the main volume of alkyds in production. Glycerol is the principal alcohol used in alkyds, but glycol, pentaerythritol, mannitol, and sorbitol are used for some applications. In 1954, the production of alkyds based on phthalic acid was 382,367,000 lb; production based on all other dibasic acids, such as maleic, sebacic, and adipic acids, was 71,234,000 lb.[1] The monobasic acids are usually the crude acid mixtures that are obtained by saponifying natural oils, such as linseed, soybean, castor, or cottonseed oils. These materials are proportioned so as to give the desired physical characteristics. A formulation and procedure for preparing a typical simple alkyd resin modified by linseed oil is given below:[2]

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[1] *U.S. Tariff Commission Rep.* 196, Synthetic Organic Chemicals, U.S. Production and Sales, 1954.

[2] Monsanto Chemical Co., The Chemistry and Processing of Alkyd Resins, 1952.

	Parts by weight
Linseed oil	2,000
Glycerol	500
Lime	2
Phthalic anhydride	1,400
Glycerol (secondary)	80

The linseed oil and glycerol are heated to 425°F (218°C) in about 2 hr, the lime is added and heating is continued to 450°F (232°C). Phthalic anhydride is added slowly to prevent rapid cooling. The remaining glycerol is added and the temperature maintained at 232°C until an acid value of 6–10 and the required solution viscosity are obtained.

In order that the esterification may go to completion, the water that is formed must be eliminated, but before it can escape, it must diffuse to the surface, which, in a large commercial batch, may involve considerable travel. Diffusion is slow in these mixtures which are fairly viscous at the start and become much more so toward the end. The operations are commonly carried on at relatively high temperatures, 200–300°C, at which the viscosities are considerably reduced but are still high. At these temperatures, sulfuric acid and like catalysts, which are so efficient at lower temperatures, cannot be used. A wide variety of catalysts, such as lead, calcium, zinc, phosphoric acid, zinc chloride, triphenyl phosphite, and *p*-toluenesulfonic acid, have been used.

Equipment and Operation.[1] Most of the standard equipment for processing alkyd resins is constructed of austenitic stainless-steel alloys. The resistance of stainless steel to chemical corrosion is a distinct advantage over other metals, and products having a pale color are obtained in equipment of stainless steel. The size of the resin kettle should be as large as possible, consistent with the volume of production desired. A single large kettle almost invariably has lower installation and operating costs than two smaller ones, each of about half the capacity. The average size of kettle used is between 1,000 and 3,000 gal. As the kettle size is increased, the rate of heating up the contents of the kettle is lowered, because of the diminishing ratio of heating surface to the weight of the charge in the kettle.

The source of heat for the resin kettle may be direct heat by coke, gas, oil, or electricity, or by circulating liquids, such as steam or Dowtherm. A temperature rise of 107°C per hr is practical when Dowtherm is used. This is about as fast as the best heat-up rate obtained with direct firing. The Dowtherm heating system offers the advantages of rapid cooling of the batch by circulation of cold liquid Dowtherm through the jacket and elimination of the danger of charring and discoloration at the heated surface.

Thorough agitation in the reaction kettle is a necessity because of the im-

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[1] HOVEY, *Ind. Eng. Chem.*, **41**, 730 (1949).

miscibility of the ingredients and the viscosity of the mixtures. Agitation which comes as close as possible to scraping the sides of the kettle clean is the best for preventing discoloration from overheating. Baffle plates placed a few inches from the sides of the kettle cause turbulent flow, giving far better mixing, faster esterification, and better color than could be obtained by unimpeded flow at a smooth wall. In general, the material should revolve around the kettle between 30 and 60 times per minute.

Air- and water-cooled condensers are used on the resin flask when it is necessary to retain volatile ingredients. An inert gas, such as carbon dioxide or nitrogen, bubbled through the reaction mixture improves agitation, promotes better color by minimizing the possibility of oxidation, and speeds the reaction by helping to remove the liberated water. Figure 12–9 shows the effect of agitation and inert gas on the rate of reaction.

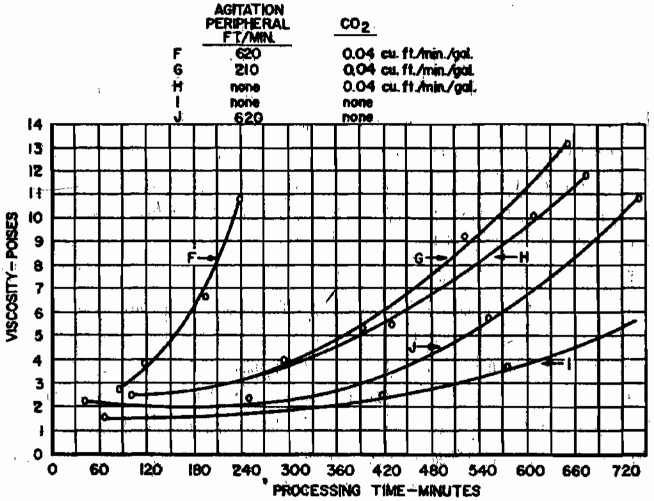


Fig. 12-9. Effect of agitation and inert gas on viscosity at 450°C. (*Monsanto Chemical Co., The Chemistry and Processing of Alkyd Resins*, 1952.)

After the esterification is completed, the resin is pressed into a thinning tank which contains a solvent, such as xylene, toluene, solvent naphtha, or treated petroleum solvents. The alkyd resin solutions are then filtered through plate-and-frame-type filter presses, which can handle a great volume of resin solution in a relatively short time and clarify it of even small-sized particles of suspended matter efficiently.

Preparation of Vinyl Acetate

The manufacture of vinyl acetate, to be used for preparing polyvinyl acetate, is preferably carried out as a vapor-phase reaction between acetylene and acetic acid. A flow sheet showing the major items of equipment for a vapor-phase process is shown in Fig. 12-10. Zinc acetate is used commonly as the catalyst for these vapor-phase processes. A suitable catalyst consists of 3–5 mm granules of a mixture of 42 parts of zinc acetate to 100 parts of activated charcoal. The catalyzers are steel boxes in which the catalyst is held between vertical plates spaced 1 in. apart. Cooling of the exothermic reaction is provided by horizontal steel tubes in the catalyst bed through which water is passed.

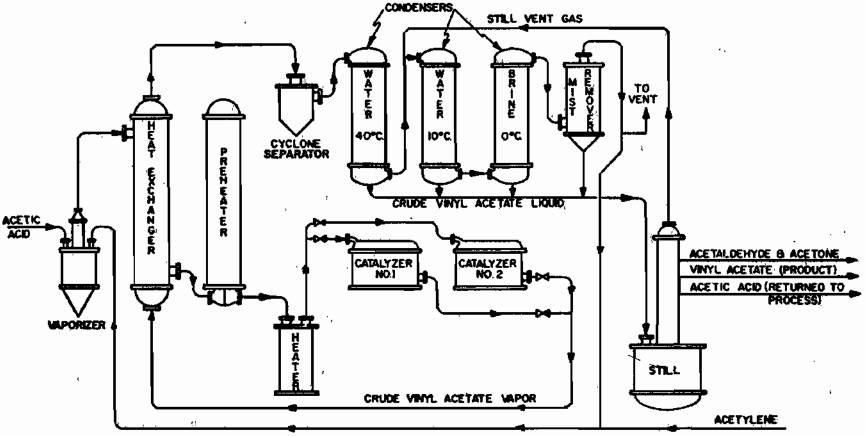


FIG. 12-10. Flow sheet of process for the production of vinyl acetate monomer. [*Greene, Chem. Eng.*, 54, 99 (1947).]

Purified acetylene, from which all traces of hydrogen sulfide and phosphine have been removed by scrubbing with sulfuric acid and passing over potassium dichromate and kieselguhr, is bubbled through acetic acid heated to 60°C in the vaporizer. The rate of flow is adjusted so that the gas leaving the vaporizer carries with it 23 per cent by weight of acetic acid. The gas, which is heated to 170°C by passing through a series of heat exchangers and heaters, flows into the catalyzer, in which the gas temperature is held at 170°C.

The conversion to vinyl acetate in the catalyzer may be regulated either by adjusting the rate of gas flow through the catalyzer or by varying the reaction temperature. The best economic balance is obtained at a conversion of 60 per cent. A charge of catalyst has a life of about two months when vinyl acetate is produced at a rate of 400–500 metric tons per month.

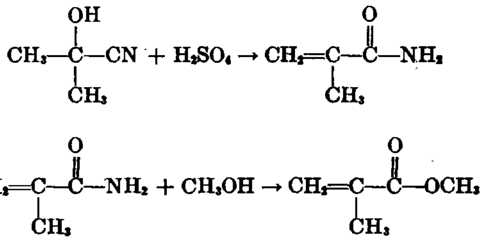
The crude vinyl acetate vapor emerging from the catalyzer passes through the heat exchanger and then to a separator where carbon dust is removed. The vapor is then passed through a series of three condensers, as is illustrated in the flow diagram (Fig. 12-10). Condensate from each of these units, plus the liquid from the mist remover, is collected in a common line which flows to the still. The condensate averages 60 per cent of pure vinyl acetate and 40 per cent of acetic acid. Resin formation during distillation is prevented by the addition of thiodiphenylamine to the crude vinyl acetate in the still. The yield of vinyl acetate varies from 92–95 per cent based on acetylene and from 97–99 per cent based on acetic acid.

Since no highly corrosive catalysts are used in the process, the materials of construction need not be special grades of highly corrosion-resistant materials. The vaporizer, heat exchanger, separator, preheater, heater, and catalyzer may be made of steel; condensers, mist remover, and still are often of stainless steel.

Long-chain vinyl esters, such as vinyl stearate, can be prepared by the liquid-phase reaction of acetylene and a long-chain acid in the presence of zinc stearate catalyst at 200 psi and 165°C in a stainless-steel autoclave.[1] Vinylation is complete in 8.5–9 hr; 3–5% of the acid is left unreacted.

Preparation of Methyl Methacrylate

Methyl methacrylate monomer, which is polymerized in large quantities in commercial practice to give the clear resinous compositions sold as Lucite and Plexiglas, is prepared from acetone cyanohydrin by a process involving dehydration and hydrolysis of the nitrile to methacrylamide, followed by alcoholysis of the amide.



$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CN + H_2SO_4 \rightarrow CH_2=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-NH_2$$

$$CH_2=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-NH_2 + CH_3OH \rightarrow CH_2=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-OCH_3$$

The synthesis of this ester starts with acetone, which is caused to react with hydrogen cyanide to yield the cyanohydrin. Alternative methods of preparing the methacrylic ester, in which the cyanohydrin is first converted into methacrylic acid, which is subsequently esterified, or in which the ester is formed before the dehydration to the unsaturated acid is carried out, have also been described. However, the method outlined above is that chiefly employed in manufacturing processes.

In the operation, a charge of acetone cyanohydrin (98 per cent pure) is placed in an enameled tank, and 1.35 molar equivalents of concentrated sulfuric acid is slowly added over a period of about 30 min at a rate such that the reaction temperature is kept at 60°C. As soon as all the acid has

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[1] Craig et al., *Ind. Eng. Chem.*, 47, 1702 (1955).

been added, the reaction mixture is heated quickly (20–25 min) to 128°C in order to complete the simultaneous dehydration and hydrolysis to methacrylamide.

The amide is then transferred to the esterifier, a brick-lined steel vessel equipped with a turbine-type stirrer of silicon-iron construction. After 1.8 moles of methanol has been added to the esterifier, water is added at a rate such that the heat of dilution plus the heat of reaction maintain the reaction temperature at 80°C. Cooling is accomplished by refluxing methanol. After a 1–1.5 hr operating cycle, the reaction mixture is dropped into a brick-lined steel tank, from which the volatile products are stripped by steam distillation. The distillate separates into an upper layer containing about 95 per cent methyl methacrylate and some water and methanol and a lower layer of methanol and water plus a trace of methyl methacrylate. The lower layer is distilled in batches to recover, in order, methyl methacrylate, dilute methanol which is recycled, and a water residue.

The upper layer is distilled continuously in bubble-cap stills of aluminum construction. About 0.025 part of phenol per part of methacrylate is added as a polymerization inhibitor. The low-boiling components are removed overhead in the first column. After this product has been washed with water, the upper monomer layer is recycled to a second continuous column which is operating at about 300 mm and which delivers pure methyl methacrylate.

Terpene Esters by Direct Addition of Aliphatic Acids

By J. N. Borglin[1]

Terpene esters can be made by the direct addition of fatty acids[2] and halogenated[3] and thiocyanated[4] fatty acids to terpene hydrocarbons, ethers, and esters. Since the bicyclic terpenes (camphene, α-pinene, and β-pinene) are more reactive than the monocyclic, they are the preferable starting materials.

Whether the ester formed is predominately secondary or tertiary depends upon the terpene used. In the case of camphene, the addition is preceded by isomerization, and the ester is secondary. The pinenes give a mixture in which the tertiary esters predominate, the ratio of tertiary to secondary depending on the reaction conditions.

The addition is carried out at a fairly low temperature, preferably below 100°C, in order that the tendency toward isomerization to monocyclic

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[1] Hercules Powder Company.

[2] Bouchardat and Lafont, *Compt. rend.*, **102**, 171 (1886).

[3] Borglin, U.S. 2,217,611; 2,217,613; 2,217,614; 2,227,059; 2,227,060 (1940); 2,239,495 (1941); 2,275,606 (1942).

[4] Borglin, U.S. 2,227,061 (1940).

terpenes and to polymerize may be minimized. On account of the corrosive nature of the fatty acids used, glass-lined equipment is required.

As a typical example: A mixture of 1,100 parts by weight of turpentine and 750 parts of monochloroacetic acid is kept at 50–55°C for 8 hr under a blanket of carbon dioxide. The product is washed with cold water to remove unreacted acid and distilled with steam to recover the uncombined terpene. The yield of isomeric esters is about 60 per cent. The product is light in color; a water-white ester can be obtained by flash distillation under vacuum.

Cellulose Esters

By James A. Mitchell[1]

Cellulose acetate is an important commercial polymer used in the manufacture of cellulose acetate yarn, plastics, photographic films and sheeting, and surface coatings. The technology of cellulose esters is complex, and only a brief outline of the commercial procedures can be presented here.

The principal commercial sources of chemical cellulose are purified cotton linters of about 99 per cent α-cellulose content and purified wood pulp of about 96 per cent α-cellulose content. Cellulose occurs in these materials as a fairly highly crystalline, high-molecular-weight polymer. It is in a fibrous form, which is insoluble in common reagents. Cellulose will not react to any significant degree with acetic acid and will react with acetic anhydride without a catalyst only at very high temperatures, at which the cellulose is degraded.

An important factor in the esterification reactivity of cellulose is the history of its method of manufacture and pretreatment or activation prior to the reaction. Since cellulose is insoluble in the acetylation solvent and is in a fibrous form, it is necessary to make the hydroxyl groups as accessible to the acetylating agent as is possible. The pretreatment or activation is designed to accomplish this. Soaking the cellulose in acetic acid or aqueous acetic acid prior to esterification greatly improves its reactivity.

Sulfuric acid is used almost exclusively in commercial practice as the catalyst for inducing the reaction of cellulose with acetic anhydride. The reaction to produce fully acetylated cellulose (44.8 per cent acetyl content) may be represented by the following equation:

$$(C_6H_{10}O_5)_n + 3n(CH_3CO)_2O \rightarrow [C_6H_7O_5(CH_3CO)_3]_n + 3nCH_3COOH$$

Sulfuric acid acts as a catalyst by initially reacting with the cellulose, preferentially at the primary hydroxyl groups. Then reaction with the acetic anhydride replaces the combined sulfuric acid, and cellulose triace-

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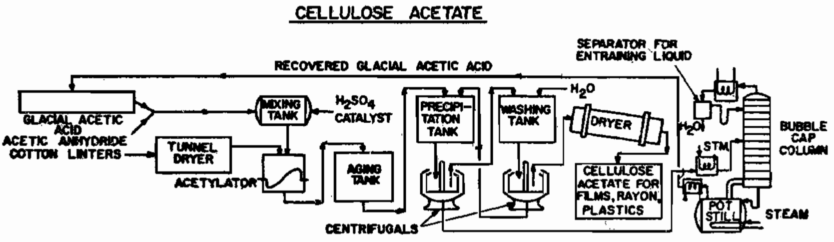
[1] Tennessee Eastman Company, Division of Eastman Kodak Company.

tate is produced. The heterogeneous reaction between the cellulose fibers and the acetic acid–acetic anhydride solution proceeds until a clear solution is obtained. The heterogeneous nature of the reaction mass and the high viscosity of the resulting product require special means of agitation in order to secure uniformity of results. The equipment for this purpose, which must be resistant to corrosion by the reagents, sometimes takes the form of a rotating vessel of the ball-mill type, with or without baffles, and, in other cases, is a heavily constructed agitated vessel of the dough-mixer type. Since cellulose triacetate is not soluble in common solvents such as acetone, it is generally hydrolyzed by aging the triester dope, which contains water and small quantities of sulfuric acid catalyst, to a lower acetyl content (39–41 per cent acetyl) to improve its solubility.

A typical commercial process is represented schematically in Fig. 12-11 and is described in the following paragraph:



COTTON LINTERS	0.7 lb.	SULPHURIC ACID	0.1 lb.	PER POUND OF CELLULOSE ACETATE
ACETIC ANHYDRIDE	2.0 lb.	DIRECT LABOR	0.12 MAN-HR.	
ACETIC ACID*	3.25 lb.			

* RECOVERY IS ABOUT 5 lb. PER lb. CELLULOSE ACETATE

FIG. 12-11. Flow sheet: cellulose acetate manufacture.

One part of cellulose (moisture content about 5 per cent) is added to 2.4 parts of acetic acid in a Werner and Pfleiderer-type stainless-steel mixer, and the mixer is run for 1 hr at 37.8°C. Four parts of acetic acid and 0.88 per cent of sulfuric acid, based on the weight of the cellulose, are added, and the mixing is continued at the same temperature for 45 min. The mixture is then cooled to 18.3°C. After 2.7 parts of 98 per cent acetic anhydride has been added, and the mixture has been cooled to 15.6°C, 6.12 per cent of sulfuric acid (based on the weight of the cellulose), which has been diluted with an equal weight of acetic acid, is added. The temperature is permitted to rise gradually to 32–35°C during an interval of 1.5–2 hr. At this stage, the reaction mixture is very viscous and free from fibers. A mixture of 1 part of water and 2 parts of acetic acid is then added during an interval of 1 hr. The reaction of the excess anhydride with the water gives a sharp temperature rise of about 5°C. After the solution has been thoroughly mixed and the temperature adjusted to 37.8°C, the solution is transferred to a hydrolysis vessel and held at 37.8°C until an ester of the desired acetyl content is obtained. The cellulose acetate is then precipitated with water by running the dope slowly into an agitated vessel where the acetic acid concentration is maintained at 25 per cent by the addition of weak aqueous solutions of acetic acid. The acid is drained from the precipitated cellulose acetate flake, and the flake is washed with water until it is free from traces of uncombined acid. Traces of calcium and magnesium salts in the wash water aid in the stabilization of the acetates, and small quantities of these salts may be added for optimum stability. The material is centrifuged or pressed to reduce water content and then dried in a moving belt tunnel drier.

One important variation of this general procedure which is in commercial practice is the use of a chlorinated solvent, such as methylene chloride, as the solvent in the reaction. Since methylene chloride has a low boiling point, the temperature of the reaction is controlled by refluxing. Another process, which has been used to a lesser degree, is a fibrous acetylation process. In this method, the reaction is carried out in the presence of several parts of benzene or a similar nonsolvent. The cellulose does not dissolve, but is converted to cellulose triacetate while remaining in fibrous form. The catalyst in this process is generally perchloric acid.

The cellulose acetate used commercially for acetate yarn has an acetyl content of about 39.5 per cent and has a degree of polymerization of about 400. Material of this composition is soluble in acetone, and spinning dopes of about 25 per cent solids concentration can easily be prepared. Materials having a 39–41 per cent acetyl content can be made into plastics by compounding the cellulose acetate with plasticizers such as diethyl phthalate. Cellulose triacetate (43.0–44.8 per cent acetyl content) is finding increased commercial use. By coating from appropriate solvents, a film base of greatly improved physical properties has been produced. Triacetate yarns are now in commercial production.

Other cellulose esters which are made commercially are cellulose acetate propionate, cellulose propionate, and cellulose acetate butyrate. These materials are made by a process generally similar to the solution process for cellulose acetate except that propionic anhydride and acid or butyric anhydride and acid are substituted for part or all of the acetic anhydride and acid. In general, milder esterification conditions and more effective activation are required. The ratio of the combined butyryl or propionyl to combined acetyl is a function of the relative molar quantities of the components of the acetylation mixture in either acid or anhydride form.

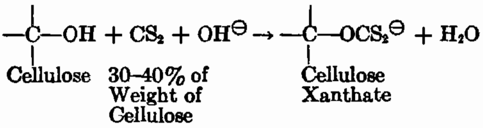
Xanthation of Cellulose

By M. T. O'Shaughnessy[1]

The reaction of an alkali cellulose with carbon disulfide to form cellulose xanthate (the cellulose monoester of unstable dithiocarbonic acid, H_2COS_2) forms the basis of the viscose process industry, by which of the order of 2 billion lb of wood and cotton cellulose is converted to rayon fibers and cellophane film annually.

Chemically, the reaction is a heterogeneous esterification of the hydroxyl groups of an alkali cellulose by carbon disulfide in vapor form, at approximately 30°C. The alkali cellulose is a semidry material which consists of approximately 32 per cent cellulose (of degree of polymerization 350–500) and 15 per cent sodium hydroxide and water and has been shredded into a fluffy mass of low bulk density. Previous steeping in 17–19 per cent sodium hydroxide has swollen the cellulose structure greatly and converted the remaining cellulose crystallites from the native lattice to the sodium cellulose I lattice, but the native fibrous structure remains largely intact. It is the task of the xanthation operator to effect a sufficiently uniform esterification of cellulose hydroxyls throughout the structure so that the resulting xanthate will dissolve smoothly in dilute alkali to form a viscose spinning solution of good filterability.

The xanthation reaction may be formulated:



$$\underset{\text{Cellulose}}{-\overset{|}{\underset{|}{C}}-OH} + \underset{\substack{\text{30–40\% of}\\ \text{Weight of}\\ \text{Cellulose}}}{CS_2} + OH^{\ominus} \rightarrow \underset{\substack{\text{Cellulose}\\ \text{Xanthate}}}{-\overset{|}{\underset{|}{C}}-OCS_2^{\ominus}} + H_2O$$

In practice, a degree of substitution of 0.5–0.6 xanthate groups per glucose unit is sufficient to yield a soluble xanthate. Hydrolysis of carbon disulfide by alkali is an unavoidable side reaction which consumes 20–30 per cent of the carbon disulfide charged.

$$3CS_2 + 6OH^{\ominus} \rightarrow 2CS_3^{\ominus} + CO_3^{\ominus} + 3H_2O$$

The finished xanthate, colored a strong red-orange by the trithiocarbonate by-product, is dissolved in dilute caustic to form viscose (typically, 6–9 per cent cellulose and 5–8 per cent sodium hydroxide plus by-products of carbon disulfide hydrolysis, of viscosity 30–50 poises at 20°C). Viscose, in turn, yields regenerated cellulose fibers or film when extruded into an acid coagulating and regenerating bath. The instability of the xanthate half-ester under acid conditions makes rapid regeneration possible.

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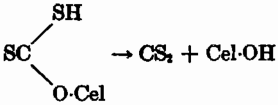
[1] American Viscose Corporation.



$$SC(SH)(O{\cdot}Cel) \rightarrow CS_2 + Cel{\cdot}OH$$

Technically, xanthation is carried out in batches in slowly rotating jacketed hexagonal or round "barattes" or "churns," fitted for evacuation and subsequent introduction of the carbon disulfide charge as a fine spray. The batches contain several hundred pounds of cellulose and tend to be larger in more recent equipment. Of all the steps in the viscose process, xanthation has been the least amenable to continuous operation, but it is likely that this obstacle will be overcome in the future and the entire viscose process embodied in integrated continuous equipment.

Manufacture of Glyceryl Trinitrate (Nitroglycerine)

Glycerol is a sirupy liquid at ordinary temperatures but freezes when exposed for a long time to temperatures below 10°C. Glycerol produced for the manufacture of glyceryl trinitrate, $C_3H_5(O{\cdot}NO_2)_3$, generally contains not less than 98.72 per cent glycerol (sp gr, 1.2620 at 15.6°C/15.6°C).

Since the freezing point of glyceryl trinitrate is about 13.3°C (56°F) and many commercial explosives are required for use in cold weather, the freezing point of nitroglycerine is lowered by adding varying percentages of ethylene glycol to the glycerol before nitration. Commercial ethylene glycol for nitration should contain not less than 99 per cent ethylene glycol. The specific gravity should be 1.116–1.119 at 15.6°C/15.6°C. Ordinary cane sugar (sucrose, $C_{12}H_{22}O_{11}$) also may be dissolved in dynamite glycerol and nitrated satisfactorily. Therefore, the nitrated product prepared for use in commercial explosives may be glyceryl trinitrate or a mixture of this ester with varying percentages of either one or both of ethylene dinitrate and sucrose octanitrate.

The process of making nitroglycerine consists of adding glycerol slowly to a suitable charge of mixed nitric and sulfuric acids to form nitroglycerine and spent acid, separating nitroglycerine from the spent acid, and neutralizing the acids remaining in the nitroglycerine by means of an alkali to give a neutral and stable nitroglycerine.

Calculations show that 100 lb of pure glycerol should produce 246.6 lb of glyceryl trinitrate and should require 205.3 lb of nitric acid. In practice, an excess of 10–15 per cent of nitric acid is provided in the mixed acid and is recovered from the spent acid (see Chap. 4, Nitration).

In the average practice in the United States, the yield of nitroglycerine is 96–97 per cent of the theoretical amount, while approximately 3 per cent is lost by solution in the spent acid. Small amounts are also lost by solution in the wash waters.

The manufacture of glyceryl trinitrate and similar esters is an extremely hazardous operation unless conducted under suitable conditions and in properly designed equipment. It should never be undertaken, even on a small scale, by anyone who is not fully informed and not protected by approved safety devices.

The Biazzi Process. For many years, the process for preparing nitroglycerine has been carried out in small batch operations, and the procedure has varied only slightly. In recent years, a modern continuous process, developed by Mario Biazzi of Switzerland, has been gradually replacing the older manufacturing methods. The apparatus (Fig. 12-12) consists of a nitrator, a separator, and three mechanically stirred washers. The entire nitrating unit is fabricated of polished stainless steel, which prevents the accumulation of pockets of nitroglycerine.

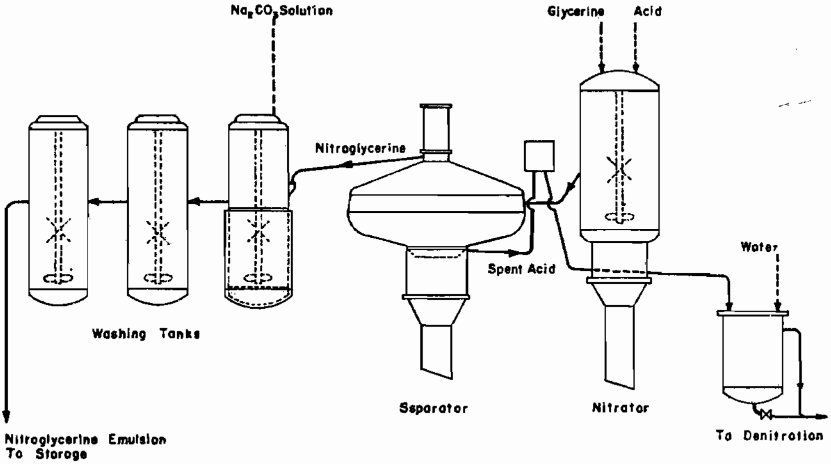


FIG. 12-12. Flow diagram for Biazzi nitroglycerine plant.

The nitrator (see Fig. 4-10) is cooled by a sealed spiral system of coils in which sodium nitrate brine at −5°C is circulated during nitration to maintain a reaction temperature of 10–15°C. Agitation is provided by a high-speed stirrer, which causes the emulsion to circulate around the cooling coils before it flows off continuously through an overflow to the separator.

A metered stream of glycerol and mixed acid (45 per cent nitric acid and 55 per cent sulfuric acid) is fed in at the top of the nitrator. After circulating about the cooling coils, the emulsion of nitroglycerine and spent acid which is formed in the reaction enters the circular separator tangentially, imparting a rotating movement to the contents. This movement helps to accelerate the separation of the nitroglycerine from the spent acid. Sight glasses in the separating vessel permit the separating process to be observed.

The separated nitroglycerine flows off continuously from the separator into the first of three wash vessels which are agitated by high-speed stirrers. In these vessels, a fine emulsion of the nitroglycerine and an equal volume of 12 per cent sodium carbonate solution is formed by the action of the stirrers and specially designed baffles. The emulsion flows through the three washers to the final storage house. The three vessels provide adequate contact time between the sodium carbonate solution and the acidic nitroglycerine to ensure complete neutralization.

The whole system can be controlled and observed at a control center removed beyond a protective barrier about the nitration room. Free nitroglycerine occurs only in the separator, and of the 1,350 lb of nitroglycerine in the nitrating room (in a unit having an output of 2,500 lb per hr), only 125 lb occurs free, the remainder being in the comparatively safe emulsions.

The Biazzi process initially produces nitroglycerine of quality suitable for use in dynamites. If the product is to be used to prepare smokeless powder, higher-purity product is required and additional washing and separating vessels are provided. At the end of a run the apparatus is shut down: (1) the glycerine feed is stopped; (2) the mixed-acid feed is stopped; (3) the nitrator stirrer is stopped; (4) spent acid from an overhead tank is then admitted to the bottom of the nitrator, displacing nitroglycerine upward until it has all been transferred to the separator; (5) the spent acid overflow line from the separator is then raised until all the nitroglycerine in the separator has been displaced to the first washer; (6) the washers are emptied in sequence after the sodium carbonate solution flow is stopped. Agitation is then stopped, all nitroglycerine and sodium carbonate solutions flowing to the storehouse by gravity. When shutting down overnight, spent acid is used to fill the nitrator and separator partly and facilitates start-up the following day. For more prolonged shut down, the spent acid is withdrawn through the diluter for recovery.

Klassen and Humphreys[1] have described the Biazzi installation at the

TABLE 12-8. COMPARISON OF BIAZZI AND BATCH NITRATORS

(Output 2,500 lb. Nitroglycerine per Hour)

	Biazzi	Batch
Nitrator capacity, U.S. gal	32	810
Total cooling surface, sq ft	122	258
Unit cooling surface, sq ft/gal	3.81	0.32
Time in nitrator, min	4.2	50
Heat transfer, Btu/(sq ft) (hr) (°F)	150	69
Brine inlet temperature, °F	28	−13 to −3
Nitroglycerine in nitrator (at 4.7:1 acid ratio), lb	170	3,500

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[1] KLASSEN and HUMPHREYS, *Chem. Eng. Progr.*, **49**, 641 (1953).

Calgary plant of Canadian Industries Limited. They give the interesting comparisons shown in Table 12-8 for the batch and continuous processes. They also compare raw-material usage for the batch and Biazzi process, as shown in Table 12-9.

TABLE 12-9. RAW MATERIALS AND LABOR REQUIRED BY BIAZZI AND BATCH PROCESSES

(Per 100 Lb Dry Nitroglycerine)

	Biazzi	Batch
Glycerine (50% ethylene glycol), lb	42.8	42.8
Sulfuric acid, †lb	101	99
Nitric Acid, †lb	104	99
Sodium carbonate, lb	8.0	1.7
Operating labor, man-hours	0.09	0.18
Maintenance labor, man-hours	0.04	0.08

† Gross input as 100 per cent acid. No allowance for recovery from spent acid.

CHAPTER 13

HYDROLYSIS

By William F. Hamner and Stewart J. Lloyd

I. DEFINITION AND SCOPE

The term *hydrolysis* is applied to reactions of both organic and inorganic chemistry wherein water effects a double decomposition with another compound, hydrogen going to one component, hydroxyl to the other:

$$XY + H_2O \rightarrow HY + XOH$$
$$KCN + H_2O \rightarrow HCN + KOH$$
$$C_5H_{11}Cl + H_2O \rightarrow HCl + C_5H_{11}OH$$

For inorganic chemistry, hydrolysis is usually the reverse of neutralization, but in organic chemistry its scope is broader. Here it includes, among other things, the inversion of sugars, the breaking down of proteins, the saponification of fats and other esters, and the final step in the Grignard reaction, all of which can be carried on with water alone, albeit slowly and incompletely. For convenience, the meaning of the term has been extended to cover also the numerous cases in which an alkali is added to the water and in which the alkali salt of an acid is usually one of the final products:

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Even more common is the application of the term to reactions in which an acid is added to the water in large or small amounts. This addition, like that of alkali, invariably hastens the hydrolysis even if it does not initiate it. The saccharification of cellulose, wherein glucose is produced as an intermediate product in the making of alcohol from wood, and the enormous production of glucose from starch fall in this category. Accelerating agents other than acid and alkali are known but, with the single exception of enzymes, are not important. The enzymes (organic catalysts) are of surpassing importance in vital processes, both animal and plant, especially in preparing food for use in the body, and many of the reactions catalyzed by them are hydrolytic.

The use of alkali in aqueous solution leads naturally to another type of hydrolytic reaction, namely, *alkali fusion*, wherein the proportion of alkali is greatly increased and that of water correspondingly reduced, for example:

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

followed by

$$2C_6H_5ONa + H_2SO_4 \rightarrow 2C_6H_5OH + Na_2SO_4$$

Quite a number of important preparations, such as that of β-naphthol, fall under this heading and may conveniently be classed as cases of hydrolysis, even though oxidation and reduction may be involved[1] and water plays but a minor part.

The line between hydrolysis and hydration is not very sharply drawn. The reaction

$$BaCl_2 + 2H_2O \rightarrow BaCl_2 \cdot 2H_2O$$

is surely hydration, whereas the saponification of a nitrile

$$C_2H_5CN + H_2O \rightarrow C_2H_5CONH_2$$

or the conversion of starch into glucose, whether wisely or not, has always been regarded as hydrolysis. Because of this relationship some interesting and industrially important cases of hydration involving olefins and acetylene are included, regardless of consistency.

We may recognize, then, five types of hydrolysis:

1. Pure hydrolysis where water alone is used.
2. Hydrolysis with aqueous acid, dilute or concentrated.
3. Hydrolysis with aqueous alkali, dilute or concentrated.
4. Alkali fusion, with little or no water but at high temperatures.
5. Hydrolysis with enzymes as catalysts.

Still another classification would be to divide all cases of hydrolysis into

1. Those taking place in the liquid phase or phases.
2. Those taking place in the vapor phase.

Class 1 contains most of the commercial operations, but vapor-phase reactions are becoming increasingly important. The passage of chlorobenzene vapor and steam at an elevated temperature over a solid catalyst to produce phenol and hydrochloric acid is an example of the latter type, as is the direct hydration of ethylene to produce ethyl alcohol.

In this chapter, the subject matter will be presented as follows:

1. A brief review of the chief hydrolyzing agents.
2. A list of the materials susceptible to hydrolysis.
3. A discussion of the kinetics, thermodynamics, and mechanism of hydrolysis.
4. Equipment, materials of construction, etc., for hydrolysis.
5. Technical operations involving hydrolysis.

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[1] FRY and BUTZ, *Rec. trav. chim.*, **52**, 129–138 (1933).

II. HYDROLYZING AGENTS

Although the word hydrolysis means decomposition by water, cases in which water unaided brings about *effective* hydrolysis are rare, and high temperatures and pressures are usually necessary even then. For complete and speedy reaction, an accelerating agent of some kind is nearly always indispensable, whatever the mechanism of its reaction may be. The most important of these are alkalies, acids, and hydrolyzing enzymes, although ion-exchange resins[1] have also been used. A succinct survey of the use and peculiarities of these three important agents, preceded by a list of cases in which water alone may be used, is given next.

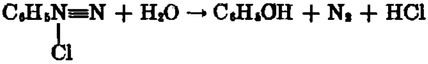
Water. The Grignard reagent, so useful in synthesis, is hydrolyzed quickly and completely by water, as are the less manageable zinc alkyls and other organometallic compounds.

The acid anhydrides, lactones, lactides, and other internal anhydrides such as ethylene oxide are readily hydrolyzed by water alone, acetic anhydride reacting much more rapidly than either benzoic or phthalic. Mixed anhydrides, among which, for convenience, are included the acid halides, react with vigor, especially acetyl chloride, which is more reactive than acetic anhydride itself. In general, the stronger the two acids in these mixed anhydrides, the more vigorous the hydrolysis; e.g., acetyl chloride is more readily hydrolyzed than butyryl bromide. Benzoyl chloride, however, reacts with less readiness than acetyl chloride, despite the greater strength (dissociation) of benzoic acid. This is probably due to the lower solubility of benzoyl chloride in water.

Alkyl halides of complex composition react with water alone, though the simple halides like ethyl chloride are but slightly affected. Mustard gas, for example, probably owes some of its effect to the reaction

$$ClH_4C_2—S—C_2H_4Cl + 2H_2O \rightarrow HOH_4C_2—S—C_2H_4OH + 2HCl$$

which takes place fairly rapidly. Diazonium salts when heated with water hydrolyze completely:



$$C_6H_5\underset{\displaystyle|\atop \displaystyle Cl}{N}{\equiv}N + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

Phenol can thus be made, though not economically, from aniline. The alkyl sulfates, e.g., ethyl hydrogen sulfate, hydrolyze when heated with water. The sodium salt of acetoacetic ester is completely hydrolyzed by water, as are the metallic alcoholates and a few other unimportant substances. A slight degree of hydrolysis seems to occur with numerous materials—esters, proteins, carbohydrates, etc.—especially upon boiling, but it should be emphasized again that water by itself is able to bring about

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[1] HELFERRICH, *Angew. Chem.*, **66**, 241–249 (1954).

complete and rapid hydrolysis of only very few substances. For all others, the intervention of a third reactant of some kind or other is required.

The use of steam instead of liquid water has brought results in a few cases. Benzenesulfonic acid with steam yields benzene and sulfuric acid

$$C_6H_5SO_3H + H_2O \text{ (steam)} \rightarrow C_6H_6 + H_2SO_4$$

and similarly α-naphthalenesulfonic acid hydrolyzes to naphthalene. Steam and chlorobenzene passed through porous silica at 575°C give a 95 per cent yield of phenol, while similar results but with smaller yields have been obtained with other aryl and alkyl halides. The Twitchell and the continuous processes of making fatty acids from fats might almost be included, though both use a small amount of catalyst.

Acid Hydrolysis. In 1811, Kirchhoff observed that starch was transformed by aqueous mineral acids into glucose and showed that no acid was used up in the process. Braconnot, in 1819, hydrolyzed linen (cellulose) with strong sulfuric acid, obtaining a fermentable sugar. This use of acid in hydrolysis was rapidly extended to other classes of organic materials—the esters, sugars, amides, etc.—and it was found that, wherever water brought about hydrolysis, acid accelerated the reaction. In addition, the latter seemed in many cases to initiate reaction where water alone failed. The acid hydrolysis of acetate esters has come to be a sort of proving ground for theories of catalysis. It is customary to attribute the effect of acid to the hydrogen-ion content, and with dilute acid in many reactions, there is at least a rough proportionality between the velocity of reaction and the hydrogen-ion concentration. Like many other generalizations in chemistry, this relation is more honored in the breach than the observance, and with concentrated acids, it does not hold at all. The undissociated acid and the negative radical have both been called upon from time to time to account for certain anomalous results.

Hydrochloric and sulfuric acids are naturally the most commonly used, though many others have been explored. Formic and trichloroacetic appear to be lower in activity than would be expected, whereas oxalic and benzenesulfonic are more active than sulfuric. Concentrations from very high to very low are used in both laboratory and commercial practice.

Sulfuric acid is particularly useful because it forms, with many types of organic substances, intermediate compounds that themselves readily undergo hydrolysis. This is exhibited in the acid process of fat splitting to make fatty acids, in making alcohol from ethylene, and probably also in the hydration of acetylene to make aldehyde. In all these, sulfuric acid exhibits a specific action, distinct from its hydrogen-ion concentration, and cannot be replaced by other acids.

The preparation of individual amino acids by the hydrolysis of proteins is generally very difficult because these natural materials are composed of some 20 amino acids having similar chemical properties. Generally, no one amino acid constitutes more than 10–20 per cent of the protein. Because of this inherent difficulty, the industrial production of amino acids from casein and soybean proteins awaits further progress in current research.

One protein that is used in multi-million-pound quantities annually is wheat gluten—which is valued for its relatively high (35–40 per cent) content of glutamic acid, $HOOC(CH_2)_2CH(NH_2)COOH$. Monosodium glutamate is a condiment that is being used in increasing quantities for imparting a meatlike flavor to soups and other foodstuffs. The usual procedure for making monosodium glutamate involves hydrolysis of the gluten with a constant-boiling 20 per cent hydrochloric acid solution; removal of excess HCl by distillation; and filtration from humin followed by successive crystallizations of glutamic acid hydrochloride, glutamic acid, and monosodium glutamate in the presence of decolorizing carbon.[1]

Although acid and alkali may frequently be used interchangeably on the same materials to give essentially the same products, this is not invariably true. The action of acid on acetoacetic ester and its derivatives leads to acetone, carbonic acid, and alcohol and its related products, while alkali on the same ester produces acetic acid and alcohol.

Alkali Hydrolysis. We may distinguish three different cases of hydrolysis with alkali:

1. The use of low concentrations of alkali in the hydrolysis of esters and similar materials: Here the hydroxyl ion is supposed to catalyze the reaction as the hydrogen ion does in catalysis by dilute acid. Since one of the products of reaction is usually an acid that reacts immediately with the hydroxyl ion, this case is of significance only in theoretical studies, where an instantaneous value of a reaction velocity is desired.

2. The use of sufficient caustic under pressure and in high concentrations to unite with all the acid produced:

$$C_6H_5Cl + NaOH\ aq. \rightarrow C_6H_5OH + NaCl + H_2O$$

sometimes followed by

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

A variant of this is the passage of the vapors of chlorinated hydrocarbons mixed with steam over solid alkaline materials, such as lime, yielding alcohols.

$$2CH_3Cl + Ca(OH)_2 \xrightarrow{\text{steam}} 2CH_3OH + CaCl_2$$

3. The fusion of organic materials with caustic soda or potash: This develops naturally from case 2 by decreasing the ratio of water. The

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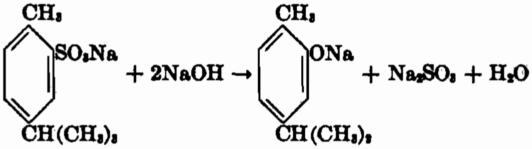
[1] OLCOTT, *Food Inds.*, **16**, 541, 576 (1944).

formation of carvacrol from sodium *p*-cymenesulfonate is an example:



with, of course, the subsequent acidulation of the sodium salt.

This alkali fusion process is limited essentially to sulfonic acids, though the elimination of carbon dioxide is sometimes accomplished in this way.[1] Chlorinated and nitrated compounds do not seem to have been successfully subjected to this mode of treatment.

Alkali is used only to a limited extent in the hydrolysis of carbohydrates. Cellulose is rather resistant to alkali and, when attacked, is broken down but not distinctly hydrolyzed. The carbohydrates in corn cobs undergo deep-seated changes when heated at 240°C with a concentrated caustic solution, oxalic and acetic acids being the principal products. When invert sugar is treated with two molar equivalents of sodium hydroxide—as a 50 per cent solution—lactic acid is obtained.[2]

Caustic soda is the base most commonly used, but the alkali carbonates and bicarbonates as well as the alkaline-earth hydroxides all find occasional application. Potassium compounds show no advantage over the cheaper sodium materials, except that potassium hydroxide in some alkaline fusions permits the use of a lower temperature. Ammonium hydroxide and ammonium salts are rarely used. Chloroform has occasionally been used as a solvent.

Compression of solid catalysts like silica gel used for hydrolysis reactions has been studied in Russia, the results showing that in the particular case in question the improvement in yield passed through a maximum with increasing pressure.[3]

Enzymatic Hydrolysis. Comparatively few large-scale operations depend upon enzymes for hydrolysis, though one or two enzymes (urease) are used for analytical purposes. Molasses is converted by invertase in the manufacture of industrial alcohol, and, of course, the whole brewing industry depends upon the complex hydrolysis of starch into maltose and glucose by the amylases. Despite its occasional industrial application, enzymatic hydrolysis is, however, primarily the concern of the biochemist.[4]

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[1] PHILLIPS, *Ind. Eng. Chem.*, **13**, 759 (1921).

[2] Lock, U.S. 2,382,889 (1945).

[3] FREIDLIN, VERESCHAGIN, and NUMANOV, *Doklady Akad. Nauk S.S.S.R*, **88**, 1011–1014 (1953).

[4] WALDSCHMIDT-LEITZ, "Enzyme Actions and Properties," trans. and extended by R. P. Walton, John Wiley & Sons, Inc., New York, 1929; GORTNER, "Outlines of Biochemistry," pp. 714–716, John Wiley & Sons, Inc., New York, 1929.

III. MATERIALS SUSCEPTIBLE TO HYDROLYSIS

There do not appear to be any general rules or far-reaching generalizations that will enable us to predict the behavior of organic materials toward hydrolyzing agents. For this reason, it is necessary to review one by one the chief types of compounds and to describe explicitly their behavior.

Hydrocarbons. Saturated aliphatic hydrocarbons apparently do not suffer hydrolysis directly. There is no record of the reaction

$$C_nH_{2n+2} + H_2O \rightarrow C_nH_{2n+1}OH + H_2$$

taking place to the slightest degree, even with caustic or acid or enzymes or at high temperatures and pressures or any combination of these, nor has the reverse reaction been recorded.

With unsaturated hydrocarbons, the case is different. The reaction

$$C_nH_{2n} + H_2O \rightarrow C_nH_{2n+1}OH$$

has been effected on a large scale with ethylene, through the formation of an intermediate compound with strong sulfuric acid; even less difficulty is experienced with the homologues (propylene, butylene, etc.). The *direct* addition of water vapor in the presence of a catalyst has also been successfully developed. Both processes are described in the technical section of this chapter. The reverse reaction whereby ethylene is made from alcohol vapor passed over a solid catalyst, such as alumina, is well known.

The addition of water to acetylene

$$C_2H_2 + H_2O \rightarrow CH_3CHO$$

whereby acetaldehyde and ultimately acetic acid are produced has long been recognized and is today practiced on a large scale. Sulfuric acid containing either dissolved mercury sulfate or suspended mercuric oxide serves as the hydration catalyst.

This addition of water to the olefins and acetylene just mentioned takes place in the liquid phase. Benzene vapor when passed with steam through a hot quartz tube (650°C) gives rise to detectable amounts of phenol:[1]

$$C_6H_6 + \underset{\text{Steam}}{H_2O} \rightarrow C_6H_5OH + H_2$$

This result has been confirmed by Lloyd, who obtained a conversion into phenol of 0.3 per cent of the benzene passed through the tube.[2] Various solid catalysts such as chromium oxide and zinc ferrite had little effect on the yield.

Carbohydrates. Cellulose is hydrolyzed to glucose by acids and to cellobiose by its own specific enzyme cellulase. Alkali is not effective.

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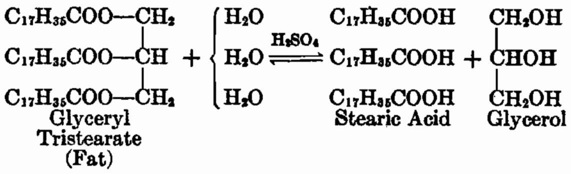
[1] FISCHER, *Ges. Abhandl. Kenntnis Kohle*, **5**, 417 (1920).

[2] LLOYD, unpublished research.

The hydrolysis of wood is an enormous potential source of foodstuff. In a percolation process,[1] wood chips are hydrolyzed to a high-glucose feed by the use of 0.5 per cent sulfuric acid. A modified Rheinau process obtains an 85 per cent of theoretical yield of dextrose from wood wastes, using 41 per cent hydrochloric acid at 21°C (70°F).[2] Furfural, acetic acid, levulinic acid, and formic acid may also be obtained from wood hydrolysis.[3] The 12-carbon sugars—sucrose, maltose, etc.—yield monosaccharides on hydrolysis with enzyme or dilute acid, but alkali brings about other changes in them. The pressure hydrolysis of sucrose with hydrated lime gives encouraging (70 per cent) yields of lactic acid. Enzymes and dilute acids hydrolyze starch into maltose and glucose, whereas inulin yields only fructose by this treatment. Other carbohydrates, such as pectins, xylan, and araban, suffer corresponding changes with acids or enzymes. It should be emphasized that alkalies are not, as a rule, useful with this class of substances.

Esters. Organic esters of all kinds, including the esters of carbohydrates, are quite subject to hydrolysis with acids, bases, and, in many cases, enzymes. In this connection, the term *saponification* is commonly used instead of hydrolysis. The most important example is that of the saponification of fats and oils to make glycerol and either soap or fatty acids. The decomposition of ethyl and methyl acetates by water plus a catalyst has probably received more attention than any other case of hydrolysis by reason of its bearing on the general subject of catalysis. Hydrolysis of esters is reversible, unlike that of the carbohydrates, so that the equilibrium point may be approached from both sides. The following equations represent typical cases of ester hydrolysis:

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{HCl} CH_3COOH + C_2H_5OH$$



$$\begin{array}{l} C_{17}H_{35}COO-CH_2 \\ \qquad\qquad\quad | \\ C_{17}H_{35}COO-CH \\ \qquad\qquad\quad | \\ C_{17}H_{35}COO-CH_2 \end{array} + \left\{\begin{array}{l} H_2O \\ \\ H_2O \\ \\ H_2O \end{array}\right. \xrightleftharpoons{H_2SO_4} \begin{array}{l} C_{17}H_{35}COOH \\ \\ C_{17}H_{35}COOH \\ \\ C_{17}H_{35}COOH \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

The esters of inorganic acids, ethyl and methyl sulfates, ethyl hydrogen sulfate, the alkyl phosphates, glyceryl nitrate, etc., may all be hydrolyzed, generally speaking, by acids and bases.

Ethers (Organic Oxides). Ether may be hydrolyzed to ethyl alcohol in the presence of a dilute aqueous acidic catalyst, such as 10 per cent sulfuric

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[1] GILBERT, HOBBS, and LEVINE, *Ind. Eng. Chem.*, **44**, 1712–1720 (1952); LOCKE and JOHNSON, *ibid.*, **46**, 475–482 (1954).

[2] *Chem. Eng.*, **61** (2), 138–142 (1954).

[3] WILEY, HARRIS, SAEMAN, and LOCKE, *Ind. Eng. Chem.*, **47**, 1397–1405 (1955).

acid, at a temperature of 272°C, and under pressure of over 225 psi.[1] A 46 per cent conversion of ether to alcohol has been obtained at 275–300°C and 120 atm pressure with aluminum oxide containing 5 per cent nickel oxide.[2] Secondary alcohols are more readily formed from ethers than primary. Ethylene oxide and trimethylene oxide hydrolyze fairly readily with water to form ethylene and propylene glycols, respectively. The higher polymethylene ethers are less reactive with water; the penta- and hexamethylene ethers have exceedingly stable ring systems, as is to be expected from the Baeyer strain theory. The addition of water to diphenyl oxide has been studied in connection with the production of phenol by the hydrolysis of chlorobenzene and is favored by a large excess of caustic alkali:

$$(C_6H_5)_2O + H_2O \xrightarrow{NaOH} 2C_6H_5OH$$

Hydrolysis of phenol and naphthol ethers with concentrated hydrochloric acids shows that meta derivatives decompose the least and para derivatives the most and that acidic groups increase the stability.[3]

Organic Halides. These useful compounds differ markedly in their behavior toward hydrolyzing agents, the acid halides, like acetyl chloride, reacting readily with water alone, whereas varying degrees of resistance are shown by the alkyl and aryl compounds. Alcoholic solutions of caustic potash convert alkyl chlorides into the corresponding alcohols.[4]

$$C_2H_5Cl + KOH\ (alcohol) \rightarrow C_2H_5OH + KCl$$

The hydrolysis of the amyl chlorides with sodium oleate and caustic soda solution to form the corresponding alcohols is the basis of a flourishing industry and is discussed on another page. The ease of removal of halogen increases markedly from chlorine to iodine and with increasing complexity of the compound. Ethylene chlorohydrin, for example, is easily and smoothly hydrolyzed to ethylene glycol by aqueous sodium bicarbonate:

$$CH_2OHCH_2Cl + NaHCO_3\ aq. \rightarrow CH_2OHCH_2OH + CO_2 + NaCl$$

A differentiation should be made between the hydrolysis of simple halogen compounds and chlorohydrins, since a difference in reaction mechanism, and in many cases a difference in order of magnitude of yield, is involved. Ethylene oxide is considered to be an intermediate between ethylene chlorohydrin and ethylene glycol.[5] The aromatic halides are much more difficult to hydrolyze. Acids are without effect upon them, save in the

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[1] U.S. 2,045,785 (1936).

[2] Balandin, Shuikin, Nesvizhskii, and Kozminskaya, *Ber. deut. chem. Ges.*, **65B**, 1557–1561 (1932); see also Mason, U.S. 2,519,061 (1950).

[3] Kolhatkar and Ghaswalla, *J. Indian Chem. Soc.*, **8**, 511–516 (1931).

[4] Grant and Hinshelwood, *J. Chem. Soc.*, **1933**, 258.

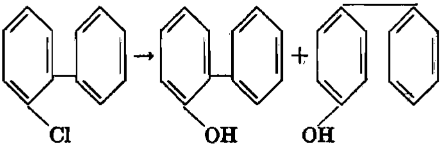
[5] Schrader, "The Glycol Industry," *Z. angew. Chem.*, **42**, 541–546 (1929).

case of meta-chlorinated pyridine, while in the Dow process for making phenol from chlorobenzene a pressure of 4,200 lb and a temperature of 360°C are required to make alkali effective. The presence of small amounts of copper speeds up this last reaction immensely but increases the relative amount of by-products.

$$C_6H_5Cl + 2NaOH\ aq. \xrightarrow{Cu} C_6H_5ONa + NaCl + H_2O$$

Similar results have been reported for naphthol. *p*-Chloronitrobenzene has likewise been commercially converted into *p*-nitrophenol by heating to 160°C with aqueous caustic soda.[1]

It has been found by Britton that when an aryl or alkyl-substituted aromatic halohydrocarbon is hydrolyzed at a relatively high temperature, i.e., 300–400°C, in the absence of copper, there is formed a substituted phenol in which the hydroxyl group is in a position that is ortho or para to the original position of the halogen, together with a certain amount of the expected phenol.[2] For example, both *o*-phenylphenol and *p*-phenylphenol are prepared from *o*-chlorobiphenyl.



The hydroxy compounds are not convertible into isomers by treatment with alkalies in like manner. Similar results were obtained in the production of naphthols from bromo- and chloronaphthalenes.[3]

Hydrolysis in the "silicones" is usually just a special case of the reaction with organic halides. The most important reaction is the preparation of siloxanes by the hydrolysis of chlorosilanes and the subsequent condensation to form the commercially important polysiloxanes (see Chap. 15). Diethyl silane diol, $(C_2H_5)_2Si(OH)_2$, and the corresponding di-*n*-propyl and di-*n*-butyl diols have been made by hydrolyzing the dichlorosilanes.[4] The trimethyl and triethyl silicon hydroxides have been prepared by the hydrolysis of complex organic silicon compounds containing the aceto and the amino group, respectively.[5]

Nitrogen Compounds. Aliphatic and aromatic amines—ethylamine and aniline—resist hydrolysis even under extreme conditions, though the production of α-naphthol from α-naphthylamine under pressure is recorded.

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[1] *B.I.O.S. Final Rept.* 1153, Item 22 (British Intelligence Objectives Sub-committee).

[2] U.S. 1,996,744 (1935).

[3] U.S. 1,996,745 (1935).

[4] George, Sommer, and Whitmore, *J. Am. Chem. Soc.*, **75**, 1585–1588 (1953).

[5] Shostakovski, Shikhiev, Kochkin, and Belyaev, *J. Gen. Chem.* (*U.S.S.R.*) **24**, 2202–2206 (1954).

1-Naphthol-4-sulfonic acid is produced in a "reverse Bucherer reaction" by the hydrolysis of naphthionic acid with bisulfite. Amides are hydrolyzed to the ammonium salt of the corresponding acid when heated with water, but, in the presence of acids and bases, there is a marked increase in the rate of hydrolysis.

$$CH_3CONH_2 + H_2O \rightarrow (CH_3COOH + NH_3) \rightarrow CH_3COONH_4$$

The hydrolysis of two fairly important nitrogenous sweetening substances —dulcin and saccharin—has been minutely studied by Täufel and associates.[1] Dulcin (*p*-phenetylcarbamide) in strongly acid or alkaline solution is converted to ammonia and *p*-phenetylcarbamic acid, but in boiling water more complicated changes occur. The conclusion is drawn that this material, when used for sweetening purposes, should be added *after* cooking. Saccharin boiled in neutral water does not hydrolyze appreciably but in alkaline media changes to *o*-sulfoamidobenzoic acid, while acid catalysts carry the hydrolysis farther to the ammonium salt. A temperature of 100°C in the foodstuffs to which it is added does not cause appreciable hydrolysis.

Nitriles undergo a fairly complete but peculiar form of hydration when heated with water, especially if alkali or acid be present. Thus, the hydrolysis of ethyl cyanide does *not* proceed as follows:

$$C_2H_5CN + H_2O \rightarrow C_2H_5OH + HCN$$

Instead, the bond between the carbon and nitrogen is broken, and we have

$$C_2H_5CN + 2H_2O \rightarrow C_2H_5COONH_4$$

Benzonitrile acts in a similar way to form benzoic acid but requires sulfuric acid in the reacting mixture. Nicotinic acid amide (nicotinamide) has been prepared by the mild hydrolysis of 3-cyanopyridine,[2] and acrylamide by the partial hydrolysis of acrylonitrile.[3] Acrylonitrile may also be hydrolyzed to acrylic acid with mineral acids or with alkalies.[4] Polyacrylonitrile is partially converted to the amide by nitric acid,[5] and the nitrile groups of a number of polymers and copolymers have been hydrolyzed to amide and carboxylic acid groups to produce water-soluble polyelectrolytes.[6] Isocyanides are stable toward alkalies but hydrolyze in the presence of acids to form an acid and an amine:

$$CH_3NC + 2H_2O \rightarrow CH_3NH_2 + HCOOH$$

[1] TÄUFEL, *Z. Elektrochem.*, **34**, 115–127; 281–291 (1928).

[2] U.S. 2,471,518 (1949).

[3] SCHULZ, RENNER, HENGLEIN, and KERN, *Makromol Chem.*, **12**, 20–34 (1954); Weisgerber, U.S. 2,535,245 (1950).

[4] KASZUBA, *J. Am. Chem. Soc.*, **67**, 1227 (1945); Jones, U.S. 2,734,915 (1956).

[5] Polson, U.S. 2,579,451 (1951).

[6] Mowry and Hedrick, U.S. 2,625,471 (1953).

Alkylamines may be produced by the alkaline hydrolysis of the corresponding N-substituted formamide,[1] and amino acids such as alanine and isoleucine may be prepared by the hydrolysis of hydantoins.[2]

Nitro compounds, such as nitrobenzene and nitromethane, are not readily hydrolyzed. Indeed, nitroethane may be distinguished in this way from ethyl nitrite, which hydrolyzes readily with caustic alkali:

$$\underset{\text{Ethyl Nitrite}}{C_2H_5ONO} + NaOH \rightarrow C_2H_5OH + NaNO_2$$

Sulfonic Acids. The sulfonic acids require rather drastic methods of hydrolysis. The aliphatic members of the group do not hydrolyze; e.g., ethylsulfonic acid, $C_2H_5SO_3H$, may be boiled with caustic soda solution or with concentrated acids without decomposition, whereas the ester ethyl hydrogen sulfate hydrolyzes readily:

$$C_2H_5OSO_3H + H_2O \rightarrow C_2H_5OH + H_2SO_4$$

Benzenesulfonic acid, when treated with steam under pressure, yields benzene and sulfuric acid:

$$C_6H_5SO_3H + \underset{\text{Steam}}{H_2O} \rightarrow C_6H_6 + H_2SO_4$$

but when fused with caustic soda, sodium phenoxide is the product:

$$C_6H_5SO_3H + 3NaOH \xrightarrow{\text{fusion}} C_6H_5ONa + Na_2SO_3 + 2H_2O$$

The action of steam on α-naphthalenesulfonic acid similarly yields naphthalene. Practically all aromatic sulfonic acids may be hydrolyzed with mineral acids to the parent hydrocarbons, but each sulfonic acid requires a specific minimum temperature. α-Naphthalenesulfonic acid hydrolyzes at a much lower temperature than the beta compound. However, the beta compound with fused caustic acts quite like the corresponding benzenesulfonic acid to give β-naphthol, sodium sulfite, and water. Under certain conditions, steam may replace the more expensive fused caustic alkalies in the hydrolysis of aromatic sulfonates that are volatile with steam:

$$RSO_3M + ROM + H_2O \rightleftharpoons M_2SO_3 + 2ROH$$

IV. KINETICS, THERMODYNAMICS, AND MECHANISM OF HYDROLYSIS

The preceding part of this chapter has dealt with the reagents of hydrolysis and the behavior of the organic materials undergoing the reaction. A study of the equilibrium state and the rate and mechanism of attaining

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[1] Smolin, *J. Org. Chem.*, **20**, 295–301 (1955); Thurston, U.S. 2,689,868 (1954); Ritter, *J. Am. Chem. Soc.*, **70**, 4048 (1948).

[2] Pfister and Leanza, U.S. 2,658,912 (1953); White, U.S. 2,642,459 (1953); Duschinsky, U.S. 2,593,860 (1952).

that state provides a basis for understanding these hydrolytic processes. Classical thermodynamics furnishes much information about the equilibrium state, under a given set of conditions, but provides little or no information on reaction rates and mechanism. This latter problem is one of chemical kinetics. A study of these two problems separately is desirable to avoid confusion when considering the effect on the reaction of variables such as temperature, pressure, concentrations, and catalysts. A bridge between the problems of equilibrium and kinetics has, however, been established by the application of quantum-statistical methods. All thermodynamic functions may be expressed in quantum-statistical terms, and thus such factors as the equilibrium constant may be calculated from fundamental principles. The theory of absolute reaction rates, where the rate is expressed in terms of an equilibrium between activated complex and reactants, affords a similar means of calculating the reaction velocity.

Thermodynamics of Hydrolytic Reactions

The extent to which a chemical reaction may proceed under a given set of conditions is given by the equilibrium state. The driving force of the reaction is the change in free energy, which is related to the equilibrium constant (K) by

$$\Delta F^\circ = -RT \ln K$$

where superscript ° indicates that all reactants and products are in the standard state. The thermodynamic relation $\Delta F^\circ = \Delta H^\circ - T\,\Delta S^\circ$ relates the change in free energy to the heat of reaction ($-\Delta H^\circ$). ΔS° is the change in entropy accompanying the reaction. If the free energy change is negative the reaction is spontaneous and becomes more favorable with increasing ($-\Delta F^\circ$); on the other hand if the free energy change is positive and greater than 10 kg-cal per mole the reaction is not suitable for practical application.

We need to know the equilibrium constant (or ΔF°), therefore, to ascertain the conditions necessary for a high yield and to avoid wasted efforts on reactions that are thermodynamically impossible. There are several methods for obtaining data from which the equilibrium constant may be calculated. Some of these are illustrated in discussing the thermodynamics of the following hydrolytic reactions.

Hydration of Ethylene.

$$C_2H_4\ (g) + H_2O\ (g) = C_2H_5OH\ (g) \qquad \Delta H_{298} = -11{,}000 \text{ cal per mole}$$

The free energy change accompanying this reaction has been calculated by Aston and coworkers[1] at various temperatures, employing the methods of statistical mechanics. A comparison (Table 13-1) with experimentally

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[1] ASTON, ISSEROW, SZASZ, and KENNEDY, *J. Chem. Phys.*, **12**, 336 (1944); ASTON, *Ind. Eng. Chem.*, **34**, 514 (1942).

TABLE 13-1. FREE ENERGY AND EQUILIBRIUM DATA FOR HYDRATION OF ETHYLENE

Temp	Exptl. $\Delta F°$	log K	Calc. $\Delta F°$	log K
298.2	−1200	0.88	−1705	1.25
351	315	−0.20	−362	0.22
403	1800	−0.98	1457	−0.79
600	7460	−2.72	7460	−2.72

determined values shows excellent agreement. It is seen that log K and thus $\Delta F°$ become zero at approximately 70°C (experimental) or 90°C (calculated). It should be noted that at temperatures below these values the formation of alcohol is favored ($K > 1$) and above, the dehydration to ethylene ($K < 1$). An estimate of the free energy change can be made from the heat of reaction together with the entropy change. This latter may be taken as 30 cal per deg per mole (e.u.) for each change in number of moles between product and reactant in a gaseous reaction or estimated by the method of Meissner.[1] A value of −30 e.u. for $\Delta S°$ gives a $\Delta F°_{298}$ of −2000 cal per mole, which is in fair agreement with the values above.

Hydrolysis of Alkyl Chlorides.

$$RCl + H_2O = ROH + HCl$$

An estimation of the change in heat content (enthalpy) from bond energies[2] shows this hydrolysis to be endothermic. ΔH is given by summation of energies of bonds broken minus bonds formed.

Bonds broken:	C—Cl	66.5 kg-cal	Bonds formed: C—O	70.0 kg-cal
	H—O	110.2 kg-cal	H—Cl	102.7 kg-cal
		176.7 kg-cal		172.7 kg-cal

ΔH = 4.0 kg-cal per mole

A combination of the two reactions:

$$C_2H_5Cl = C_2H_4 + HCl \qquad \Delta H = 15.3 \text{ kg-cal}$$
$$C_2H_4 + HOH = C_2H_5OH \qquad \Delta H = -11.0 \text{ kg-cal}$$

gives a ΔH of 4.3 kg-cal well in agreement with the above calculation. For the hydrolysis of mixed amyl chlorides to pentasol, high temperatures would be desired. At high temperatures, however, the equilibrium between branched-chain chloride and alkene greatly favors the latter; at moderate temperatures, the primary chlorides hydrolyze very slowly, so that a technical problem is presented. The hydrolysis by aqueous NaOH using sodium oleate as an emulsifying agent makes this reaction possible.

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[1] MEISSNER, *Ind. Eng. Chem.*, **40**, 904 (1948).

[2] PAULING, "The Nature of the Chemical Bond," 2d ed., pp. 53, 131, Cornell University Press, Ithaca, N.Y., 1940.

Hydrolysis of Ethyl Acetate.

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

The equilibrium constant for the reverse, esterification, reaction has been measured by Berthelot and Péan de St. Gilles[1] and found to be 3.96, corresponding to 66.57 per cent esterification. The forward reaction would thus reach equilibrium at 33.43 per cent hydrolysis with K equal to 0.253. The equilibrium position was shown to be independent of the temperature. A calculation of the heat of reaction by the method of bond energies gives a value of zero, since the bonds broken are of the same type as the bonds formed. From the van't Hoff equation (see later section) the condition for a zero temperature coefficient of equilibrium is that ΔH be zero. The heat of reaction for the hydrolysis of ethyl acetate, therefore, is negligible. At a temperature of 60°C and a pressure of 5,000 atm, the equilibrium position remained at approximately 33 per cent hydrolysis.[2] This is to be expected, since an equal number of molecules appears in reactants and products.

A mixture of equivalent amounts of ethyl acetate and steam kept in contact with silica gel gave the following figures:

Temp, °C	*% Hydrolyzed*
150	15.3
200	16.7
250	21.7
300	25.1

This could indicate a slightly endothermic reaction. A small heat of reaction, however, would indicate that the entropy factor ($T\ \Delta S$), although small, plays a part in determining the equilibrium position. A calculation from the free energies of formation of the gases at 25°C gives $\Delta F^\circ = 1.1$ kg-cal per mole for the vapor-phase hydrolysis.

Inversion of Sucrose. Many hydrolytic reactions, including the decomposition of esters, are reversible; but others such as sucrose inversion and protein hydrolysis, though not necessarily complete, have not been reversed. The heat effects of these reactions, however, are important. The inversion of sucrose, for example, is an exothermic reaction with ΔH at 25°C approximately -3.6 kg-cal per mole.[3]

Effect of Temperature and Pressure on Equilibrium. The van't Hoff equation relating the heat of reaction, the equilibrium constant, and the temperature is valid here, as elsewhere:

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[1] Berthelot and Péan de St. Gilles, *Ann. chim. et phys.*, **65**, 385 (1862); **66**, 5 (1862); **68**, 225 (1863).

[2] Newitt, Linstead, Sapiro, and Boorman, *J. Chem. Soc.*, **1937**, 876.

[3] Sturtevant, *J. Am. Chem. Soc.*, **59**, 1528 (1937).

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

where K is the equilibrium constant, ΔH° the heat absorbed, and T the absolute temperature. If the hydrolytic reaction is accompanied by an evolution of heat, it will proceed further at low temperatures, and vice versa.

The standard free-energy change ΔF° and, consequently, the equilibrium constant are independent of the pressure. In reactions involving a change in the number of molecules, however, the equilibrium position is shifted according to the Le Châtelier principle. Therefore, *exact* thermodynamic data on vapor-phase reactions of this type are not necessary since the equilibrium position may be shifted at will with changes of pressure.

Kinetics and Mechanism of Hydrolysis

In commercial processes, whether a reaction goes fast or slow is extremely important, and thus the rate at which a chemical reaction approaches equilibrium is significant. If the reaction is thermodynamically possible but proceeds with a velocity that is not economically practical, some means must be found by which the rate is increased. In addition to the variation of temperature, pressure, and concentration ratios, a catalyst may be employed to bring about the desired results. Although reaction conditions and catalysts are usually determined experimentally, a discussion of typical hydrolytic reactions from the theoretical point of view may throw some light on the mechanism of these reactions and make the approach to future problems less arbitrary.

The data obtained on reaction rates may be interpreted through either the collision theory or the theory of absolute reaction rates. The former places emphasis on the energy of activation as the rate-determining factor. This may be related to the temperature (T) and the rate constant (k) by a modified form of the Arrehenius equation:

$$k = PZe^{-E/RT} \tag{1}$$

where E is the energy of activation, R the gas constant, Z the frequency of collision at unit concentration of reactants, and P a probability factor. This last term accounts for considerable deviation in some cases between theory and experiment. Z may be calculated from kinetic theory. The newer theory,[1] also called transition-state theory, places emphasis on the *free* energy of activation and is concerned with the thermodynamic probability of attaining an "activated complex," or transition state. One form of the rate constant expression is

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[1] GLASSTONE, LAIDLER, and EYRING, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, 1941.

$$k = \frac{k'T}{h} e^{-\Delta F\ddagger/RT} = \frac{k'T}{h} K\ddagger \tag{2}$$

$$k = \frac{k'T}{h} e^{-\Delta H\ddagger/RT} e^{\Delta S\ddagger/R} \tag{3}$$

where $\Delta F^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are the standard free energy, heat content, and entropy of activation; $K^\ddagger$ is the equilibrium constant for the activation; and $k'T/h$ is a universal frequency constant. These quantities may be calculated by the methods of statistical thermodynamics, and replacement by quantum-statistical expressions gives the rate constant in terms of the potential energy of activation and the partition functions of the reactants and the activated complex. A comparison of the two shows that E of Eq. (1) may be related to $\Delta H^\ddagger$ of Eq. (3), and since $k'T/h$ is constant and Z is of the same order for a given series, P is related to the entropy term.

Since the collision theory is the older and simpler, Eq. (1) has been used in the analysis of most of the published results. Table 13-2 lists the values of constants for this equation for some typical hydrolytic reactions.

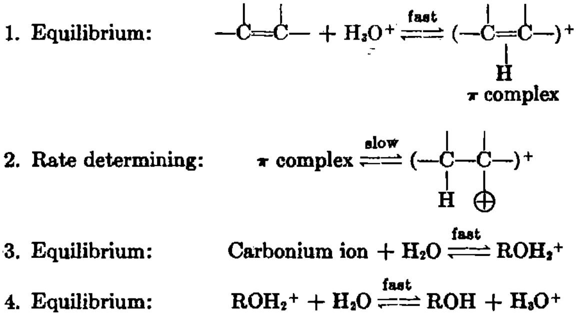
TABLE 13-2. CONSTANTS FOR THE EQUATION, $k = PZe^{-E/RT}$, FOR SOME TYPICAL HYDROLYTIC REACTIONS

Hydrolysis	Condition	Solvent	Temp, °C	k, sec^{-1}	$\log_{10} PZ$	E, kg-cal/mole	Ref.*
Methyl acetate.........	Acid	Aq. acetone	25	5.49×10^{-5}	7.6	16.2	1
	Alkaline	Aq. acetone	25	1.37×10^{-1}	7.6	11.5	1
Ethyl acetate...........	Acid	Aq. acetone	30	4.27×10^{-3}	9.3	16.2	2, 3
	Acid	Aq. acetone	40	10.10×10^{-3}	9.3	16.2	2, 3
	Acid	Alcohol-water	100	4.03×10^{-6}	7.53	16.2	4
	Alkaline	Aq. acetone	20	2.13	7.6	9.8	2, 3
	Alkaline	Aq. acetone	30	3.74	7.6	9.8	2, 3
Ethyl thiolacetate.......	Acid	Aq. acetone	30	1.34×10^{-4}	9.0	17.8	2
	Alkaline	Aq. acetone	30	3.45	10.9	14.4	2
Cellulose acetate........	0.1 N alkali	....	25	0.226	8.04	11.7	5
Ethylene chlorohydrin...	Neutral	Alcohol-water	79	1.27×10^{-8}	8.4	26.2	6
Propylene α-chlorohydrin	NaOH	....	25	0.27	14	19.9	7
Isopropyl chloride.......	....	Aq. ethanol	25	1.9×10^{-9}	8.32	23.2	8
Tertiary butyl chloride..	....	Aq. ethanol	25	9.14×10^{-6}	11.89	23.1	8

* (1) NEWLING and HINSHELWOOD, *J. Chem. Soc.*, **1936,** 1357; (2) SCHAEFGEN, *J. Am. Chem. Soc.*, **70,** 1308 (1948); (3) DAVIES and EVANS, *J. Chem. Soc.*, **1940,** 339; (4) TIMM and HINSHELWOOD, *J. Chem. Soc.*, **1938,** 862; (5) HOWLETT and MARTIN, *J. Textile Inst.*, **38,** T212 (1947); (6) COWAN, MCCABE, and WARNER, *J. Am. Chem. Soc.*, **72,** 1194 (1950); (7) PORRET, *Helv. Chim. Acta*, **30,** 701 (1947); (8) COOPER and HUGHES, *J. Chem. Soc.*, **1937,** 1183.

The order of a reaction and "molecularity" must be included in discussing chemical kinetics. The order of a reaction is determined from the mathematical expression showing the dependence of rate on the concentration of the reactants, and the molecularity by the number of molecules involved in the reaction.

Hydration of Ethylene. Taft and associates[1] have proposed the following mechanism for the hydration of olefins in an aqueous acid medium:



1. Equilibrium: $$-\overset{|}{C}=\overset{|}{C}- + H_3O^+ \xrightleftharpoons{\text{fast}} (-\overset{|}{C}=\underset{\underset{H}{|}}{\overset{|}{C}}-)^+$$ π complex

2. Rate determining: $$\pi \text{ complex} \xrightleftharpoons{\text{slow}} (-\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{\oplus}{|}}{\overset{|}{C}}-)^+$$

3. Equilibrium: $$\text{Carbonium ion} + H_2O \xrightleftharpoons{\text{fast}} ROH_2^+$$

4. Equilibrium: $$ROH_2^+ + H_2O \xrightleftharpoons{\text{fast}} ROH + H_3O^+$$

From the relation between the activity coefficient ratios and the acidity function (H_0), it is concluded that the transition state must be effectively a conjugate acid of the olefin which is not firmly bound to any water molecule. Since the reactants are olefin and hydronium ion, such a transition state can be formed only by the isomerization from one unstable intermediate to another. The unimolecular isomerization of the π complex to the carbonium ion fits the requirements and constitutes the rate-determining step. Water molecules do not enter the transition state, thus the molecularity of the reaction is zero with respect to the solvent water.

Mace and Bonilla[2] have established a rate equation for the direct hydration of ethylene over supported tungsten oxide catalyst which indicates that hydration proceeds by a surface reaction without preferential adsorption of either ethylene or water and without retardation by strong adsorption of ethyl alcohol.

Hydrolysis of Esters. Extensive study of the hydrolysis of esters has shown that the reaction is reversible and is catalyzed by both oxonium (H_3O^+) and hydroxyl (OH^-) ions. The addition of acid speeds up the reaction but scarcely shifts the equilibrium position, whereas the addition of sufficient base not only increases the rate but also causes the reaction to go to completion by neutralization of the acid product.

Ingold[3] has proposed eight possible mechanisms for ester hydrolysis. He denotes these $B_{AC}1$, $B_{AC}2$, $B_{AL}1$, $B_{AL}2$, $A_{AC}1$, $A_{AC}2$, $A_{AL}1$, $A_{AL}2$, where B stands for basic hydrolysis, A for acidic, subscripts AC and AL stand for acyl and alkyl oxygen fission, respectively, and 1 stands for unimolecular and 2 for bimolecular processes. All but $B_{AC}1$ and $A_{AL}2$ have been observed experimentally.

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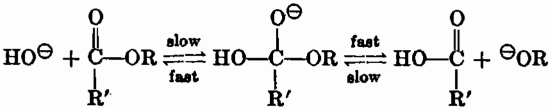
[1] TAFT, PURLEE, RIESZ and DEFAZIO, *J. Am. Chem. Soc.*, **77**, 1584–1587 (1955).

[2] MACE and BONILLA, *Chem. Eng. Progr.*, **50**, 385–395 (1954).

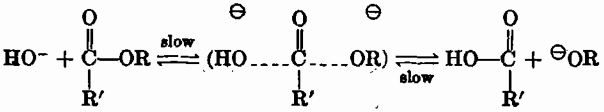
[3] INGOLD, "Structure and Mechanism in Organic Chemistry," pp. 754–782, Cornell University Press, Ithaca, N.Y., 1953.

The most common case of basic hydrolysis follows the $B_{AC}2$ mechanism, which is represented as follows:



$$HO^{\ominus} + \overset{O}{\overset{\|}{\underset{R'}{C}}}\text{—}OR \underset{fast}{\overset{slow}{\rightleftharpoons}} HO\text{—}\overset{O^{\ominus}}{\underset{R'}{C}}\text{—}OR \underset{slow}{\overset{fast}{\rightleftharpoons}} HO\text{—}\overset{O}{\overset{\|}{\underset{R'}{C}}} + {}^{\ominus}OR \qquad (1)$$

or, considering the intermediate to be a transition state of nucleophilic substitution:



$$HO^{-} + \overset{O}{\overset{\|}{\underset{R'}{C}}}\text{—}OR \overset{slow}{\rightleftharpoons} (\overset{\ominus}{HO}\cdots\overset{O}{\overset{\|}{\underset{R'}{C}}}\cdots\overset{\ominus}{OR}) \underset{slow}{\rightleftharpoons} HO\text{—}\overset{O}{\overset{\|}{\underset{R'}{C}}} + {}^{\ominus}OR \qquad (1a)$$

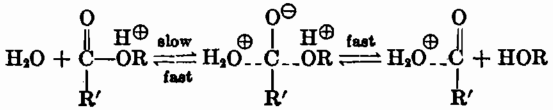
the presence of base drives the reaction to completion:

$$R'COOH + {}^{\ominus}OR \xrightarrow{fast} RCOO^{\ominus} + ROH \qquad (2)$$

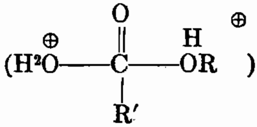
Polanyi and Szabo[1] by using isotopic oxygen in the alkaline hydrolysis of amyl acetate showed that the acyl oxygen bond was broken.

For acid hydrolysis the $A_{AC}1$ and $A_{AC}2$ are typical. The following equations illustrate the $A_{AC}2$ mechanism:

$$R'COOR + H^{\oplus} \overset{fast}{\rightleftharpoons} R'COO\overset{\oplus}{H}R \qquad (3)$$



$$H_2O + \overset{O}{\overset{\|}{\underset{R'}{C}}}\text{—}\overset{H^{\oplus}}{OR} \underset{fast}{\overset{slow}{\rightleftharpoons}} \overset{\oplus}{H_2O}\cdots\overset{O^{\ominus}}{\underset{R'}{C}}\cdots\overset{H^{\oplus}}{OR} \overset{fast}{\rightleftharpoons} \overset{\oplus}{H_2O}\cdots\overset{O}{\overset{\|}{\underset{R'}{C}}} + HOR \qquad (4)$$



or the transition state $(\overset{\oplus}{H^2O}\text{——}\overset{O}{\overset{\|}{\underset{R'}{C}}}\text{——}\overset{H}{OR}\ )^{\oplus}$ may be written for the intermediate

$$R'COOH_2^{\oplus} \underset{fast}{\overset{fast}{\rightleftharpoons}} RCOOH + H^{+} \qquad (5)$$

The kinetics of hydrolysis of benzoate esters labeled in the carbonyl group with O^{18} have been studied by Bender.[2] The exchange observed between carbonyl oxygen of the ester and the solvent indicates that a true intermediate, rather than a transition state, occurs during hydrolysis. Upon partial hydrolysis the remaining ester contains less O^{18} than originally. This is explained by the formation of an intermediate in which the carbonyl oxygen participates:

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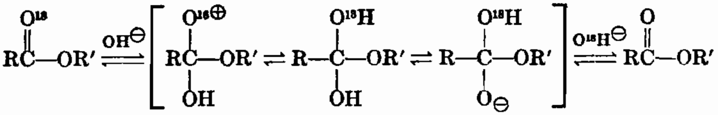
[1] Polanyi and Szabo, *Trans. Faraday Soc.*, **30**, 508 (1934).

[2] Bender, *J. Am. Chem. Soc.*, **73**, 1626–1629 (1951).



$$R\overset{O^{18}}{\overset{\|}{C}}-OR' \xrightleftharpoons{OH^{\ominus}} \left[R\underset{OH}{\underset{|}{\overset{O^{18}\oplus}{\overset{|}{C}}}}-OR' \rightleftharpoons R-\underset{OH}{\underset{|}{\overset{O^{18}H}{\overset{|}{C}}}}-OR' \rightleftharpoons R-\underset{O^{\ominus}}{\underset{|}{\overset{O^{18}H}{\overset{|}{C}}}}-OR' \right] \xrightleftharpoons{O^{18}H^{\ominus}} R\overset{O}{\overset{\|}{C}}-OR'$$

The activation energies for alkaline hydrolysis are usually 5–7 kg-cal lower than corresponding acid hydrolyses.

The hydrolysis of acetal is catalyzed by acids but not by bases, and the rate of reaction is proportional to the hydrogen-ion concentration.

Hydrolysis of Amides. Amides may be hydrolyzed by aqueous acids or alkalies to give the organic acid or salt. The proposed mechanisms for the hydrolysis of amides are similar to those of the esters and generally follow the $B_{AC}2$ or $A_{AC}2$ schemes.

Hydrolysis of Fats and Starches. The acceleration of hydrolysis of fats by alkali under pressure of 100 atm has long been known and practiced. In general, the rate of hydrolysis of the glycerides of stearic, palmitic, etc., acids increases in the order tri-, di-, and monoglyceride.

The hydrolysis of starches seems to provide first-order reactions with the rate varying with kind.[1] The speed approximately doubles for a 5° rise in temperature between 90 and 100°C.[2]

Alkyl Halides. There are two possible mechanisms[3] for the reaction:

$$R-Cl + H_2O \rightarrow ROH + HCl$$

which is assumed to be a nucleophilic substitution of OH^- for Cl^- on the alkyl group.

1. The bimolecular mechanism:

$$HO^- + RCl \rightleftharpoons HO-R-Cl \rightleftharpoons HOR + Cl^-$$

This type is designated S_N2, indicating that it is a bimolecular nucleophilic substitution.

2. The unimolecular mechanism, designated S_N1:

$$RCl = R^+ + Cl^- \text{ (slow)}$$
$$R^+ + OH^- = ROH \text{ (fast)}$$

In the S_N2 type, the repulsion between the attacking nucleophilic reagent (OH^-) and the center of reaction (R—) is important. The ionizability of the C—Cl bond controls the S_N1 mechanism. The hydrolysis of tertiary butyl chloride is a first-order reaction[4] and proceeds rather rapidly. The S_N1 mechanism is applicable in this case.

The resonance and inductive effects present in unsaturated halides,

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[1] Schrenk, Andrews, and King, *Ind. Eng. Chem.*, **39**, 113 (1937).

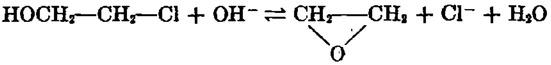
[2] Suen and Chien, *J. Chem. Eng. China*, **8**, 19 (1941).

[3] Hughes and Ingold, *J. Chem. Soc.*, **1935**, 244.

[4] Swain and Ross, *J. Am. Chem. Soc.*, **68**, 658 (1946).

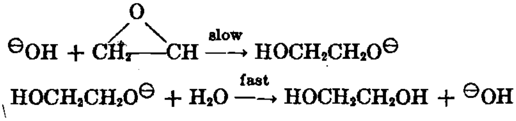
such as vinyl chloride and allyl chloride, play a determinant role in the mechansim. In allyl chloride, for example, the resonance effect ($CH_3\overset{\curvearrowright}{=}CH—CH_2\overset{\curvearrowright}{—}Cl$) increases the ionizability of the C—Cl bond and thus favors the S_N1 path. The inductive effect ($CH_3{=}CH—CH_2 \leftarrow Cl$) would favor the S_N2 mechanism.

Allyl chloride, crotyl chloride, and 1,3-dichloropropane show bimolecular reactions with water and are S_N2 reactions.[1] The effect of solvent is shown by the hydrolysis of benzyl chloride[2] which is bimolecular in 50 per cent aqueous acetone and almost unimolecular in water. The formation of ethylene oxide from ethylene chlorohydrin is a reversible reaction:



When sodium hydroxide is used, the reaction is first order with respect to both ethylene chlorohydrin and hydroxide ion.

The product thus formed may be further hydrolyzed to produce ethylene glycol. The base-catalyzed hydrolysis of ethylene oxide is a first-order reaction and follows the S_N2 mechanism:



Effect of Temperature on the Rate of Hydrolysis. More important than the effect upon the equilibrium point is the influence of temperature upon the speed of reaction. The necessity of completing the operation in a minimum of time has led to the use of the highest temperatures practicable in order to take advantage of the greater speed of reaction, regardless of the possibly unfavorable shift of the equilibrium point. Hydrolytic reactions, like most others, follow the rule that the rate doubles approximately for every 10° rise in temperature. For the ratio $k_{25°C}:k_{35°C}$, the hydrolysis of esters has values between 1.7 and 2.4; the acid hydrolysis of amides, a value of 3.4; organic acid anhydrides, 1.84; acetal, 3.2; and cane-sugar inversion, 4.

Figure 13-1 illustrates the relation between temperature and time of heating necessary to secure a 92 per cent yield of phenol from chlorobenzene and aqueous caustic.[3] At 370°C, 12 min is sufficient; at 295°C, 3 hr.

Unpublished experiments by Lloyd show that in a vapor-phase reaction the rate of formation of phenol from chlorobenzene and steam in the presence of silica gel is negligible at 350°C but exceedingly rapid at 575°C.

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[1] ANDREWS and KEPNER, *J. Am. Chem. Soc.*, **70**, 3456 (1948).

[2] OLIVIER, *Rec. trav. chim.*, **53**, 891 (1934).

[3] HALE and BRITTON, *Ind. Eng. Chem.*, **20**, 117 (1928).

Effect of Concentration of Reactants. Increase in the concentration of the hydrolyzing reagent would naturally be expected to speed up the reaction, other things being equal, but a high concentration sometimes leads to undesirable by-products. The effect of alkali concentration on the hydrolysis of allyl chloride is shown in Table 13-3. It is seen that a high alkalinity leads to an increase in the side reaction which forms diallyl ether and a lower yield of the primary product, allyl alcohol.

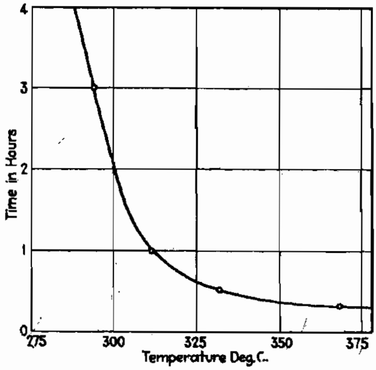

FIG. 13-1. Relation between the temperature and the time necessary to secure a 92 per cent yield of phenol from chlorobenzene and aqueous caustic.

Effect of Pressure on Rate of Hydrolysis. The effect of pressure on the rate of a reaction is shown by the following relationship from the transition-state theory:[1]

$$\frac{d \ln k}{dp} = \frac{-\Delta V^{\ddagger}}{RT}$$

where $\Delta V^{\ddagger}$ is the change in volume between the reactants and the activated complex. For the saponification of ethyl acetate over a pressure range 250–500 atm, the calculated value for $\Delta V^{\ddagger}$ is -11. Thus the rate should increase with increased pressure; this is in agreement with experiment.

TABLE 13-3. EFFECT OF ALKALINITY ON YIELD OF ALLYL ALCOHOL AT VARIOUS CONCENTRATIONS OF SODIUM HYDROXIDE*

NaOH strength, wt %	pH	Allyl alcohol, %	Diallyl ether, %	Unreacted allyl chloride
10	12–13	84.4	13.7	1.9
10	10–11	85.8	11.1	3.1
10	8	79.0	12.9	8.1
5	12	88.9	9.3	1.8
5	10–11	91.9	7.0	1.1
5	8.9	91.8	6.2	2.0
2.5	12–13	93.3	4.6	2.1
2.5	11–12	92.9	4.8	2.3
2.5	10–11	91.5	3.9	4.6

* FAIRBAIRN, CHENEY, and CHERNIAVSKY, *Ind. Eng. Chem.*, **43**, 280 (1947).

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[1] GLASSTONE, LAIDLER, and EYRING, *op. cit.*, p. 473.

The observed value of −5.5, however, is somewhat smaller than the calculated.

V. EQUIPMENT FOR HYDROLYSIS

Materials of Construction. *General.* If the examples of commercial hydrolysis later described are examined carefully, it will be seen that they take place, almost without exception, either in acid or in alkaline media. The acids used are confined largely to sulfuric or hydrochloric; the bases include caustic soda or potash and the alkaline salts of weak acids. The acids may be dilute or concentrated; the bases, aqueous or fused. It is obvious that different materials of construction are required for these different cases. Alkaline processes have, in general, the great advantage that, with rare exceptions, they may be carried out in iron or steel vessels. Only in a few cases do we find caustic soda attacking iron to produce hydrogen. In general, no great difficulties are encountered with materials of construction in alkaline hydrolysis. Even the severe treatment experienced by the cast-iron pots used for caustic fusion does not shorten their life so much as might be expected.

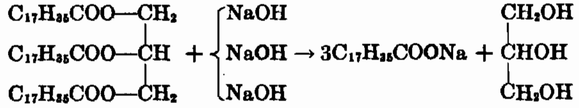
Only two acids—sulfuric and hydrochloric—require serious consideration under acid hydrolysis. Until the advent of Duriron (high-silicon iron), lead-lined equipment was essential for all processes in which sulfuric acid was used, except for very concentrated acid. Saccharification of wood with very dilute sulfuric acid takes place in lead-lined or refractory-brick apparatus, while the absorption of olefins requires acid of specific gravity 1.84, and lead-lined containers are not needed. The hydrolysis of the resulting sulfate, whereby dilute acid is produced, must, however, be conducted in lead equipment, which may further be protected by close-fitting pyrex glass bricks. Duriron is successfully used in acetylene hydration, where dilute sulfuric acid is encountered, but it is not so adaptable or easily fabricated as lead. Recent years have seen the development of Inconel and various types of stainless steel, which have found wide use in hydrolysis, especially under pressure. Different types of plastics have also been employed as surface coatings; and the Haveg resin-asbestos products are available in the form of large tanks and other vessels.

Hydrochloric acid as a hydrolyzer and as a product of hydrolysis in the absence of alkali has been the source of much trouble as it is one of the most corrosive chemicals known. However, even at slightly elevated temperatures, completely dry hydrogen chloride gas has very little corrosive action and is easily handled in iron equipment. Nickel and Monel metal are fairly resistant to low hydrochloric acid concentrations. With dilute acid, several of the copper-base alloys, such as phosphor bronze, aluminum bronze, manganese bronze, and Everdur metal, have fairly good resistance and can often be used in applications where corrosion can be offset by a heavy wall thickness. A general penetration rate for good resistance is below 10×10^{-6} cm per day.[1] Many nonmetallic materials of construction, such as rubber, stoneware, fused silica, glass, and plastic materials such as Tygon and Proflex, have excellent resistance to hydrochloric acid.

In the laboratory, glass and silica are, of course, satisfactory, but their use is limited in commercial work. The starch-glucose transformation takes place in an acid concentration of less than 1 per cent and at low temperature (125–140°C), so that bronze and copper metal containers suffice. The difficulty of handling wet hydrochloric acid gas has been one of the retarding factors in the development of vapor-phase hydrolysis of organic halides, but the use of tantalum is finding favor in continuous processes involving large production. The discovery that Toncan metal (an alloy of iron, molybdenum, and copper) is preferentially wetted by an organic material rather than by aqueous acid and is, therefore, much less subject to corrosion may be of significance.[2] An iron-nickel-molybdenum alloy (Hastelloy A) shows similar properties.

VI. TECHNICAL OPERATIONS INVOLVING HYDROLYSIS

Soap, Glycerol, and Fatty Acids. Oils and fats are glycerol esters of fatty acids, similar and dissimilar, saturated and unsaturated. By hydrolyzing these fats with steam or acid or enzymes, we obtain the glycerol and fatty acids directly; if we add caustic soda to the water in hydrolyzing, common soap results instead of the fatty acids.



$$\begin{array}{l} C_{17}H_{35}COO—CH_2 \\ \qquad\qquad\qquad\;\; | \\ C_{17}H_{35}COO—CH \\ \qquad\qquad\qquad\;\; | \\ C_{17}H_{35}COO—CH_2 \end{array} + \left\{ \begin{array}{l} NaOH \\ NaOH \\ NaOH \end{array} \right. \rightarrow 3C_{17}H_{35}COONa + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glyceryl Tristearate Sodium Stearate Glycerol

Most of our soap is made through the process described by the above equation. In ordinary soapmaking, the fats are placed in a large steel pan (kettle) provided with a perforated steam coil; steam is blown in until the resulting liquid is heated to 80°C; and some water from the condensed steam appears at the bottom of the kettle. Caustic soda is then gradually added, while live steam keeps the mass stirred and emulsifies it. At this stage, one of the three acid radicals combined with the glycerol is removed. More alkali is added, and the boiling with steam is continued until the solution of soap is pasty, a condition indicating that the second acid radical has been properly hydrolyzed off from the glycerol.

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[1] DURGIN, LUM, and MALOWAN, *Trans. Am. Inst. Chem. Engrs.*, **55**, 643 (1937).

[2] AYRES, *Trans. Am. Inst. Chem. Engrs.*, **22**, 23 (1929).

Salt is added to the mass at the proper time to salt out the soap that rises to the top, while the salty aqueous solution containing glycerol settles to the bottom and may be drawn off. More alkali is now added, boiling renewed, and the soap again salted out. This operation may be repeated to ensure complete hydrolysis of the fat, or as often as desired, depending upon the nature and quality of soap desired. Finally the pan is covered, to retain the heat, and the contents are separated into three layers, of which the top is good soap. This layer is skimmed off and put in frames to solidify.

A process for producing directly a low-moisture-content soap consists of subjecting the semidry ingredients to intensive smearing and shearing at low temperatures. Almost stoichiometric amounts of caustic are used, and complete hydrolysis is effected in a short time.[1]

Not only in its manufacture but in its use does soap involve hydrolysis. Like other salts of strong bases and weak acids, sodium stearate and the other sodium soaps spontaneously hydrolyze somewhat in water, and upon this hydrolysis to some extent depends the detergent (cleansing) effect of soap.

Fatty Acids. The above process is an old and direct method by which to make soap; but if fatty acids are wanted, and their use is increasing, the addition of alkali must be avoided unless subsequent treatment with acid at additional expense is to be incurred. For making these fatty acids several processes may be used, the autoclave and the traditional Twitchell method, which are batch operations, and the more modern continuous-countercurrent procedures developed by Colgate-Palmolive-Peet and by The Procter & Gamble Company. Darkening of the resulting products from this type of operation is retarded by the use of hydroxy aromatic compounds as stabilizers.[2]

Since oil or liquified fat is insoluble in water, two liquid phases exist during hydrolysis, and the reaction rate, of course, depends upon their surface of contact—the greater the surface, the faster the saponification. The best way to secure a large surface of contact between two liquids is to emulsify them thoroughly. For example, although pure glycerides react slowly with caustic, the soaps produced from the free fatty acids that are always present to the extent of 2–5 per cent in commercial soap stocks promote emulsification, thereby increasing the rate of reaction. Lascaray,[3] however, claims to have shown that the hydrolysis is really effected by the water which dissolves in the oil phase, so that anything which increases this solubility will hasten the reaction.

Twitchell discovered that a small amount (2 per cent) of a sulfoaromatic

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[1] Bradford, U.S. 2,730,539 (1956).

[2] Ross and Trent, U.S. 2,619,494 (1952).

[3] Lascaray, *J. Ind. Eng. Chem.*, **41**, 786 (1949).

compound added to the system produced such an excellent emulsion that a current of steam without any mineral acid or base effected complete saponification. His reagent may be made by adding concentrated sulfuric acid to benzene and oleic acid at a temperature below 30°C.

$$C_6H_6 + C_{17}H_{33}COOH + H_2SO_4 \rightarrow C_6H_4(SO_3H)(C_{17}H_{33}COO) + H_2O$$

In the Twitchell process the fat is first freed from foreign matter by boiling in a lead-lined tank with dilute sulfuric acid and is then transferred to a second lead-lined tank with a close-fitting cover. After the addition of one-third its weight of water, the mixture is treated with 1.0 per cent of the Twitchell reagent and heated with live steam for 24 hr. Ninety per cent of the fatty acids is set free in this time. The glycerol-water lower layer is drawn off, and the fatty acids that have risen to the surface are boiled again with fresh water for 12 hr, and the separation is repeated. Low-grade fats and greases can be effectively treated in this way.

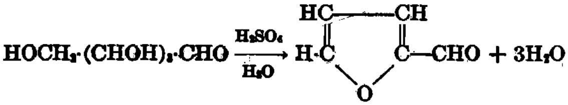
Glycerol. From all these different processes for hydrolyzing fats into soap or fatty acids, glycerol is recovered and refined for the various purposes to which it is now applied. Practically all glycerol refining is now accomplished by distillation with steam under diminished pressure.

In the continuous countercurrent system (Fig. 13-2) the oil is fed at a controlled rate to the bottom of a stainless-steel hydrolyzing tower 70 ft high and 3 ft in diameter, while water is being fed into the top of the tower. The fatty acids, upon discharge from the top, are separated from the accompanying water, while aqueous glycerine flows from the bottom. The tower normally operates at 252°C (480°F) and 700 psig and will hydrolyze 98 per cent of the glycerides, yielding a 15 per cent glycerine solution. Hours rather than days are required to make fatty acids through this process.

Hydrolysis of Carbohydrates

The chief carbohydrates are the sugars, cellulose, and starch with its related polysaccharides. Of these, the only ones hydrolyzed in large-scale industrial operations are the pentoses, from which furfural is obtained, and starch, from which glucose is produced.

Furfural. The commercial production of furfural depends on the conversion of the pentosans of oat hulls and other cereal products. Using xylose as an example, the hydrolytic reaction may be represented as follows:



Ordinarily, oat hulls, which have a relatively high pentosan content and which are available as a by-product of cereal manufacture, are used. The need for furfural has greatly increased in recent years largely because of its use in the extraction of butadiene from petroleum dehydrogenation operations and for the production of hexamethylenediamine for nylon manufacture. As a result, corncobs, rice hulls, and cottonseed bran are now extensively employed. The yields of furfural per 100 lb of such pentoses-containing materials on a dry basis are closely as follows:

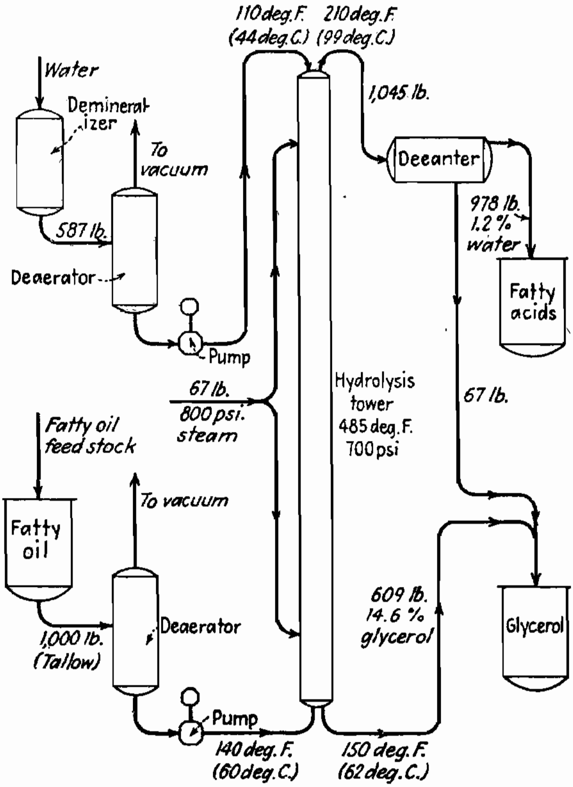


FIG. 13-2. Flow diagram of Colgate continuous-countercurrent hydrolysis of fats.

	Pounds
Rice hulls	7.5
Corncobs	11.0
Cottonseed bran	12.5
Oat hulls	13.5

The raw materials are conveyed from storage (Fig. 13-3),[1] loaded into rotating digesters together with dilute (5–10 per cent) sulfuric acid, and

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[1] HITCHCOCK and DUFFEY, *Chem. Eng. Progr.*, **44** (9), 669 (1948).

cooked under 50–100 lb steam pressure for approximately 2 hr. The furfural that is formed is carried out by the steam when the digester pressure is released and is separated by distillation and then further purified by fractional distillation. Methanol is separated from the furfural and is sold as a by-product. Acetic acid produced in small amounts is not recovered. The residue from the digesters is either burned to produce steam for the plant or is sold as a conditioner for fertilizers. Approximately 1/5 lb of sulfuric acid is consumed per 100 lb of material treated.

Economics. The general economics of furfural production have been discussed by Duffey and Wells.[1] Raw materials such as corncobs, sugarcane bagasse, paper-mill wastes, oat hulls, and cottonseed hulls are plentiful; thus, the manufacturer must be competitive in handling and processing these raw materials. The two greatest costs in the manufacture of furfural are the raw-material costs and the costs associated with a large plant investment.

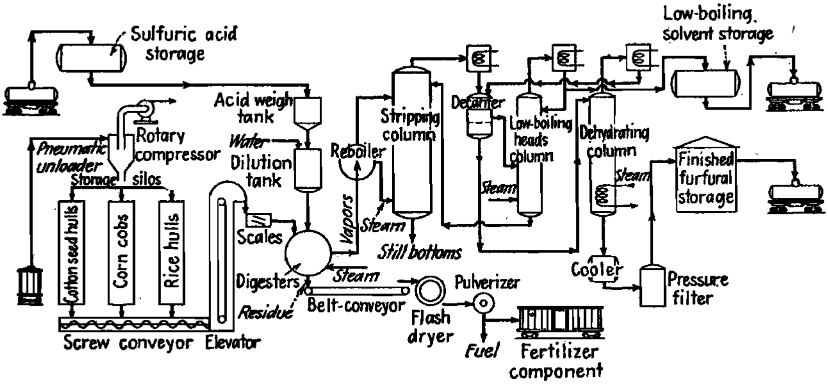

FIG. 13-3. Flow diagram of Quaker process for manufacture of furfural.

The cost of raw material is the sum of six items: (1) cost at point of production, (2) cost of collection, (3) cost of transportation, (4) cost of storage to ensure year-round supply, (5) cost of preparation for use, (6) and cost of disposing of by-products. The cost at the point of production is most subject to variation.

Since the plant investment relative to the value of the product is large, it is necessary to operate at high capacity on a continuous basis. The principal risks involved in a furfural plant are fluctuations in raw-material prices and supply and ability to maintain profitable markets.

Hydrolysis of Starch to Sirup and Dextrose.[2] The hydrolysis of starch using an acid catalyst is an old process dating back to the Russian, Kirch-

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[1] DUFFEY and WELLS, *Ind. Eng. Chem.*, **47**, 1408–1411 (1955).

[2] Contributed by Corn Industries Research Foundation, Inc.

hoff, in 1811. It has been used commercially for over 100 years and today represents approximately a 2-billion-lb operation. In the United States, corn is the cheapest source of starch and hence is the raw material of preference, although starch from any botanical source would be equally suitable from a technologic standpoint.

A high polymer of dextrose, starch is composed of anhydroglucose units linked with carbon 1 of one anhydroglucose unit glucosidically bonded to an adjacent anhydroglucose unit, usually, but not always, on carbon 4 of the adjacent unit. In the presence of water the catalytic effect of acids is to cleave these glucosidic linkages and at the same time introduce the elements of water at the point of cleavage. The reaction is accelerated by increased temperature and by increased acid concentration (lower pH). It also may be somewhat accelerated by decreased carbohydrate percentages in the system. Under the influence of considerably elevated temperatures or increased acid concentration, a secondary degradative reaction sets in which produces color and flavor bodies. These are of the furfural type and of the type produced by the Maillard browning reaction. In order to minimize the formation of these impurities, commercial hydrolysis is carried on at a temperature and an acid concentration which is a compromise between the speed of the hydrolysis and the undesirable formation of these side-reaction products.

The extent to which the hydrolysis will approach completion is a function of the proportion of carbohydrate to water. Starting with a starch slurry of about 40 per cent dry substance, the reaction will go roughly 80 per cent to completion. If the starch concentration is reduced to approximately 20 per cent, the reaction appears to go about 87 per cent to completion. If the concentration is reduced to 1 per cent, which is in the range of the analytical method for determination of starch substance, the reaction goes about 99 per cent to completion. Even at a concentration of 0.25 per cent, there is still some polymeric material present. Under conditions of moderate concentration in the 50–80 per cent range, the unhydrolyzed polymers consist chiefly of randomly linked disaccharides, apparently with isomaltose, the alpha-linked 1,6 disaccharide, predominating.

Commercially in the United States the hydrolyzates of starch are found in two broad classes: sirups, which are partial hydrolyzates and do not crystallize readily upon standing; and sugars, which are more nearly completely saccharified and do crystallize readily upon standing. The methods of manufacture are similar, differing largely in the selection of the specific hydrolytic conditions. Sirups generally are hydrolyzed at about 40 per cent starch concentration, with hydrochloric acid at 0.016 normal, and at a temperature of 140–150°C. The time required for hydrolysis is in the order of 20–25 min. Sugars are hydrolyzed at about 20 per cent dry-substance starch concentration, using hydrochloric acid of approximately 0.030 normality, a temperature of 150°C, and a reaction time of about 40–45 min. The extent of hydrolysis is customarily measured by the content of reducing sugars. This is usually determined by the Lane and Eynon technique with Fehling's solution, the reducing power being calculated as dextrose and expressed as a percentage of the total dry substance in the system. This value is referred to as the dextrose equivalent (D.E.).

In a typical refinery, a batch for corn sirup consists of 3,400 gal of 24° Bé starch suspension and 50 lb of 20° Bé commercial muriatic acid. The total time for conversion is 28–30 min, but the charge is under actual conversion steam pressure of 30 psi for only 6–8 min. The resulting product is a partly hydrolyzed solution containing dextrose, maltose, and higher saccharides and is the basis of ordinary commercial sirup. Varying proportions of dextrose, maltose, and higher saccharides may be obtained by changing the cooking period, concentration of starch, or quantity of acid used.

The corn sirups usually fall in a D.E. range of 24–60. The progress of the hydrolysis is commonly followed by plotting the D.E. of the reaction mixture against time. However, the specific rotation bears an exact relationship to the D.E. and can be used instead of D.E. for following the course of this reaction. Starch, being insoluble, has no measurable specific rotation, but its hydrolytic products in the early stages rotate about +200 deg. As the hydrolysis proceeds, the specific rotation of the mass decreases until theoretically it reaches the rotation of pure dextrose (+52.5 deg). Research by the Corn Industries Research Foundation (1956) has resulted in reasonably precise analyses of sirup hydrolyzates in the range of 15–67 D.E. The components of the hydrolytic mixtures have been characterized in the mono-, di-, tri-, tetra-, penta-, hexa-, and heptasaccharide classes, the balance being referred to as higher saccharides. These data with an expected accuracy of ±1 per cent are given in Table 13-4.

Prior to World War II, a two-step or dual-hydrolysis sirup was developed[1] and placed on the market. The first step in its manufacture is similar to the hydrolysis already described. After the neutralization of the acid, filtration, and partial concentration of the sirup, a saccharifying enzyme is added. By the end of 48 hr a considerable increase in the dextrose and maltose and a decrease in the higher-saccharide content result. The final product is considerably sweeter and not nearly so viscous as straight acid-conversion sirup.

For the manufacture of corn sugar, a typical 3,200-gal batch of 10° Bé starch suspension is converted with 90 lb of muriatic acid at a steam pressure of 45 psi, with a total conversion time of 40 min. In this conversion the hydrolysis of the starch is carried as far as is practical. In the

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[1] U.S. 2,201,609 (1940).

case of the acid conversion of both sirup and sugar, there are variations in time, temperature, and acid from plant to plant, depending on the equipment used, the type and character of raw material processed, and the end product desired.

The corn sugars fall in a D.E. range of 82 and higher. If crystalline dextrose is not required, the sugar liquors may be refined, concentrated, and cast, under which condition they set up to a solid cake. This cake can then be shipped as such or chipped and bagged. Such so-called "crude" sugars are not generally used directly for edible purposes but find utility as fermentation substrates, as a base for the manufacture of caramel color, in the finishing of leather, and in the manufacture of viscose rayon.

TABLE 13-4. CARBOHYDRATE COMPOSITION OF CORNSTARCH HYDROLYZATES

D.E.*	Per cent saccharides							
	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Higher
Acid-converted Products								
10	2.3	2.8	2.9	3.0	3.0	2.2	2.1	81.7
15	3.7	4.4	4.4	4.5	4.3	3.3	3.0	72.4
20	5.5	5.9	5.8	5.8	5.5	4.3	3.9	63.3
25	7.7	7.5	7.2	7.2	6.5	5.2	4.6	54.1
30	10.4	9.3	8.6	8.2	7.2	6.0	5.2	45.1
35	13.4	11.3	10.0	9.1	7.8	6.5	5.5	36.4
40	16.9	13.2	11.2	9.7	8.3	6.7	5.7	28.3
45	21.0	14.9	12.2	10.1	8.4	6.5	5.6	21.3
50	25.8	16.6	12.9	10.0	7.9	5.9	5.0	15.9
55	30.8	18.1	13.2	9.5	7.2	5.1	4.2	11.9
60	36.2	19.5	13.2	8.7	6.3	4.4	3.2	8.5
65	42.5	20.9	12.7	7.5	5.1	3.6	2.2	5.5
67	45.1	21.4	12.5	6.9	4.6	3.2	1.8	4.5
Acid-Enzyme (Dual-conversion) Sirup								
62–63	38.8	28.1	13.7	4.1	4.5	2.6	. .	8.2†

* Dextrose equivalent (D.E.) is defined as the reducing sugar content calculated as dextrose and expressed as a percentage of the total dry substance.

† Includes heptasaccharides.

If crystalline dextrose is sought, corn-sugar liquors are crystallized in motion by slow cooling over a period of about 100 hr, and the crystalline dextrose is then centrifuged from the magma. Under usual crystallizing conditions pure dextrose crystallizes as the monohydrate, in which the crystal structure is an alternating lattice of one molecule of water crystallized with each molecule of dextrose. If desired, this product can be remelted or redissolved in a strike pan at high temperature with supersaturation maintained by continued evaporation. Under these conditions, dextrose can be caused to crystallize in the anhydrous form, and by proper control of the exact crystallizing conditions, either the alpha or the beta configuration can be induced.

Whether the desired product is a corn sugar or a corn sirup, the elements of processing are identical. The starch is hydrolyzed to the desired degree controlled by the D.E., the acid is neutralized with sodium carbonate, the insoluble nonstarch impurities are mechanically removed, the soluble impurities are reduced by adsorption on a refining agent, and the resulting clarified and refined hydrolyzate is concentrated to the desired percentage of solids, usually measured with a hydrometer on the Baumé scale.

In the hydrolysis of starch, as in any hydrolytic process, the elements of water added to the hydrolytic fragments become a true part of the dry substance of the hydrolyzate. Thus, whereas in some processes the yields may *approach* 100 per cent, in hydrolysis the yield is over 100 per cent of the starting dry-substance starch. For most of the corn sirups, this so-called "chemical gain" amounts to 4–5 per cent, depending upon the degree of hydrolysis; for crude corn sugars, it may amount to about 9 per cent, again depending upon the degree of hydrolysis; and for crystalline dextrose, the theoretical chemical gain is 11.1 per cent, but there is an accompanying loss in the mother liquor. It is important to remember this fact in any consideration of the economics of the process.

Continuous Starch Hydrolysis. A commercial continuous converter installation for dextrose manufacture employing a continuous, automatically controlled step for the hydrolysis of starch is now in operation. A flow diagram of a modern commercial installation for continuous starch hydrolysis is shown in Fig. 13-4. The starch converter consists of an 8-in. coil, 677 ft long, which is fed by a high-pressure centrifugal pump from a continuous starch make-up tank equipped for automatic control of density (Baumé), level, and acidity. The level controller regulates the addition of 20° Bé starch suspension, the Baumé controller operates the water valve, and a conductivity instrument controls the addition of acid. The head end of the converter coil has an entry chamber to separate noncondensables, and the feed is instantaneously heated with live steam through a jet heater.

The temperature of the "pasted" starch is measured at the outlet of the entry chamber, and this temperature controls the steam addition. Because the coil is operated under pressure, a control valve on the discharge end is operated by a level control in the entry chamber; as the level goes up, the valve opens to send more "liquor" forward in the process. As hydrolyzate is flashed from the discharge end of the converter, the vapor and liquid are

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[1] DLOUHY and KOTT, *Chem. Eng. Progr.*, **44** (5), 399 (1948).

separated and the liquid goes to subsequent stations for refining, concentration, crystallization, separation, and drying. The most important advantages of continuous hydrolysis are the ability to maintain a high production rate and the uniform control of quality. Since there is a minimum of holding time, the same quantity of material can be produced with fewer tanks and less equipment.

Operating Conditions. By a proper choice of operating conditions, a number of hydrolysis coil products serving various purposes of manufacture can be produced. The extent of hydrolysis is followed by analyzing the coil end product for the relative amount of reducing sugars to determine its dextrose equivalent. By varying acid concentration, holding time, or temperature within the system, the D.E. produced in the hydrolyzed product can be varied over a wide range. At very low D.E., the product has a pastelike consistency because of the high percentage of incompletely hydrolyzed starch. As the D.E. level is raised, the product becomes more fluid and less pasty, the viscosity decreasing as D.E. increases. Where a considerable change in product composition is required, as, for example, from dextrose liquors to sirup liquors, or pastes, all three variables may be altered. However, in the case of minor adjustments of D.E. due to underhydrolysis or overhydrolysis, a shift in the operating temperature is usually

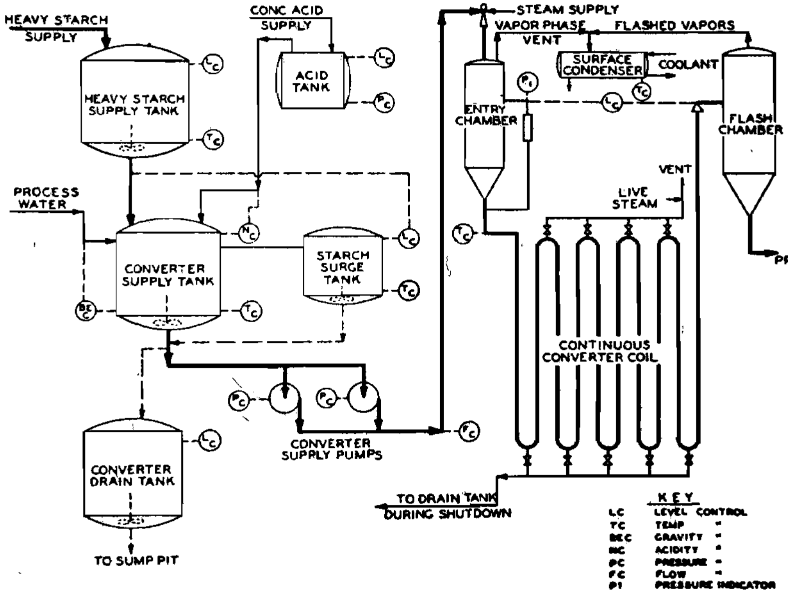

FIG. 13-4. Flow diagram for the continuous hydrolysis of starch.

the most convenient method of correction. Typical sets of operating conditions are presented in Table 13-5.

TABLE 13-5. OPERATING CONDITIONS FOR DEXTROSE, SIRUP, AND LOW D.E. PASTES

Hydrolysis coil product	Acid catalyst	Normality of acid catalyst in coil	Time in coil, min	Temp in coil, °C	D.E. expected
Dextrose........	H_2SO_4	0.030	18	158	90
Sirup.............	HCl	0.016	10.5	148	58
Sirup..............	HCl	0.016	13	142	42
Paste..............	HCl	0.010	6	142	16
Paste..............	HCl	0.007	6	132	5

Preparation of Amyl Alcohols from Chloropentanes

New and enlarged uses for the amyl alcohols and their derivatives, particularly in pyroxylin lacquers, have called for enlarged production, which could not remain dependent upon incidental fusel oil from molasses and potato fermentation. This new production has come from the pentanes of natural gasoline through the chlorination-hydrolysis process developed by Ayres.[1]

This process consists in the isolation from natural gasoline of two of the three pentanes, their chlorination (see Chap. 6) to form monochlorides as far as possible, the hydrolysis under moderate pressure of these monochlorides by water containing sodium oleate and caustic soda, and, finally, the distillation of the alcohols from the reacting mixture. From the chlorination to the distillation inclusive, the process is continuous.

Hydrolysis is accomplished in a system of reservoirs, heaters, and pumps through which a hot emulsion of amyl alcohol, water, and sodium oleate is circulating at the rate of 500 gpm. Amyl chlorides and an aqueous solution of caustic soda are continuously pumped into this circulation material, and two products are continuously withdrawn: (1) a saturated salt solution, which is returned to electrolytic cells for manufacture of chlorine and caustic soda, and (2) a vapor containing principally amyl alcohols. Three hundred gallons of amyl chloride is present at all times in the hydrolysis system, and 300 gal is hydrolyzed each hour.

The vapors from hydrolysis are separated by a train of fractionating columns into five components: (1) unchanged amyl chlorides, which are returned to hydrolysis, (2) amylene, which is later hydrated to amyl alcohol, (3) diamyl ether, (4) amyl alcohol fractions that are cut out for special uses, and (5) the mixture of amyl alcohols marketed under the trade

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[1] AYRES, *Ind. Eng. Chem.*, **21**, 899 (1929).

name Pentasol for use in pyroxylin lacquers. The general layout is given in Fig. 13-5.

A condensed but inadequate description of the chlorination and hydrolysis is given by the equations

$$C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$$
$$C_5H_{11}Cl + NaOH \rightarrow C_5H_{11}OH + NaCl$$

The operation of the hydrolysis can be followed from the accompanying diagram (Fig. 13-5). The mixture of water, caustic, sodium oleate, and amyl chloride is circulated through two digesters (only one is shown in the figure), one of which is larger than the other and serves also as a still. About 2 per cent of the amyl chloride present is hydrolyzed during each cycle. Like all other heterogeneous reactions, this one proceeds more rapidly the more thoroughly the mixture is emulsified; and it has been found that by introducing the caustic soda *before* the circulating pump, the agitation due to the latter much improves the emulsification. A temperature of 170°C is maintained by a steam heater placed outside the digesters and through which the mixture is continually circulated.

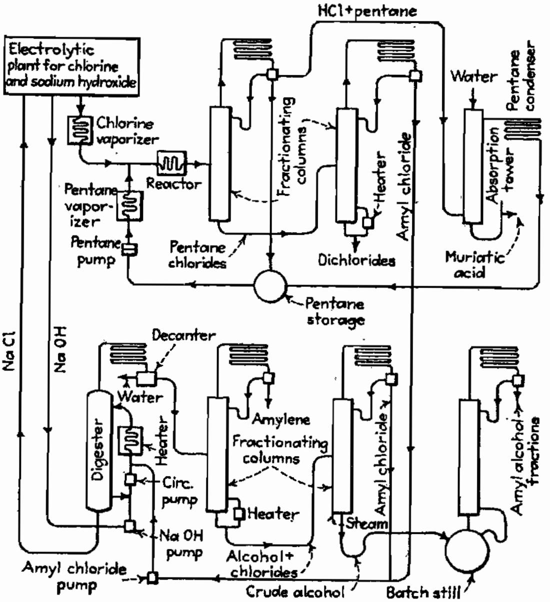

FIG. 13-5. Plant for production of amyl alcohols from pentane. (*According to E. E. Ayres.*)

Two pentanes (normal and iso) serve as starting products for chlorination, and these give rise to primary, secondary, and tertiary chlorides.

The tertiary and secondary chlorides will hydrolyze with water; the primary and secondary, with sodium oleate. This catalyst really acts therefore in two ways: (1) It puts water in colloidal contact with amyl chloride, thereby promoting *rapid* hydrolysis of the secondary and tertiary chlorides; (2) it is itself in colloidal contact with the chorides so that the primary and secondary compounds can form with it the amyl oleates, which are readily decomposed by caustic. Amyl chloride must not be present in excess over sodium oleate; or amylene will form in quantity.

The reaction is a surface one, and a coating of sodium oleate forms over the caustic, which must be mechanically dispersed; hence, the necessity for efficient agitation.

Preparation of Alcohols from Olefins

An abundant and relatively cheap raw material is almost sure to find in time a use to which it can be economically put. The cracking of petroleum, especially vapor-phase cracking, produces tremendous volumes of olefin gases, which are now extensively used as raw materials for alcohol production. The alcohols made by this procedure are ethyl from ethylene, isopropyl from propylene, normal butyl indirectly from ethylene, secondary butyl from normal butylene, tertiary butyl from isobutylene, and secondary and tertiary amyl from amylenes.

All these alcohols are produced through reactions common apparently to all olefins—the union of the gas with concentrated sulfuric acid (or phosphoric acid) to form the corresponding monosulfate and the subsequent hydrolysis of this ester.

$$C_nH_{2n} + H_2SO_4 \rightarrow C_nH_{2n+1}OSO_3H \qquad (1)$$

$$C_nH_{2n+1}OSO_3H + H_2O \rightarrow C_nH_{2n+1}OH + H_2SO_4 \qquad (2)$$

The water molecule that enters the olefin distributes itself in such a way that the hydroxyl ion becomes attached to the carbon having the least hydrogen, so that secondary and tertiary alcohols—not primary—result.

The more complex the olefin, the lower the temperature and pressure at which reaction (1) will take place. Furthermore, ethylene requires a more concentrated sulfuric acid for efficient absorption than its homologues. Both mono- and dialkyl sulfates are formed simultaneously when ethylene or propylene is absorbed in sulfuric acid. An appreciable amount of diethyl sulfate is formed when the acid has reacted with about $\frac{1}{3}$ mole of ethylene. In addition, appreciable amounts of the corresponding ethers are produced. Ethyl ether, for example, is formed to a considerable extent by the reaction of alcohol with diethyl sulfate.[1] Polymer formation, particularly for higher olefins, is also an undesirable side reaction.

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[1] BROOKS, *Ind. Eng. Chem.*, **27**, 283 (1935).

Some processes use *dilute* acid under high pressures,[1] an increased yield of alcohol being obtained with a corresponding decreased yield of ether. The yield of ether may be also decreased by removal of alcohol from contact with unreacted sulfate liquor, as rapidly as it is formed, by immediate distillation in hot water.[2] Brooks and others have shown the advantages of absorption of ethylene under pressure.[3] Various catalysts are used in these processes,[4] and ethyl alcohol has also been prepared by the direct combination of ethylene with water in the presence of catalysts and under pressure.[5] The two most promising catalysts are supported phosphoric acid[6] and promoted tungsten oxide.[7]

The Shell process, now in commercial operation (see process description) uses a phosphoric acid–on Celite catalyst to effect a 4.2 per cent oncethrough conversion. Mace and Bonilla[7] showed that a tungsten oxide–on silica gel catalyst was the most effective of several types investigated. Yields of 4.0 mole per cent were obtained at optimum conditions of 580°F (300°C), 2,000 psi pressure, steam:ethylene mole ratio of 1, and a space velocity of 1,500 reciprocal hours.

The direct hydration of propylene and higher olefins has also been accomplished. The tungsten oxide type of catalyst was the best found, although supported phosphoric acid gave good results.[8]

Preparation of Ethanol from Ethylene. *Via Ethyl Hydrogen Sulfate.*[9] Ethylene is scrubbed, purified, and piped in gaseous form direct to processing in the alcohol plant (Fig. 13-6). On entering an absorber, ethylene comes into contact with sulfuric acid of 95 per cent concentration or higher. The resulting liquid is a mixture of monoethyl and diethyl sulfate. The esters leave the bottom of the absorber and are pumped into the bottom of a hydrolyzer column along with a measured volume of water. Here the esters formed in the absorber are converted to alcohol, ethyl ether, weak sulfuric acid, and small volumes of other materials.

Crude alcohol and other products pass to a stripping column. Steam

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[1] U.S. 1,951,740; 1,955,417 (1934); 2,045,842; 2,050,442; 2,050,443; 2,050,444; 2,050,445 (1936).

[2] U.S. 2,038,512 (1936).

[3] Brooks, U.S. 1,885,585; 1,919,618 (1933); 1,960,633 (1934); *Ind. Eng. Chem.*, **31**, 518 (1939); Strahler and Hachtel, *Brennstoff-Chem.*, **15**, 166 (1934).

[4] U.S. 1,977,632 (1934); 1,999,620; 2,014,740 (1935); 2,051,046; 2,064,116 (1936); 2,087,290 (1937); 2,472,618; 2,473,224 (1949).

[5] Bliss, *Ind. Eng. Chem.*, **29**, 19 (1937).

[6] Nelson et al., U.S. 2,579,601 (1951); Brit. 651,275 (1951); Schrader et al., U.S. 2,673,221 (1954).

[7] Thomson and Reynolds, Brit. 665,214 (1952); Mace and Bonilla, *Chem. Eng. Progr.* **50**, 385 (1954).

[8] *F.I.A.T. Final Rept.* 968 (1947) (Field Information Agency); Runge et al., *Brennstoff-Chem.*, **1953** (11), 330; Levy and Thomson, Brit. 667,391 (1952).

[9] *Chemical Engineering*, Staff Report, November, 1945.

carries off the alcohol, ether, and a small volume of acidic material. The remainder of the water together with the dilute acid is withdrawn from the bottom of the tower. The acid goes to an acid cooler and then to storage where it remains until concentrated for reuse.

The vaporized mixture of alcohol, ether, and water leaves the stripping column at the top and goes to a caustic scrubber, entering at the bottom.

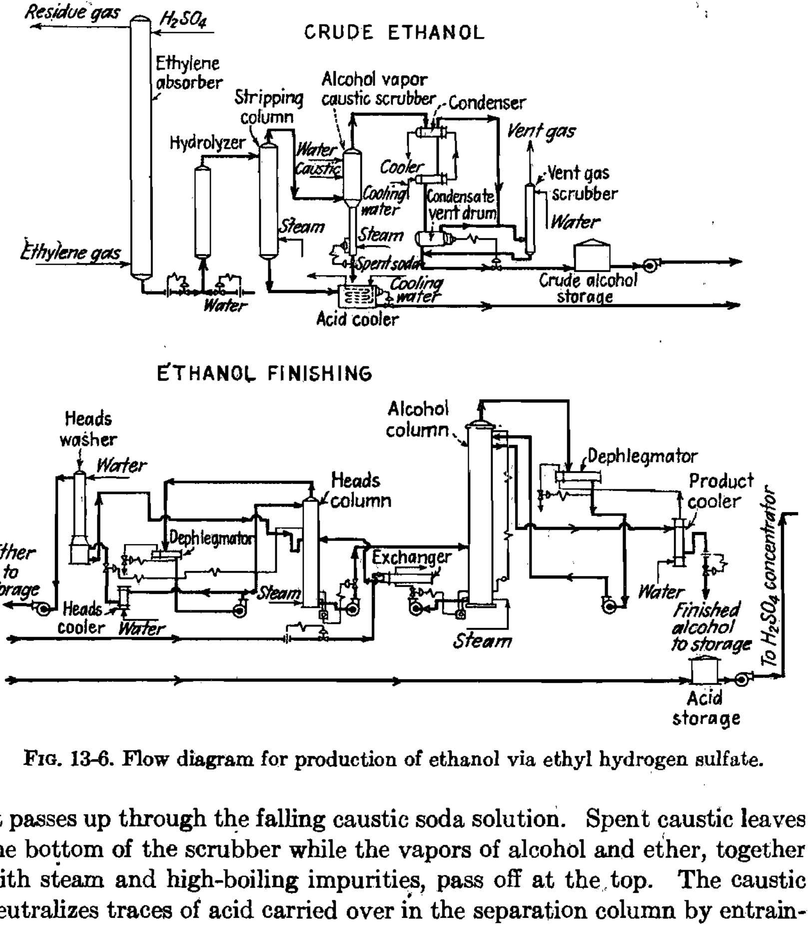

FIG. 13-6. Flow diagram for production of ethanol via ethyl hydrogen sulfate.

It passes up through the falling caustic soda solution. Spent caustic leaves the bottom of the scrubber while the vapors of alcohol and ether, together with steam and high-boiling impurities, pass off at the top. The caustic neutralizes traces of acid carried over in the separation column by entrainment. The vapors are condensed and pumped to the crude-alcohol storage tanks at the finishing building.

Ether Removal. At this point there is only a small amount of ether in the mixture, which is mostly crude alcohol and water. The first step in finishing is to remove the ether. This is done in an "ether" column. Steam at the proper temperature enters the column, vaporizing the ether and carrying it off at the top of the tower. The overhead from the column, a mixture of ether and alcohol, is water-scrubbed. The alcohol is returned to the alcohol column, and the ether is condensed and conveyed to storage for shipment.

Crude-alcohol bottoms are fed into an efficient, large fractionating column, and alcohol of 190–192 proof (95–96 per cent) is driven overhead. Water and high-boiling impurities go to the sewer. The alcohol is then cooled and pumped to storage.

Concentration of Sulfuric Acid. Returning now to the dilute sulfuric acid leaving the stripping column in the crude alcohol unit, this acid flows to an acid reboiler which is really a concentrating unit (not shown in Fig. 13-6). Sufficient water is evaporated to raise the acidity to 70 per cent. Water evaporated from the acid is returned as vapor to the base of the generator in which it is used as a stripping medium. The acid is cooled and pumped to storage tanks. The primary purpose of the reboiler is to concentrate spent acid. The reason for this particular setup is to utilize the water evaporated and thereby save the cost of stripping steam consumed in the generator.

For further concentration of the acid, a two-stage vacuum acid system is used. Acid is pumped continuously from storage into the constant-level feed tank. The acid rate to the concentrators is controlled by hand and is metered by a rotometer. The 70 per cent acid enters the first-stage evaporator operated at an absolute pressure of 2.5 in. Hg. Here the acidity is raised to 89 per cent. The acid then overflows into the second-stage evaporator operating at an absolute pressure of 0.4 in. Hg. The acid concentration is raised to the final desired strength.

Effect of Temperature Gradients. Operation of the ethylene absorption tower under a temperature gradient increasing from the top to the base of the tower is evidently conducive to a greater absorption of ethylene by sulfuric acid.[1] The quantity of ether formed is, however, higher, and in general this is economically disadvantageous. According to Alcohol Tax Unit reports, about 4.3 lb ethylene is used per gallon of alcohol produced, which indicates that at least 88 per cent of the olefin is converted to ethyl hydrogen sulfate.

Ethanol via Direct Hydration. The Shell Process.[2] The production of ethanol by the direct addition of water to ethylene is being carried out successfully on a commercial scale. In the Shell process a phosphoric acid–on Celite catalyst is used in the reaction:

$$C_2H_4 + H_2O \xrightarrow{H_3PO_4} C_2H_5OH + 19{,}000 \text{ Btu/lb mole}$$

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[1] Morrell and Robey, U.S. 2,545,161 (1951).

[2] Nelson and Courter, *Chem. Eng. Progr.*, **50**, 526–531 (1954); Johnson and Nelson, *Chemistry & Industry*, **1953**, S 28–31; Nelson and others, U.S. 2,579,601 (1951); Brit. 651,275 (1951); Sherwood, *Petroleum Engineer*, **28**, C33–42 (1956).

Products from the principal side reactions are diethyl ether from the dehydration of ethyl alcohol, acetaldehyde from the hydration of acetylene impurity, and olefinic polymers. None of these, however, is produced in large quantities.

The reaction section shown in Fig. 13-7 is one of several parallel units. The feed ethylene is compressed to approximately 1,000 psi before joining the larger recycle stream. Water is added to give a ratio of 0.6 mole of water per mole of ethylene and the mixture preheated to 570°F (300°C) by means of a gas-fired furnace. After entering the top of the reactor, the feed passes downward through the catalyst bed where a fraction of the mixture is converted to ethyl alcohol. Since the reaction is exothermic, the product leaving the reactor is at a higher temperature than the feed.

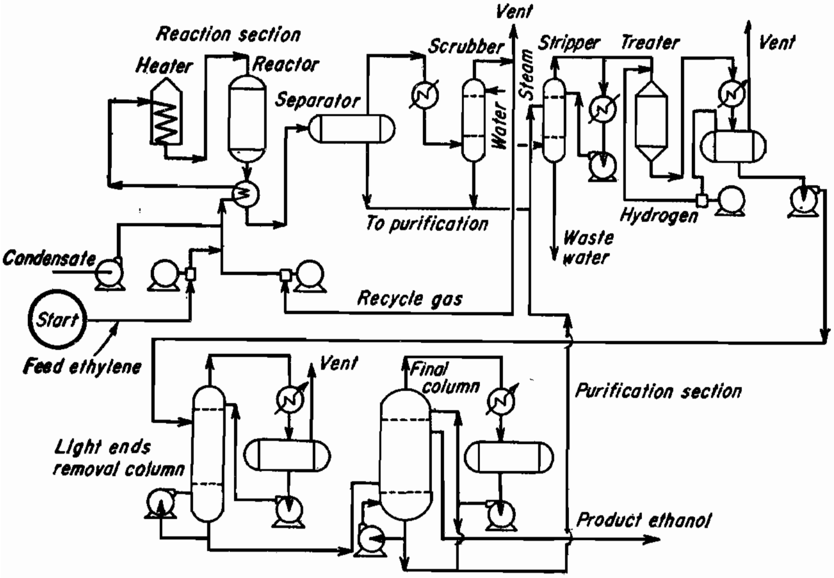


FIG. 13-7. Flow diagram of Shell process for manufacture of ethanol. [*Petroleum Refiner*, **34** (12), 145 (1955), *by permission*.]

The reactor effluent passes into a feed-product heat exchanger, where it is partially condensed. After washing with dilute caustic soda to neutralize traces of phosphoric acid, it passes into a second exchanger and on to a high-pressure separator to give a liquid and a vapor stream. The condensate goes to purification and the vapor to recycle. The vapor is cooled by the recycle-gas cooler and scrubbed with water to remove alcohol. The build-up of impurities like methane and ethane is controlled at this point by venting a small stream of the recycle gas.

The condensate and the alcohol-water solutions of the various parallel units are combined and separated in a low-pressure separator. This crude product enters a stripping column where the ethyl alcohol is concentrated in the overhead. A recycle hydrogen stream is combined with the alcohol before it enters the treater. In the treater, traces of aldehydes are hydrogenated over a supported nickel catalyst to the corresponding alcohols. The product from this reactor is condensed, separated, and sent to the light ends column where light by-products, principally diethyl ether, are taken overhead. Product ethanol is removed as a side stream from the final purification column.

The operating conditions used are:

Reaction temperature	570°F (300°C)
Reaction pressure	1,000 psig
Feed ethylene concentration	85%
Make-up ethylene concentration	97%
Water:ethylene mole ratio	0.6
Space velocity, VSVM (vol. of gas at 60°F (15.5°C) and 1 atm/min/vol. catalyst)	30
Ethylene conversion per pass	4.2%
Over-all process yield	97% or better
Product purity	95%

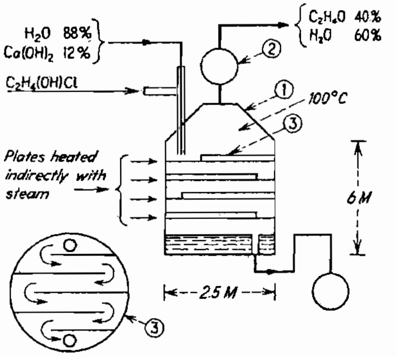
Catalyst. The support for the phosphoric acid must have sufficient pore volume to hold relatively large quantities of the acid and be sufficiently resistant to conditions in the reactor to remain physically strong. Celite, a calcined and pelleted diatomaceous earth, has proved to be a superior catalyst support.

During operation a small amount of acid is carried from the reactor by the gases, with a resultant decrease in catalytic activity of the bed. In practice, the injection of a stream of phosphoric acid at the inlet to the reactor maintains activity of the catalyst.

Effect of Operating Variables. The direct hydration of ethylene is an equilibrium reaction (see Sec. V) which is favored by low temperatures, high pressures, and high steam:ethylene ratios. The catalytic activity of the phosphoric acid catalyst increases with increasing temperature, decreases with increasing pressure because of lower concentration, and decreases with high steam:ethylene ratios at high pressures because of moisture absorption. Thus, the process conditions that favor ethanol production adversely affect the catalyst activity. For this reason, operating conditions must necessarily be chosen on the basis of economic considerations.

Temperature. The equilibrium concentration of ethyl alcohol decreases rapidly with an increase in temperature while the activity of the catalyst increases. By-product formation is also a function of temperature. Low temperatures favor diethyl ether formation, and high temperatures increase the amount of polymeric materials. The optimum temperature at which rate and equilibrium give a maximum alcohol production for the process is 300°C at a space velocity of 28 VSVM (volumes of gas at 60°F (15.5°C) and 1 atm/min/vol. of catalyst).

Pressure. Equilibrium is favored by an increase in pressure, and activity is adversely affected. Variations in space velocity and ethylene:water ratios may be made to compensate for this decreased catalyst activity; however, economic considerations relating to high-pressure equipment lead to an optimum pressure of 1,000 psig.



① *Saponifier C.I. 2.5MΦ × 6M*
② *Dephlegmotter to reduce loss of water with product*
③ *Plates, steam heated, with vertical baffles to give long tortuous path for reaction mixture*

FIG. 13-8. Ethylene oxide from ethylene chlorohydrin.

Ethylene Purity. The ethylene purity in the recycle is a function of feed purity and vent rate. An economic balance between the size of the reactor and ethylene purification facilities results in a recycle purity of 85 per cent and make-up feed of 97 per cent ethylene.

Materials of Construction. The reactors and the first of the two heat exchangers are lined with copper to prevent corrosion. Since the small amount of acid carried over is neutralized, the other parts of the reaction system and the purification unit are constructed of steel. One of the economic advantages of the direct hydration process over the sulfuric acid process is the use of steel in a large part of the plant.

Manufacture of Ethylene Glycol. Ethylene glycol can be made by the hydrolysis of ethylene chlorohydrin with sodium acid carbonate solution:

$$CH_2OHCH_2Cl + NaHCO_3 \rightarrow CH_2OHCH_2OH + NaCl + CO_2$$

The above reaction, although apparently simple, has not been employed industrially because of the difficulty in obtaining a pure product. Instead, the chlorohydrin is first converted to ethylene oxide (Fig. 13-8), which is then hydrated to ethylene glycol.[1]

$$C_2H_4 + Cl_2 + H_2O \rightarrow ClCH_2CH_2OH + HCl \qquad (1)$$

$$ClCH_2CH_2OH + \tfrac{1}{2}Ca(OH)_2 \rightarrow C_2H_4O + \tfrac{1}{2}CaCl_2 + H_2O \qquad (2)$$

$$C_2H_4O + H_2O \rightarrow HOCH_2CH_2OH \qquad (3)$$

The freshly prepared solution of ethylene chlorohydrin and hydrochloric acid in water (see Chap. 6) is led to a vertical steel saponifier that contains a

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[1] *B.I.O.S. Final Repts.* 1059 and 1618, Item 22; *F.I.A.T. Final Repts.* 874 and 1311.

number of baffles. Just before the solution enters the saponifier, a 10–12 per cent milk of lime slurry at 90°C is added. The mixture is delivered to the top plate, where it is brought to a boil with live steam. Under these conditions, the chlorohydrin is converted to ethylene oxide [reaction (2)], and this together with the ethylene dichloride originally present in the chlorohydrin solution is removed as vapor with the steam. A reflux condenser returns about 30 per cent of the distillate to the hydrolyzer. The steam used is about ten times the weight of ethylene and is distributed at about a 2:1 ratio on the top and bottom plates of the hydrolyzer. The base temperature is about 102°C and the pressure 80 mm Hg gauge.

It is known that about 60 per cent of the theoretical quantity of calcium hydroxide can be replaced with sodium hydroxide. When a greater proportion is used, there is a decrease in the yield of ethylene oxide.

The effluent from the hydrolyzer passes to a settling basin and to thickeners where the solids are removed and the liquid is discarded. The vapors, leaving the dephlegmator above the hydrolyzer at 80°C and containing about 75 per cent water, 20 per cent ethylene oxide, and 5 per cent ethylene dichloride, enter a cooler which operates in conjunction with the primary ethylene oxide still. The vapors are cooled with water to 40–50°C and enter a vessel where the condensed liquid, mostly ethylene dichloride, separates from the vapors of ethylene oxide. The former flows to the seventeenth plate of the first ethylene oxide distilling column, and the latter goes to the vapor space above the top (30 to 50) plate.

Steam is regulated on the still to give a temperature of 55°C at the base, the reflux ratio being 0.5–1.0:1 of product removed to storage. The dephlegmator is cooled with brine at − 14°C. The ethylene oxide coming overhead in the first column is further purified in the second column, while the liquid from the base of both still columns is pumped to a secondary column where the remaining ethylene oxide is separated from the ethylene dichloride.

Operating Procedure for Glycol. After nitrogen has been purged, the reaction tower is filled with water and heated by blowing in steam at the base until the temperature reaches 165–170°C. When this temperature is reached, steam is shut off and a feed comprising 1 part by volume of ethylene oxide and 6 parts by volume of water is pumped in. The pressure rises because of the vapor pressure of the ethylene oxide, a working pressure of 15–21 atm being used.

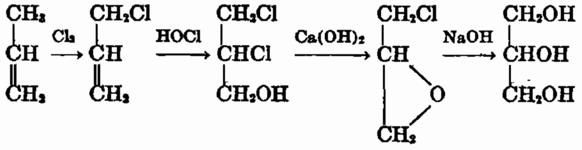
The liquid in the reactor is maintained at constant level by adjusting the drawoff. The temperature rises because of the exothermic reaction and is maintained at 200–210°C by lowering the temperature of the liquid feed. The ethylene oxide feed to the mixing vessel is at about −10°C. The water (condensate from evaporators) should not be above 20°C and must be below pH 7.

The reaction products leaving continuously via the drawoff are cooled from 180 to about 90°C and pass to an aerator tank where they are blown with nitrogen to drive off any acetaldehyde or crotonaldehyde. The liquid drawn from the bottom of the aerator tank is adjusted to a pH of 7–8 by means of a 30 per cent solution of sodium hydroxide.

The crude glycol passes to a storage tank and is then pumped through a preheater to the calandria of the first effect of a triple-effect evaporator. The concentrated glycol leaving the evaporator contains 5–15 per cent water. The removal of the remaining water is accomplished in a tall column operating at 10 mm Hg. The crude glycol from the base of this column is delivered to another column where ethylene glycol is removed overhead as a distillate. The higher glycols are removed at the base and rectified in separate stills. The percentage ratio of each product is 88.5 per cent ethylene glycol, 9.3 per cent diglycol, and 2.2 per cent triglycol.

Ethylene Oxide by Direct Oxidation of Ethylene. The ethylene oxide required for the preparation of glycol can also be obtained by the direct oxidation of ethylene. Air and ethylene are reacted in the presence of a silver catalyst at 220–240°C. Two reactors in series are used. The gas entering the first reactor contains 2.9 per cent by volume of ethylene, while the exit gases contain about 1.1 per cent ethylene oxide, 1.8 per cent carbon dioxide, and 0.9 per cent ethylene. This stream is enriched with ethylene to 2.9 per cent and introduced into the second reactor. The gas leaving this reactor contains 2.2 per cent ethylene oxide, 3.6 per cent carbon dioxide, and 0.9 per cent ethylene. About 90 per cent of the ethylene fed undergoes reaction. Approximately 60 per cent is converted to ethylene oxide and 40 per cent to carbon dioxide. The over-all yield of ethylene oxide based on ethylene fed is 50–55 per cent.

Preparation of Glycerol. When propylene is chlorinated at temperatures above 200°C, yields of 85–90 per cent of allyl chloride are obtained. This can be converted to glycerol by a number of procedures, one of which is depicted below.



A flow diagram for the production of glycerine[1] from propylene is shown in Fig. 13-9. The allyl chloride is converted to a mixture of dichlorohydrins by reaction with hypochlorous acid. This mixture is fed to a stirred reactor and contacted with a lime slurry at less than 140°F (57°C) where almost

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[1] *Petroleum Refiner*, **34** (12), 158–159 (1955); MINER and DALTON (eds.), Glycerol, ACS Monograph 117, pp. 80–83, 1953; *Chem. Eng.*, **55** (10), 134–137 (1948).

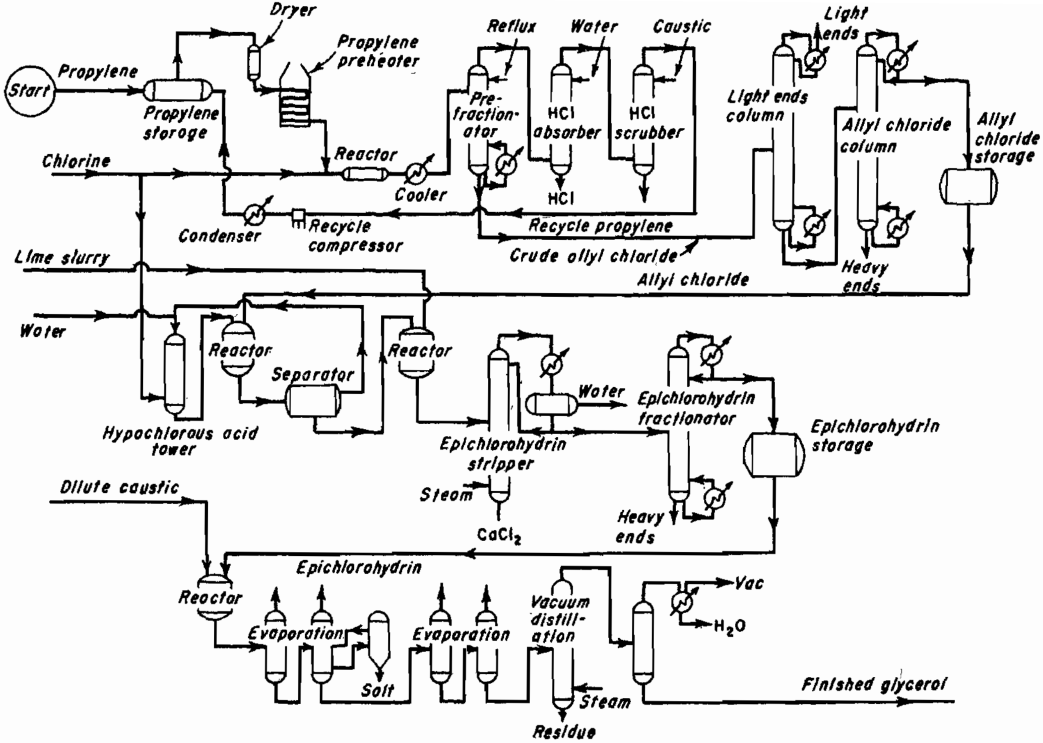

FIG. 13-9. Flow diagram for synthesis of glycerol. [*Petroleum Refiner*, **34** (12), 159 (1955), *by permission.*]

complete conversion to the epichlorohydrin is obtained. Glycerol is then formed from the epichlorohydrin by hydrolysis with dilute (10 per cent) sodium hydroxide in a stirred reactor. The product from this reaction is a dilute solution of glycerol containing salt. The salt and water are removed by evaporation. The salt crystalizes at an intermediate point in the multiple-effect evaporation system and is removed from the bottom of the evaporator. Crude glycerol is obtained from the final stage of evaporation where reduced pressures are used. This desalted glycerol may be extracted with a hydrocarbon solvent to remove color bodies and other impurities. High-purity glycerine is obtained from a final vacuum distillation. The product is stored in nickel-lined tanks and shipped in special aluminum tank cars. A tentative new process for synthetic glycerine likewise starts with propylene but proceeds by sulfuric acid treatment through isopropanol (a hydrolysis step) which is then reacted with acrolein to give ally alcohol. By hydroxylation with hydrogen peroxide, glycerol is obtained.[1]

Manufacture of Synthetic Phenol[2]

Synthetic phenol from benzene affords examples of three commercial methods of manufacture by hydrolysis. The process that dominated the field at first involves the caustic fusion of sodium benzenesulfonate. In this process, a seemingly large number of separate operations are required to effect the simple transformation

$$C_6H_6 \rightarrow C_6H_5OH$$

Although the by-products in each step of this process are advantageously employed in some phase of the synthesis, it is obvious, from the description below, that relatively large quantities of materials (4.3 lb per lb phenol) have to be handled. The process of the Dow Company, which accounts for a substantial percentage of domestic production, starts from chlorobenzene, hydrolyzing it under high pressure in an aqueous alkaline solution with copper as catalyst.

Patents[3] by Raschig and his associates describe processes whereby chlorobenzene is prepared from benzene by use of hydrochloric acid and oxygen at temperatures above 200°C, the chlorobenzene then being hydrolyzed by steam at temperatures above 350°C. The phenol and hydrochloric acid formed are separated from the reaction products while they are still in the gaseous state.

$$C_6H_6 + HCl + \tfrac{1}{2}O_2 \rightarrow C_6H_5Cl + H_2O$$
$$C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$$

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[1] *Chem. Week*, **78** (12), 44 (1956); *Petroleum Refiner*, **34** (12), 160 (1955).

[2] *B.I.O.S. Final Repts.* 1246 and 1841, Item 22; *F.I.A.T. Final Rept.* 768; *C.I.O.S. Rept.* XXIII–25, Item 22 (Combined Intelligence Objectives Sub-committee).

[3] Raschig, Fr. 730,462 (1932); 756,814 (1933); Ger. 588,649 (1933); U.S. 2,009,023 (1935); 2,035,917 (1936).

Another still more recent process which starts with cumene (isopropyl benzene) has attained considerable prominence. It does not involve hydrolysis, but consists of the oxidation of cumene to the hydroperoxide and the subsequent decomposition of the latter by sulfuric acid to phenol and acetone. Like the sulfonation process, it depends for its commercial success upon the sale of its by-products, chiefly acetone.

Sulfonation and halogenation of benzene are described in other chapters of this book. The initial discussion of phenol production will start with sodium benzenesulfonate and chlorobenzene as raw materials.

Phenol from Benzenesulfonic Acid. The reactions involved in the preparation of phenol via benzenesulfonic acid are as follows:

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O \tag{1}$$

$$2C_6H_5SO_3H + Na_2SO_3 \rightarrow 2C_6H_5SO_3Na + H_2SO_3 \tag{2}$$

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O \tag{3}$$

$$2C_6H_5ONa + H_2SO_3 \rightarrow 2C_6H_5OH + Na_2SO_3 \tag{4}$$

A simplified flow sheet of operations is shown in Fig. 13-10[1] in which the four

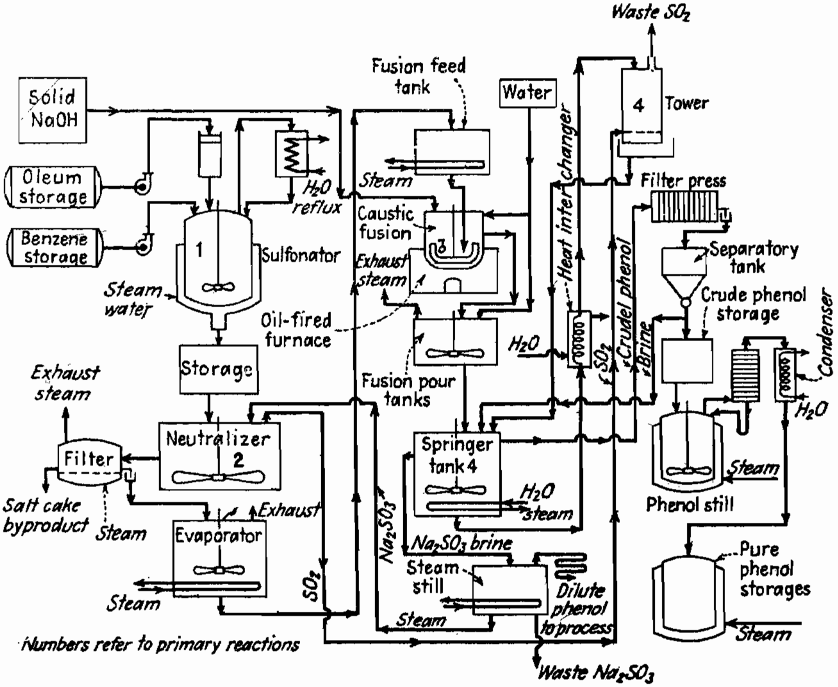

FIG. 13-10. Flow diagram for production of phenol via benzene sulfonic acid.

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[1] Callaham, *Chem. Met. Eng.*, **49**, 76 (1942).

primary reactions shown above are related to the entire process by numerals.

Sodium Benzenesulfonate. Benzenesulfonic acid prepared continuously in a cascade series of six 2,000-gal cast-iron vessels is fed to a neutralizer system.[1] Sodium sulfite slurry from reaction (3) is fed into the neutralization tank at a constant rate while the benzenesulfonic acid flow is regulated to keep the reaction mixture distinctly acid. Sulfur dioxide is liberated [Eq. (2)] and piped for acidification of sodium phenoxide [Eq. (4)], and some is sent to another plant for purification and liquefaction.

The slurry of sodium benzenesulfonate and sodium sulfate is transferred from the neutralizer (2), to a lead-and-brick-lined tank with agitator. Here, steam is blown in to remove the remaining sulfur dioxide. The slurry is then delivered to a final "adjusting" tank and made alkaline with sodium hydroxide solution. The mixture of sodium sulfate in aqueous sodium benzenesulfonate is fed to a battery of three solid-bowl continuous centrifuges. The first two effect the major separation of sodium sulfate from the solution. The separated sulfate, slurried with a small quantity of water, is sent to the third centrifugal. The solution of sodium benzenesulfonate from the first two centrifugals goes to the evaporators; solution from the third is used in neutralization. The washed sodium sulfate from the third centrifugal is kiln-dried and sold.

Evaporation. The solution of sodium benzenesulfonate, NaBS, enters the body of a standard cone-bottom evaporator, circulates through a system of three tubular heat exchangers, and then returns to the body of the evaporator. Vapors from the evaporator are scrubbed with sodium hydroxide to remove phenol, while sodium sulfate solution is continuously drawn off from the base. The NaBS from the evaporator is continuously delivered to steel settling tanks.

Fusion. Fusion of sodium benzenesulfonate is carried out in cast-iron pots (3) having vertical sides and dished-up bottoms which cause flattening rather than elongation at the temperature of operation. Sodium hydroxide (70 per cent) from an adjacent steam-heated tank is pumped by a nickel centrifugal pump into the warm fusion pot and evaporated nearly to dryness. When the temperature reaches 300°C, agitation of the molten mass is started and NaBS solution is pumped in at a metered rate under the surface of the caustic melt.

The temperature is maintained at 305–310°C for 6 hr and brought up to 330°C for an hour before the run is completed. Since the sodium sulfite formed is practically insoluble in a concentrated solution of caustic soda containing sodium phenoxide, the fusion mass is run into a vessel containing a measured quantity of sodium phenoxide wash waters from previous

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[1] **Kenyon** and **Boehmer**, *Ind. Eng. Chem.*, **42**, 1446–1455 (1950).

charges. The sodium sulfite separates out and is filtered off by pumping the aqueous suspension onto a nickel gauze or into a centrifugal filter. A saturated solution of sodium sulfite[1] or organic solvents[2] may be used to extract the sodium phenoxide from the sodium sulfite.

The water from previous washes is taken for the first wash and added to the solution of sodium phenoxide. The next two washes are saved for use in the quenchers and for washes, respectively.

Neutralization of the sodium phenoxide to release the phenol [Eq. (4)] may be done by carbon dioxide, mineral acids, benzenesulfonic acid, or preferably with the SO_2 liberated when the benzenesulfonic acid is treated with the by-product Na_2SO_3 to form the required sodium benzenesulfonate. Usually, some sulfuric acid must be finally added to ensure complete neutralization. The phenol containing some water separates out as an upper layer over an aqueous solution containing the appropriate sodium salt. The phenolic layer is separated and distilled *in vacuo*, while the aqueous layer, which still contains some phenol, goes back to the operating cycle.

Techniques of fusion have lately been markedly advanced, and continuous fusion processes have been studied. Acidification of the sodium phenoxide has been improved, and changes in distillation methods have resulted in a 40–40.6°C phenol becoming standard instead of the former 39°C.

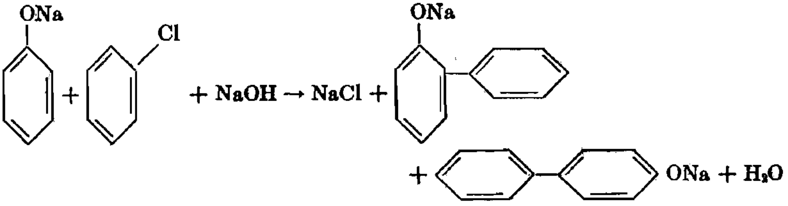
Phenol from Chlorobenzene, Dow Process. The Dow phenol process is based on the hydrolysis of chlorobenzene in caustic soda solution at temperatures of about 360°C and pressures of about 4,000 psi. Although the basic reaction was discovered in 1914 by Meyer and Bergius,[3] the development of the commercial application of the reaction had to await the introduction of satisfactory materials of construction and the solution of a number of chemical and chemical engineering problems.

The fundamental reactions are as follows:

$$C_6H_5Cl + 2NaOH \rightarrow C_6H_5ONa + NaCl + H_2O \qquad (1)$$

$$C_6H_5ONa + C_6H_5Cl \rightarrow C_6H_5{-}O{-}C_6H_5 + NaCl \qquad (2)$$

Side reactions also occur as follows:



(3)

Aylsworth showed that the reaction could be carried out by pumping the

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[1] U.S. 2,334,488 (1943).

[2] U.S. 2,281,485 (1942).

[3] MEYER and BERGIUS, *Ber. deut. chem. Ges.*, **47**, 3155 (1914).

reaction mixture at elevated temperatures through a tubular pressure system.[1] Putnam found that, by the use of heat exchange, the heat requirements of the reaction could be supplied by the exothermal reaction, thereby providing an economic basis of operation.[2] Finally, Hale and Britton showed that the diphenyl ether [Eq. (2)] produced in the process when returned as a reaction ingredient held its further production to a minimum.[3]

The plant for carrying out the process consists of a mixing tank for thoroughly mixing chlorobenzene, diphenyl ether, and caustic soda solution; a hydraulic pump capable of producing pressures up to 10,000 psi; a tubular autoclave, preferably built-in heat-exchange design, containing about 4,500 lineal feet of 1½-ft XX heavy pipe; a cooling coil; an accumulator-actuated discharge valve;[4] and the necessary storage tanks for the several products.

The reaction is carried out by placing in the mixing tank a mixture containing 2¼ moles of caustic soda as a 10 per cent solution per mole of chlorobenzene. After a good mixture has been obtained, the hydraulic pump is started and the mixture is initially heated to 350°C, which starts the reaction. With continuous pumping being carried on, the mixture enters the heat-exchange path; and after this equipment has been warmed up, the preliminary heating may be virtually eliminated because the reaction is thence continued in heat-exchange relation. The pumping rate is such that the mixture traverses the tubular autoclave in about 20 min. The pressure will be about 4,500 psi, although the vapor pressure of the solution would be only about 3,000 psi, the extra pressure being due to the pipe system itself. The accumulator discharge is set at about 3,200 psi. After many days of operation, the pressure necessary to force solution through the tubular autoclave increases owing to the formation of Fe_3O_4 in the tubes with subsequent partial plugging. This proceeds to a point where the system is completely plugged. The tubular autoclave is then dismantled, cleaned out, and repaired if necessary, and the cycle is resumed.

After the phenoxide solution is discharged from the autoclave, it is extracted with chlorobenzene to remove all alkali-insoluble material, viz., diphenyl ether and phenyl xenyl ether. The reaction mass is then acidified with hydrochloric acid to neutralize excess caustic and to liberate the phenols. The aqueous layer is put through a steaming-out tower to recover all dissolved phenol. The phenol layer is distilled to recover phenol, following which distillation is continued to recover ortho- and para-phenylphenols which are further purified for sale.

In the process, the chlorobenzene is converted to about 78 per cent phe-

[1] Aylsworth, U.S. 1,213,143 (1917).

[2] Putnam, U.S. 1,921,373 (1933).

[3] HALE and BRITTON, *Ind. Eng. Chem.*, **20**, 114 (1928).

[4] Griswold, U.S. 1,602,766 (1926).

nol, 11–12 per cent diphenyl ether, 7–8 per cent phenylphenols, 2–3 per cent higher ethers, and by-product tars and phenols. When the diphenyl ether is returned to the system as produced, the amount of chlorobenzene added is lessened by its diphenyl ether equivalent, and approximately the same amounts of products are produced.

Manufacture of Phenol by Regenerative Process.[1] The regenerative, or Raschig, process for the production of phenol is based on a combination of two well-known processes: (1) the production of chlorobenzene from benzene and hydrogen chloride and air (see Chap. 6) and (2) the hydrolysis of chlorobenzene with water vapor in the presence of a catalyst.[2]

An examination of the reactions that are involved show that the by-products obtained in one step are used in the other; thus,

$$C_6H_6 + HCl + O \xrightarrow[\text{catalyst}]{\text{copper chloride with iron chloride}} C_6H_5Cl + H_2O \tag{1}$$

$$C_6H_5Cl + H_2O \xrightarrow[\text{catalyst}]{Ca_3(PO_4)_2} C_6H_5OH + HCl \tag{2}$$

In the first step, hydrogen chloride is consumed and water is produced; in the second, water is consumed and hydrochloric acid is produced. It is clear, therefore, that by a suitable combination of the two steps, phenol can be produced in a most economical manner by the consumption of only benzene and atmospheric oxygen,

$$C_6H_6 + \tfrac{1}{2}O_2 \rightarrow C_6H_5OH \tag{3}$$

In addition to the pronounced economy in materials, there is a further advantage in that the process permits a most economical utilization of fuel, steam, and cooling water.

The process consists of two vapor-phase catalytic stages that are fundamentally simple but become complex in practice owing to the need for separating and recovering unreacted materials and the regenerated hydrochloric acid that circulates in the process.[3] In the first stage, benzene is reacted with air and hydrochloric acid to form monochlorobenzene and water. In the second, the monochlorobenzene is reacted with steam to regenerate the HCl and produce phenol. The per-pass conversion in stage I is 10–12 per cent; in stage II, 12–15 per cent.

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[1] This process is covered by a number of patents, in particular U.S. 1,963,761 and 2,035,917, which are assigned to F. Raschig, G.m.b.H. In the United States, the process was developed by Durez Plastics and Chemicals Corporation (now a division of Hooker Chemical Company) and is now used by other firms. See also *B.I.O.S. Final Repts.* 507 and 1841, Item No. 22.

[2] Redman, U.S. 2,311,777 (1943).

[3] Olive, *Chem. Met. Eng.*, **47**, 770–775, 789–792 (1940), with supplementary information by R. M. Crawford, Durez Plastics and Chemicals Corporation; Crawford, *Chem. Eng. Progr.*, **46**, 483 (1950).

It may be considered that the process starts with the preheater (Fig. 13-11).[1] Benzene vapor is preheated to 300°C and air to 150°C in separate parts of an oil-fired furnace and passed to a vapor mixer where they are mixed with hydrochloric acid vapors. The gaseous mixture enters the first-stage converters which contain a catalyst comprising copper chloride with iron chloride on alumina. The catalyst is maintained at 230–250°C by blowing air around the container tubes. This unit produces a mixture containing benzene, chlorobenzene, small amounts of dichlorobenzenes, plus residual hydrochloric acid and fixed gases. This mixture is separated by partial condensation and distillation operations which produce pure chlorobenzene for the second-stage reaction.

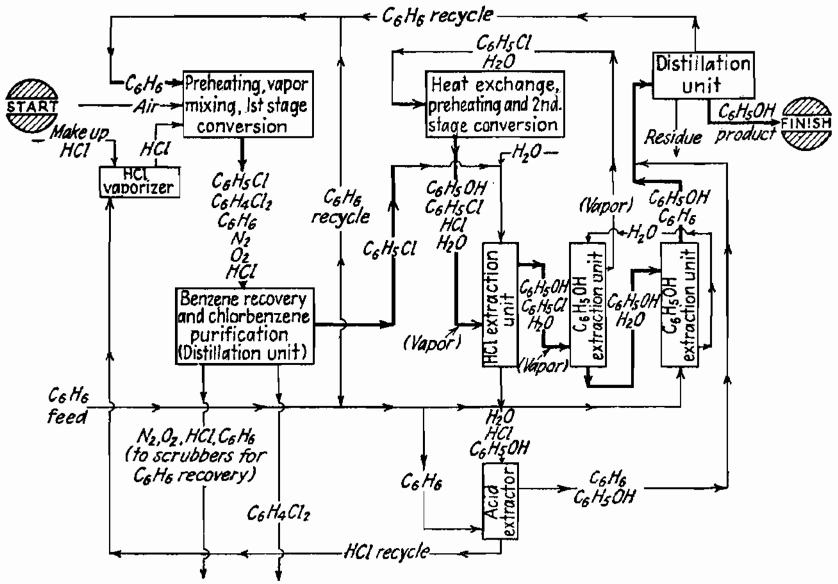

FIG. 13-11. Flow diagram for production of phenol by the (Durez-Raschig) vapor-phase catalytic process.

The logical starting point for discussion of the second-stage reaction is the introduction of the chlorobenzene and steam-vapor mixture to the heat exchangers and preheaters preceding the second-stage converters which contain a tricalcium phosphate catalyst at 450–500°C. The gases from this unit consist of a mixture of chlorobenzene, phenol, hydrochloric acid, and water. The acid is first removed by scrubbing with water in a tower which discharges the water azeotropes of chlorobenzene and phenol as an overhead product. The acid bottoms from the tower contain phenol, which

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[1] MESSING and KEARY, *Chem. Inds.*, July and August, 1948.

is recovered by benzene extraction prior to recycling of the hydrochloric acid to the first-stage reaction. The chlorobenzene and phenol mixtures are separated in a tower which utilizes hot water as a scrubbing fluid, producing a water solution of phenol as the bottoms product. The chlorobenzene-water azeotrope vapors from the top of this unit are recycled to the second-stage reaction step. Phenol is recovered from the phenol-water solution by continuous countercurrent extraction with benzene. Make-up benzene, equivalent to the quantity of phenol produced, is added at this point and utilized for this extraction. The resultant benzene-phenol mixture is then separated by distillation processes to recover benzene for recycle and to prepare the pure phenol product.

In recovering the hydrogen chloride from the hydrolytic step, it is essential to use only a limited quantity of water in the washing operations so that a 17 per cent solution is delivered to the acid evaporators. This is suitable for the subsequent step involving the halogenation of benzene. Operating in a closed cycle, the hydrochloric acid picks up impurities so that part of it must be purged continuously. This loss and that involved in the production of polychlorobenzenes constitute the replacement requirements of acid.

An over-all yield of 92 per cent of theory on benzene converted is believed to be representative.

Economic Summary. Phenol Production. A comparison of today's processes, including the cumene nonhydrolysis route, has been published by Tonn[1] and is summarized with some omissions in Table 13-6. Many of the figures in a table of this kind are necessarily uncertain, but some definite conclusions can be drawn from them.

The sulfonation process though old and sometimes regarded as out of date is showing remarkable vitality. It is a heavy user of raw materials (4.3 lb per lb of phenol produced) but furnishes as a by-product large amounts of sodium sulfate and sulfite, which find a ready market in Kraft paper mills. The recent Monsanto plant at Avon, Calif., designed to produce 24 million lb per year uses the sulfonation process.

Labor costs do not appear to differ materially among the processes; although they are highest for the sulfonation method. Continuous processing is basic to the Raschig process; it is utilized to a major extent in the chlorobenzene process and to some extent in the sulfonation process.[2]

Utility charges are highest for the chlorobenzene process chiefly because of the charge for power for electrolysis. Here the production of chlorine and chlorobenzene is considered as an integral part of the phenol process. If the chlorobenzene had to be bought, or acquired by intraplant transfer at "most favorable" market prices, the competitive position of this process would not appear so attractive. The Raschig process is the largest steam

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[1] TONN, *Chem. Eng.*, **61** (11), 157–160 (1954).

[2] KENYON and BOEHMER, *Ind. Eng. Chem.*, **42**, 1446–1455 (1950).

TABLE 13-6. PRODUCTION COST COMPARISON FOR SYNTHETIC PHENOL

	Process			
	Cumene	Benzene-sulfonate	Chloro-benzene	Raschig
Raw materials, cents/lb	9.5[*]	8.2	10.1	9.4
Utility costs, cents/lb	0.2	0.4	0.3	0.9
Power	0.05	0.15	0.075	0.20
Steam	0.10	0.16	0.188	0.60
Water	0.05	0.09	0.037	0.10
Labor costs, cents/lb	0.3	0.9	0.4	0.5
Maintenance costs, cents/lb	0.3	0.7	0.5	0.5
Depreciation and taxes, cents/lb	0.3	0.6	0.5	0.5
Manufacturing costs,[†] cents/lb	10.6	10.8	11.8	11.8
Selling price, cents/lb	18	18	18	18
Investment required, $/ton/year	280,[‡] 400[§]	270	400	420
Optimum plant size, million lb/year	15–30	15–40	50	30

[*] Based on purchased cumene.

[†] Credit given for by-products.

[‡] Phenol manufacturing facilities only.

[§] Cumene and phenol manufacturing facilities.

consumer because of relatively low per-pass conversion and consequent high distillation load. Fuel cost is highest in the sulfonation process because of the requirements for caustic concentration and fusion of sodium benzenesulfonate.

Any estimate of plant investment is necessarily approximate. Construction costs change markedly, and cost accounting is sometimes a matter of company policy. In this connection the sulfonation and chlorobenzene processes usually provide an outlet (and feedstock) for other plant products while the Raschig-Durez process depends only on contract benzene and by-product hydrochloric acid. Another item of importance is the fact that the Raschig process is a vapor-phase catalytic process while the others are liquid-phase operations involving relatively fixed relations between reactants. Assuming the possibility of achieving a 15 per cent instead of a 10 per cent per-pass conversion in either stage I (chlorination) or stage II (hydrolysis), in the Raschig process, this would represent an increased output of 50 per cent. Only minor increments of operating costs—the largest item of expense—would be incurred.

CHAPTER 14

ALKYLATION

BY R. NORRIS SHREVE AND LYLE F. ALBRIGHT

I. INTRODUCTION

Types of Alkylated Compounds. Alkylation may be defined as the introduction of an alkyl radical by substitution or addition into an organic compound. We also include under this procedure the introduction of an aralkyl radical, such as benzyl, and those alkylations presented in discussions of the Friedel-Crafts reaction in previous editions of this book. Alkylation is of six general types, depending on the linkage effected:

1. Substitution for hydrogen in carbon compounds. This is nuclear alkylation when an aromatic hydrogen is substituted. The carbon of the alkyl is bound to carbon of either aliphatic or aromatic compounds. This is carbon-to-carbon alkylation and includes the alkylations hereto classified under the Friedel-Crafts reaction, e.g.,

$$(CH_3)_3C—CH_2CH(CH_3)_2 \quad \text{and} \quad (HO)_2C_6H_3—CH_2(CH_2)_4CH_3$$

2. Substitution for hydrogen in the hydroxyl group of an alcohol or a phenol. Here the alkyl is bound to oxygen, e.g.,

$$C_2H_5O—C_2H_5 \quad \text{and} \quad C_6H_5O—CH_3$$

3. Substition for hydrogen attached to nitrogen. Here the alkyl is bound to trivalent nitrogen, e.g.,

$$C_6H_5N—(CH_3)_2$$

4. Addition of an alkyl halide or an alkyl ester to a tertiary nitrogen compound. Here the binding of the alkyl is to the nitrogen, and the trivalent nitrogen is often assumed to be converted to a pentavalent linkage. In reality, the nitrogen possesses four ordinary covalencies and one electrostatic bond, e.g.,

$$C_6H_5N—(CH_3)_3Cl \quad \text{or} \quad C_6H_5\overset{+}{N}—(CH_3)_3\overset{-}{Cl}$$

5. Alkyl-metallic compounds. Here the alkyl is bound to the metal, e.g.,

$$Pb(C_2H_5)_4 \quad \text{and} \quad C_6H_4(COONa)S{\cdot}Hg—C_2H_5$$

6. Miscellaneous alkylations. In mercaptans, the alkyl group is bound to sulfur; in the alkyl silanes, it is bound to silicon:

$$n\text{-}C_{12}H_{25}\text{—}SH \quad \text{and} \quad C_2H_5\text{—}SiCl_3$$

While the number of possible different alkyl radicals is very large, the following are the principal ones of technical importance: methyl, ethyl, propyl, butyl, amyl, and hexyl. The introduction of the aralkyl or benzyl radical, as well as the unsaturated allyl group, also is included here, for they are technically important. There are many other miscellaneous alkylations,[1] e.g., involving bonding to lithium, boron, phosphorus, germanium, thallium, selenium, etc.

Products Derived by Alkylation. An examination of the products obtained as a result of alkylation shows that this *unit process* is used in the making of anesthetics, antipyretics, alkaloids, antiseptics, detergents, dyes, explosives, flavors, hypnotics, intermediates, lubricants, medicinals, perfumes, photographic chemicals, plasticizers, plastics, resins, synthetic rubber, rubber chemicals (accelerators, antioxidants, modifiers, stabilizers), solvents, soporifics, synthetic gasoline, etc.

The petroleum industry first obtained gasoline by straight-run distillation. Next the longer molecules were cracked. Now gasoline is being synthesized on a large scale. For this purpose, the most important reaction in all probability is an alkylation wherein olefins, by the aid of catalysts, are made to combine with other molecules such as isoparaffins and aromatics.[2]

Alkylation plays an important role in the production of synthetic rubber of the GR-S type, this unit process being employed for the preparation of ethylbenzene from which styrene is derived. Much lauryl mercaptan has been manufactured for use as a modifier in making synthetic rubber.

Among our anesthetics, mention need be made only of ether and procaine, and, among antipyretics, acetophenetidine, antipyrine, and aminopyrine. In the field of alkaloids, opium contains some codeine, but to augment this supply, the phenolic hydroxyl of morphine is methylated. The caffeine market is supplied partly by methylation of theobromine, as well as by extraction and synthesis. Antiseptics include many alkylated products that exemplify several different types of alkyl linkage, hexylresorcinol and thymol being examples of nuclear alkylation, whereas in guaiacol we find oxygen alkylation, and in merthiolate, metal alkylation.

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[1] SHREVE, Alkylation, Annual Reviews, *Ind. Eng. Chem.*, **40**, 1565–1574 (1948); **41**, 1833–1840 (1949); **42**, 1650–1664 (1950); **43**, 1908–1916 (1951); **44**, 1972–1979 (1952); **45**, 1903–1912 (1953); **46**, 1789–1799 (1954); **47**, 1826–1839 (1955); **48**, 1551–1562 (1956). These annual alkylation reviews should be consulted by anyone wanting further information on *any phase* of the subject.

[2] See particularly EGLOFF and HULLA, "Alkylation of Alkanes," vol. I, Reinhold Publishing Corporation, New York, 1948; BROOKS et al., "The Chemistry of Petroleum Hydrocarbons," especially chaps. 54 and 57, Reinhold Publishing Corporation, New York, 1955.

The alkylation process enters into dye manufacture in two ways, because dyes may be formed from alkylated intermediates, or in a lesser number of instances, an intermediate may be subjected to alkylation as a final step. For instance, dimethylaniline is condensed with phosgene to give tetramethyldiaminobenzophenone (Michler's ketone). From this ketone are formed many dyes, such as crystal violet and Victoria blue. On the other hand, the alkylation process may be almost the last step in the manufacture of a dye, for example, when the disazostilbene dye, paper yellow 3G, is ethylated to give crysophenine G.

Among the booster explosives, we find trinitrophenylmethylnitramine, commonly called tetryl or tetralite. An outstanding example of an alkylated compound in the field of flavors is vanillin. Alkylation plays a striking part in the preparation of hypnotics, e.g., barbital (Veronal), phenobarbital (Luminal), and Amytal, rendering them lipoid-soluble.

Among alkylated intermediates, dimethylaniline has probably the most extensive and varied application. Other important members of this class are benzylethylaniline, benzylmethylaniline, diethylaniline, dianisidine, *m*-diethylaminophenol, and trimethylphenylammonium chloride. Alkyl silanes are used as intermediates for polymeric silicon organics which have great resistance to extreme temperatures. Perfumes include numerous instances of alkylated compounds, such as nerolin (β-naphthyl methyl ether) and artificial musk. As a photographic developer, Metol (N-methyl-*p*-aminophenol sulfate) has long held an important place. For germicides and detergents, alkyl quaternary compounds have attained an important place as either the final product or an intermediate. In the field of solvents, many new alkylated compounds have been synthesized, these being principally complex ethers of ethylene glycol, e.g., ethylene glycol ethyl ether and diethylene dioxide, or *p*-dioxane.

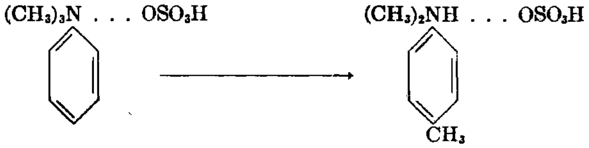
II. TYPES OF ALKYLATION

The six different types of alkylation treated in this chapter are sharply defined from a structural viewpoint. However, the linkage of alkyl to carbon, oxygen, nitrogen, or a metal can, in many instances, be effected by the same alkylating agent, e.g., ethyl chloride. Naturally, there is some variation in the conditions under which such a reagent is employed to produce these various compounds.

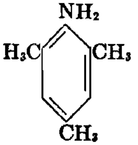
Alkyl Bound to Carbon. These compounds may be considered as being derived by the substitution of an alkyl group for hydrogen in carbon compounds. Examples are "alkylate" for synthetic gasoline, ethylbenzene for styrene entering into the manufacture of plastics and rubber, and hexylresorcinol, thymol, barbital, and other barbituric acid alkyl derivatives.

This type of alkylation is frequently referred to as alkylation of hydrocarbons, and many of the instances are nuclear alkylations. In the main, the same reagents are employed as for the other classifications.

In some instances, an alkyl bound to nitrogen or to oxygen may wander to the nucelus. For example, aniline is converted to dimethylaniline by heating to about 205°C with methanol and a small amount of sulfuric acid; if the temperature is raised to 250–300°C, considerable nuclear alkylation takes place, the reaction probably being as follows:



In the presence of excess methanol and at higher temperature (300–350°C), mesidine as well as the mono- and dimethyl derivatives are formed.



Mesidine

A similar wandering of the ethyl group in the case of diethylaniline has been studied by Johnson et al.[1] When aniline is alkylated, the alkyl group can react in many cases either nuclearly or at the nitrogen atom, depending mainly on the operating conditions. Even when the reaction is predominantly nuclear, the alkyl group is probably[2] first attached to the nitrogen atom and then wanders to the ring.

Hart and Eleuterio[3] alkylated phenols and cresols with methylphenylchloromethane. Both carbon and oxygen alkylation occurred. In the case of carbon alkylation, the reaction proceeded directly to the final product rather than via an intermediate ether. These authors[4] found, however, that alkyl aryl ethers did rearrange under the influence of fairly high temperatures so that the alkyl groups wandered to the nucleus.

Paraffins and aromatics can be alkylated with alkyl halides in the presence of catalysts, which generally are the Friedel-Crafts type. The alkyl

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[1] Johnson, Hill, and Donleavy, *Ind. Eng. Chem.*, **12**, 636–642 (1920).

[2] Kirk and Othmer, "Encyclopedia of Chemical Technology," vol. I, pp. 915–924, Interscience Publishers, Inc., New York, 1947.

[3] Hart and Eleuterio, *J. Am. Chem. Soc.*, **76**, 516–519 (1954).

[4] *Ibid.*, pp. 519–522.

group replaces a hydrogen on a carbon atom, and hydrogen halide is released.

Carbon-linkage alkylation includes the Wurtz reaction for the preparation of aliphatic compounds:

$$CH_3Br + 2Na + BrC_2H_5 \rightarrow CH_3{-}C_2H_5 + 2NaBr$$

Alcohols and ethers will often react with aromatic hydrocarbons to produce alkylated aromatics plus water. Both methanol and dimethyl ether are used[1] to alkylate various aromatics at temperatures from 250–600°C and at elevated pressures. Aluminosilicate is often employed[2] as a catalyst for these reactions. For liquid-phase reactions at lower temperatures and pressures, boron trifluoride[3] and hydrofluoric acid[4] have sometimes been found to be effective catalysts for condensing alcohols and aromatics.

Compounds which decompose readily into free alkyl radicals such as peroxides, mercaptans, etc., will alkylate hydrocarbons. Competitive reactions occur as follows:

$$R\cdot + R'H \rightarrow RH + R'\cdot \qquad (1)$$

$$R\cdot + R'H \rightarrow RR' + H\cdot \qquad (2)$$

The first reaction was found by Levy and Szwarc[5] to be predominant when methyl radicals attacked isooctane. The second reaction is predominant, however, for aromatic hydrocarbons. The free radicals formed in the above two reactions will react with each other, with other free radicals, or with impurities. The affinity of the methyl radical to attack an aromatic increases in the following order:[6] benzene, diphenyl ether, pyridine, diphenyl, benzophenone, naphthalene, quinoline, phenanthrene, pyrene, and anthracene. The ability of free alkyl radicals to interact with isopropylbenzene and cyclohexene decreases[7] in the following order: methyl, ethyl, propyl, butyl, isopropyl, *sec*-butyl, and tertiary butyl.

Olefin Alkylation of Paraffins.[8] Reactions involving paraffins and olefins may be represented as follows:

$$RH + R'CH{=}CHR'' \rightarrow R'RCHCH_2R''$$

where RH is a normal paraffin or isoparaffin and R′ and R″ are either hydrogen atoms or monovalent radicals, e.g., methyl or ethyl. Alkylation of RH involves addition of R at one of the doubly bound carbon atoms and hydro-

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[1] Morcom, Newling, and Plant, Brit. 577,314 (1946).

[2] Turova-Pollak, Levi, et al., *Doklady Acad. Nauk. S.S.S.R.*, **89**, 495–498 (1953).

[3] Hennion and Toussaint, U.S. 2,390,835 (1945).

[4] Pines et al., *J. Am. Chem. Soc.*, **73**, 4483 (1951).

[5] Levy and Szwarc, *J. Chem. Phys.*, **22**, 1621–1622 (1954).

[6] *Ibid.*

[7] Dolgoplosk, Erusalimskii, and Romanov, *J. Gen. Chem.* (*U.S.S.R.*), **24**, 1775–1782 (1954).

[8] Brooks et al., *op. cit.*, vol. 3, p. 363.

gen at the other. The R (alkyl) group sometimes wanders on the chain. Alkylations of this type form longer chain compounds of the paraffin and isoparaffin series.

Olefin Alkylation of Aromatics. Benzene, toluene, xylenes, naphthalene, and phenols are aromatics which are commonly alkylated. Either Friedel-Crafts type or protonic acid catalysts are normally used. Olefins frequently employed are ethylene, propylene, butene (isobutylene and butene-1), pentene, octene, nonene, and dodecene.

The nature of the alkylating action of normal butylene (butene-1) upon benzene[1] in the presence of sulfuric acid at 5 and 60°C follows from Fig. 14-1, which gives the solubility data for butylene in H_2SO_4. The stronger the sulfuric acid, the farther the alkylation proceeds and the higher is the boiling point of the product. The primary reactions may be represented thus:

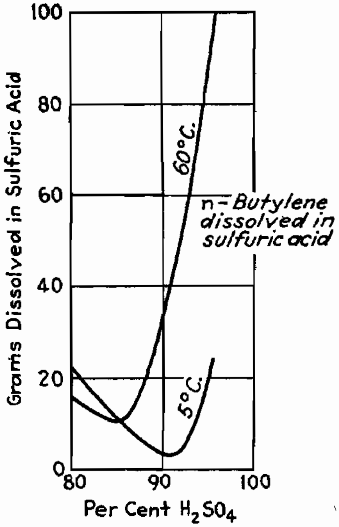
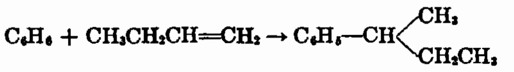


FIG. 14-1. Solubility of butene-1 in sulfuric acid.

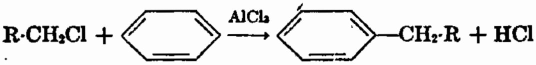


$$C_6H_6 + CH_3CH_2CH{=}CH_2 \rightarrow C_6H_5{-}CH\begin{matrix} CH_3 \\ CH_2CH_3 \end{matrix}$$

and polyalkylated products

Aluminum chloride catalyzes many alkylations. Paraffins, benzene,[1] toluene, and xylenes are alkylated by olefins and cyclopropane in the presence of aluminum chloride. Usually hydrogen chloride is needed as a promoter (see Alkylate for the Petroleum Industry).

The condensation of alkyl or aralkyl halides according to the Friedel-Crafts catalyst is a form of nuclear alkylation for the preparation of aromatic derivatives. The relative rates of alkylation for several aromatics



using Friedel-Craft type catalysts have been reported by Condon.[2] Toluene, ethylbenzene, cumene, and *tert*-butylbenzene have relative rates of 2.1, 1.8, 1.7, and 1.4, respectively, compared to benzene as 1.0. The relative rates of reaction for the meta and para positions were found to be approxi-

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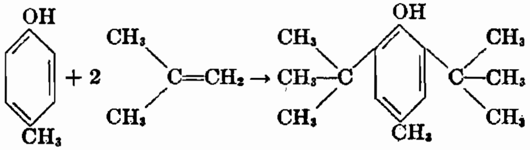
[1] IPATIEFF, W., "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, New York, 1936.

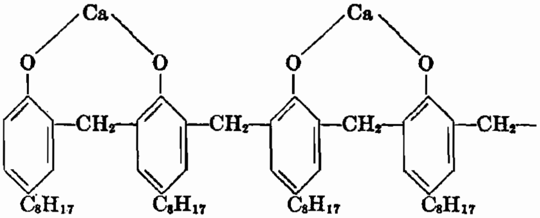
[2] CONDON, *J. Am. Chem. Soc.*, **70**, 2265 (1948).

mately equal. Steric hindrance, however, caused the rate to decrease at the ortho position as the size of the alkyl group increased.

Phenol and cresols that have been alkylated with tertiary olefins find uses as fuel additives that act as antioxidants and inhibitors.[1] The preparation of 2,6-di-*tert*-butyl-4-methylphenol is as follows:



Sulfuric acid is usually used as the catalyst, but Friedel-Crafts type catalysts are also effective for alkylations of this type. Relatively long olefins (about C_8) are employed to alkylate phenol, using sulfuric acid as a catalyst. Such alkylated phenols find use in producing oil additives. When formaldehyde is added to the alkylated phenol mixture, a condensation reaction occurs and the aromatic rings are linked together by methylene groups. Calcium hydroxide is employed to neutralize the mixture and to obtain the following oil additive:



Aromatic fractions can be alkylated with olefins to produce products which are used as *synthetic lubricants*.[2] An aromatic fraction boiling between 160 and 210°C is generally alkylated with C_{14} to C_{18} olefins in a ratio of about 2:1. A higher-boiling aromatic fraction (boiling between 210 and 260°C) is reacted with C_8 to C_{18} olefins in a ratio of 1:3. Aluminum chloride promoted with hydrogen chloride is the catalyst normally used. When the alkylated aromatics are blended with thickeners such as polyisobutylene, the mixture obtained is an excellent lubricant with a good viscosity index, stability, and pour point.

Alkyl Bound to Oxygen. The compounds of this class are generally prepared by substituting an alkyl group for a hydrogen in the hydroxyl group of an alcohol or a phenol. Typical compounds containing this alkylation linkage are the following:

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[1] Brooks et al., *op. cit.*, vol. 3, pp. 579–609.

[2] *Ibid.*

- Aliphatic ethers:
  - Cellulose ethers
  - Benzylcellulose
  - Carboxymethylcellulose
  - Ethylcellulose
  - Ethylene glycol ethers:
    - Carbitol
    - Cellosolve
  - Ethyl ether
  - Isopropyl ether
- Phenol ethers and derivatives:
  - Acetophenetidine
  - *o*-Anisidine
  - Anisole
  - Codeine (methyl ether of morphine)
  - *o*-Dianisidine
  - Guaiacol
  - *β*-Naphthyl methyl ether
  - *o*-Nitroanisole
  - Vanillin

Aliphatic Ethers. The aliphatic ethers used in industry are made usually by the action of sulfuric acid on an alcohol. Ethyl ether and isopropyl ether are thus prepared. However, more ethyl ether than the market usually absorbs is obtained as a by-product of the hydration of ethylene to alcohol. Alkyl halides react on a hydroxyl group either directly, in the presence of an alkali, or after the hydrogen of a hydroxyl group has been replaced by sodium. This is the Williamson synthesis which is particularly applicable to making mixed ethers:

$$C_2H_5ONa + CH_3I \rightarrow C_2H_5OCH_3 + NaI$$
$$C_2H_5OH + CH_3Cl + NaOH \rightarrow C_2H_5OCH_3 + NaCl + H_2O$$

Often, the cheaper and sufficiently satisfactory procedure is to react an alcohol and an alkyl halide in the presence of alkali.

The cellulose ethers are generally made by the action of alkyl or aralkyl halides on alkali cellulose. The reactions are carried out under pressure at about 100°C. The aralkyl derivative benzylcellulose, which is employed in the plastics industry, is made similarly:

$$[C_6H_7O_2(ONa)_3]_n + 3nC_6H_5CH_2Cl \rightarrow [C_6H_7O_2(OCH_2C_6H_5)_3]_n + 3nNaCl$$

Phenol Ethers. The phenol ethers are prepared similarly to the aliphatic ethers. An alkyl halide, a sodium alkyl sulfate, dialkyl sulfate, or alkyl toluenesulfonate is treated with a phenol in an alkaline medium (sodium ethylate) or in the presence of metal halides (cf. Anisole, Acetophenetidine, and vanillin). Naphthols are alkylated more easily than phenols, heating of naphthol with methanol in the presence of sulfuric acid or alumina being sufficient to give satisfactory yields.

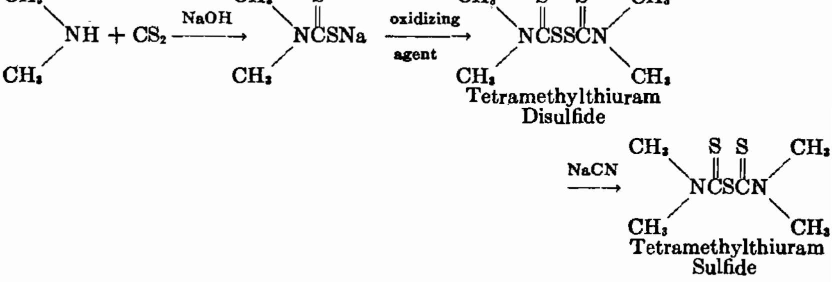
Alkaloids. Some of the most difficult oxygen alkylations are those involving the alkaloids, where the alkylation is often carried out to replace the hydrogen of the hydroxyl group in the presence of the tertiary nitrogen of the alkaloid. The best commercial example of the work that has been done with this particular group of compounds is the formation of codeine by the alkylation of the phenolic hydroxyl in morphine. Outlines of this alkylation with quaternary ammonium compounds are given under Codeine. Such a procedure is also used for theobromine, antipyrine, etc.

Alkyl Bound to Trivalent Nitrogen. In this division, the compounds may be considered as being derived by the substitution of an alkyl group for a hydrogen attached to a trivalent nitrogen. Examples of such substitutions are as follows:

- Aliphatic alkylamines:
  - Amylamines
  - Diethylamine
  - Dimethylamine
  - Adrenaline (side chain)
  - Methylamine
  - Procaine (side chain)
  - Tetramethylthiuram sulfide
  - Trimethylamine
- Heterocyclic alkylamines:
  - Pyramidone
  - Antipyrine
- Aromatic alkylamines:
  - Benzylethylaniline
  - *m*-Diethylaminophenol
  - Diethylaniline
  - *m*-Dimethylaminophenol
  - Dimethylaniline
  - Metol
  - Tetryl
- Alkaloids:
  - Caffeine
  - Codeine

Aliphatic Alkylamines. The aliphatic alkylamines are made in a variety of ways. For the lower amines, the action of an alcohol on ammonia or an amine in the vapor phase over aluminum oxide is a common method of preparation (see Chap. 8). For the higher amines, the action of an alkyl halide on ammonia in the liquid phase, often in the presence of the corresponding alcohol, is frequently used. Heat is often needed in the liquid-phase reactions, and autoclaves are then needed. The dialkyl sulfates are of particular importance because of their higher boiling points and ability to act as an alkylating agent on being heated in ordinary nonpressure vessels.

Often an alkyl group is introduced into a larger molecule by building it up from smaller molecules, one or more of which carry the alkyl group. For example, in the manufacture of the alkylated rubber accelerators, tetramethylthiuram disulfide, and sulfide [bis(dimethylthiocarbamyl) disulfide and sulfide], the alkyl groups are introduced as dimethylamine, which is itself a product of alkylation.



$$(CH_3)_2NH + CS_2 \xrightarrow{NaOH} (CH_3)_2N\overset{S}{\overset{\|}{C}}SNa \xrightarrow[agent]{oxidizing} (CH_3)_2N\overset{S}{\overset{\|}{C}}SS\overset{S}{\overset{\|}{C}}N(CH_3)_2$$

Tetramethylthiuram Disulfide

$$\xrightarrow{NaCN} (CH_3)_2N\overset{S}{\overset{\|}{C}}S\overset{S}{\overset{\|}{C}}N(CH_3)_2$$

Tetramethylthiuram Sulfide

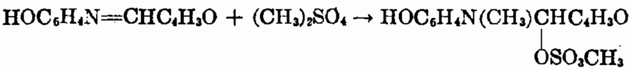
Aromatic Alkylamines. The preparation of aromatic alkylamines is exemplified in the commercial process for making dimethylaniline from methanol and aniline, using sulfuric acid as a condensing agent. A copper powder or salt is sometimes used as a catalyst.[1] Some of the methanol used in the process forms dimethyl ether, but yields of dimethylaniline higher than 97 per cent based on aniline can be obtained. Diethylaniline is made similarly, employing ethyl alcohol, but here sulfuric acid cannot be utilized because significant amounts of diethyl ether would be formed; consequently, hydrochloric acid is chosen instead.

Aniline can also be alkylated in the vapor phase at temperatures of about 400°C using methanol, dimethyl ether, ethyl alcohol, and diethyl ether. Alumina is reported[2] to be the most efficient catalyst for a continuous-flow process with aromatic amines. With other catalysts there is a greater alkylation in the ring.

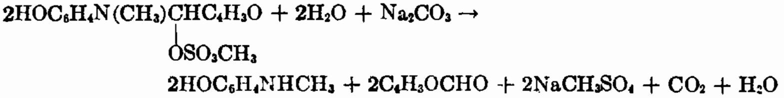
Benzyl alcohol in the presence of activated nickel and sodium benzylate has been found[3] to alkylate aniline readily. With para-substituted benzyl alcohols, the reaction rates decrease with the decreasing ability of the substituent to release electrons or in the following decreasing order: Me_3N, MeO, Me, H, and Cl. The reverse order was found when para-substituted anilines were condensed with benzyl alcohol.

The almost quantitative monoalkylation of *p*-aminophenol is claimed by Zimmerli by first forming an aldehyde amine before treating with the methylating agent.[4] With the use of furfural and dimethyl sulfate, the reaction in dry chlorobenzene as a solvent can be represented by the following equations:

$$\mathrm{HOC_6H_4NH_2 + C_4H_3OCHO \rightarrow HOC_6H_4N{=}CHC_4H_3O + H_2O} \qquad (1)$$



$$\mathrm{HOC_6H_4N{=}CHC_4H_3O + (CH_3)_2SO_4 \rightarrow HOC_6H_4N(CH_3)\underset{OSO_3CH_3}{\underset{|}{C}}HC_4H_3O} \qquad (2)$$



$$\mathrm{2HOC_6H_4N(CH_3)\underset{OSO_3CH_3}{\underset{|}{C}}HC_4H_3O + 2H_2O + Na_2CO_3 \rightarrow 2HOC_6H_4NHCH_3 + 2C_4H_3OCHO + 2NaCH_3SO_4 + CO_2 + H_2O} \qquad (3)$$

When alkylating primary, secondary, or tertiary aromatic alkylamines, much heat usually is evolved; this can be controlled by initial cooling or dilution. Such heat development is more pronounced when using dimethyl sulfate and alkyl toluenesulfonic esters than with alkyl halides, but even the latter must be handled carefully. To secure the best yields, no water must be present; if water is present, it will react with the dimethyl sulfate, yielding methyl sulfate, which will, in turn, form a salt with the amine and withdraw it from alkylation.

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[1] Kirk and Othmer, *op. cit.*

[2] Fuortes and Montagnani, *Ann. chim.* (*Rome*), **41**, 515–533 (1951).

[3] Pratt and Frazza, *J. Am. Chem. Soc.*, **76**, 6174–6179 (1954).

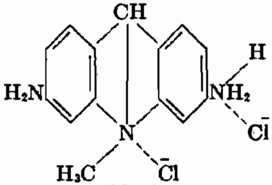
[4] Zimmerli, U.S. 1,987,317 (1935).

Heterocyclic Amines. Heterocyclic amines can be alkylated with alkyl halides or with alcohols in the presence of hydrogen plus a nickel catalyst. The Wallach reaction for the alkylation of amines by the action of aldehydes or ketones and formic acid has been studied for piperidine.[1] Reactions between toluene and cyclohexanone with piperidine and formic acid yielded 1-benzyl- and 1-cyclohexylpiperidine, respectively. An optimum amount of formic acid is desired since large amounts are harmful and wasteful.

Alkyl Bound to Pentavalent Nitrogen. In such compounds, alkylation is effected by addition, the trivalent nitrogen becoming pentavalent. There are not included here those tertiary alkyl compounds wherein the nitrogen becomes pentavalent by simple salt formation.

The preparation of this type of compound is relatively simple, in that an alkyl halide, an alkyl sulfate, or an alkyl ester is added to a tertiary amine. Details for the making of the quaternary ammonium compounds—phenyltrimethylammonium chloride and phenyltrimethylammonium tolylsulfonate—are described later under Codeine. These substances are excellent methylating agents, particularly when it is desired to methylate a phenolic hydroxyl in the presence of a tertiary nitrogen.

Acriflavine, a widely used medicinal dye containing a methylated pentavalent nitrogen, is prepared by methylating the tertiary ring nitrogen in diaminoacridine by either dimethyl sulfate or methyl *p*-toluenesulfonate in nitrobenzene or a benzene solution. Although generally the two amino groups have been protected by acetylation prior to the methylation of the ring nitrogen, this step is not necessary. The methylated product is converted by hydrochloric acid to the chloride monohydrochloride which is known as acriflavine.



Acriflavine

Quaternary ammonium compounds have in addition found use as germicides, bactericides, disinfectants, fungicides, insecticides, wetting or dispersing agents, muscle relaxers, and antispasmodic agents.

Alkyl Bound to a Metal. The alkyl group may be caused to unite with metals, such as lead, mercury, zinc, magnesium, and arsenic. Examples of this type of alkylation are tetraethyllead, merthiolate, ethyl mercury chloride, and ethyl mercury phosphate. Among the lethal poison gases

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[1] STAPLE and WAGNER, *J. Org. Chem.*, 14, 559–578 (1949).

is ethyldichloroarsine, $C_2H_5AsCl_2$, which is prepared by the following reactions:

$$C_2H_5Cl + Na_3AsO_3 \rightarrow C_2H_5AsO_3Na_2 + NaCl \quad (1)$$

$$C_2H_5AsO_3Na_2 + H_2SO_4 \rightarrow C_2H_5AsO_3H_2 + Na_2SO_4 \quad (2)$$

$$C_2H_5AsO_3H_2 + SO_2 + H_2O \rightarrow C_2H_5AsO_2H_2 + H_2SO_4 \quad (3)$$

$$C_2H_5AsO_2H_2 \rightarrow C_2H_5AsO + H_2O \quad (4)$$

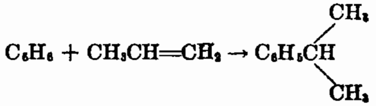
$$C_2H_5AsO + 2HCl \rightarrow C_2H_5AsCl_2 + H_2O \quad (5)$$

Alkyl Bound to Miscellaneous Elements. Several compounds in which alkyl is bound to a sulfur atom have become quite important in recent years; for example, the mercaptans, such as amyl and ethyl mercaptan, are used as warning agents in natural gas because of their intense and disagreeable odor. Mercaptans are also employed in organic syntheses as, for instance, the manufacture of sulfonal by the condensation of ethyl mercaptan (ethanethiol) with acetone, followed by oxidation. In recent years a very considerable amount of mercaptan has been used for controlling the polymerization reaction between butadiene and styrene to form synthetic rubber (GR-S).

III. ALKYLATING AGENTS

Olefins. The alkylating agents employed most extensively for carbon-carbon alkylations are ethylene, propylene, butylenes, and amylenes. Ethylene and propylene are obtained from petroleum-cracking operations. These olefins as well as butylenes and amylenes are also obtained by dehydrogenating ethane, propane, butanes, and pentanes, respectively. In general, the olefins of higher molecular weight, e.g., amylene, and most branched chains, e.g., *tert*-butyl derivatives, react more readily than do propylene and ethylene. The olefins tend to polymerize and are, therefore, often employed in the presence of an excess of the other reactant, which may be benzene or isobutane. During the course of the reaction, there is a transfer of hydrogen from the carbon of an aliphatic, aromatic, or hydroaromatic compound to the carbon of the olefin, thereby forming an alkyl radical. These reactions may be represented thus:

$$C_4H_8 + C_4H_{10} \rightarrow C_4H_9{\cdot}C_4H_9$$



$$C_6H_6 + CH_3CH{=}CH_2 \rightarrow C_6H_5CH(CH_3)_2$$

$$C_6H_6 + CH_2{=}CH_2 \rightarrow C_6H_5C_2H_5$$

In most cases, olefins are used to only a relatively limited extent for alkylations other than the carbon-carbon type, although they are employed to make other alkylating agents such as ethyl chloride and isopropyl hydrogen sulfate.

Alcohols. Methanol and ethanol have long been important alkylating agents, especially for nitrogen bonding. In practically every case, a catalyst is necessary to cause the alkylation to proceed smoothly, and in many instances, this is a mineral acid. Alcohols are used in the manufacture of ethers, such as ordinary ethyl ether, isopropyl ether, Carbitol, Cellosolve, and naphthyl methyl ether. It should be noted that, although naphthols react with alcohol in the presence of a mineral acid, the aryl alkyl ethers cannot be formed by this reaction in the case of phenols.

Dimethylaniline is made from aniline and methanol in the presence of a small amount of sulfuric acid, whereas diethylaniline is prepared from aniline and ethyl alcohol using hydrochloric acid. The ethylation does not proceed so completely as the methylation.

The alcohols are employed to effect the replacement of aromatically bound halogen atoms by heating in the presence of an alkali. In this way, *p*-nitrophenetole and *o*-nitroanisole are made by treating *p*-nitrochlorobenzene with ethanol and *o*-nitrochlorobenzene with methanol.

The lower alcohols have also been employed extensively for the catalytic vapor-phase synthesis of alkylamines and for the alkylation of phenols.

Alkyl Halides. The alkyl halides are probably the most commonly used laboratory alkylating agents and are also employed for certain manufacturing processes where the alkyl halide is available economically, as in making tetraethyllead. Most of the lower alkyl halides are now abundant and cheap because of recent developments relating to (1) addition of HCl to olefins and (2) chlorination of paraffins. These reactions are discussed at length in Chap. 6. Certain of the lower alkyl halides are so volatile that they must be used in autoclaves. While the chlorides are frequently employed because of their cheapness, other alkyl halides have occasionally given sufficiently higher yields to justify their increased cost. This has been true of alkyl bromides in certain carbon-to-carbon alkylations for the preparation of barbiturates.

The tertiary alkyl halides react vigorously and, in the case of *tert*-amyl chloride, can alkylate phenols without the intervention of a catalyst. Methyl iodide is used in the preparation of such methylated products as Pinaverdol and other sensitizing dyes, which possess a pentavalent nitrogen.

Phenols, such as *o*-nitrophenol (cf. Acetophenetidine), are alkylated by heating with alkyl chlorides in the presence of aqueous alkali. Methyl and ethyl bromides or iodides react very smoothly and, in spite of their cost, find application in the field of dyes and medicinal products, e.g., pyramidone and antipyrine, for the preparation of simple and mixed ethers and for the alkylation of phenols and amines. Allyl bromide is employed for making diallylbarbituric acid (Dial).

Alkyl Sulfates. The alkyl sulfates used most frequently are dimethyl sulfate, methyl hydrogen sulfate, and diethyl sulfate. Sulfates with longer alkyl groups are employed, however, in some cases. Dimethyl sulfate is very toxic and should be handled with care. The alkyl sulfates often give higher yields than the alkyl halides but except for methyl and ethyl sulfates are more expensive.

The alkyl sulfates are frequently employed for carbon-oxygen type alkylations to obtain compounds such as dialkyl ethers, alkyl aryl ethers, ethyl cellulose, cellosolve, and polyvinyl ethers. Alkyl sulfates have also been employed to alkylate nitrogen atoms for such compounds as caffeine, acriflavine, and diethylaniline. Both alkyl groups of dialkyl sulfates react if the reaction system is practically anhydrous. In the presence of a substantial amount of water, however, only one group reacts. In certain instances, monoalkyl sulfate may be regarded as the active alkylating reagent as, for example, in the formation of ether from ethyl alcohol and sulfuric acid.

Aralkyl Halides. Benzyl chloride is almost universally used for the introduction of the benzyl group, for instance, in the preparation of benzylethylaniline from ethylaniline. In actual practice, the benzylethylaniline is usually obtained by treating a mixture of ethylaniline and diethylaniline and fractionating. Benzyl chloride is also used in the preparation of benzylcellulose.

Arylsulfonic Alkyl Esters. The methyl or ethyl esters of *p*-toluenesulfonic acid are used to alkylate certain amines for which alcohols give unsatisfactory yields. Under Codeine (*q.v.*) is described the use of methyl benzenesulfonate and of methyl toluene sulfonate in the preparation of tetraalkylammonium compounds. The higher alkyl (C_{16} and above) esters of *p*-toluene sulfonic acid have been used[1] as alkylating agents for amines, mercaptans, and thiophenols and for phenolic groups. These higher alkyl esters of *p*-toluenesulfonic acid are more satisfactory than the sluggish higher alkyl halides and are more easily obtained than the higher alkyl sulfates.

Alkyl Quaternary Ammonium Compounds. These have long been applied in certain special fields, and their further use may well be warranted in many instances. A detailed specific example of this application is given under Codeine, where the preparation and use of phenyltrimethylammonium chloride, $C_6H_5N(CH_3)_3Cl$, is described. These quaternary alkyl substances have also been recommended for alkylations leading to phenetole, antipyrine, pyramidone, acriflavine, and caffeine.

Metallic Alkyl Derivatives. The alkylmagnesium halides are frequently too expensive for commercial application, but they can be used to make alkylphenols, to prepare other metal alkyls and silicon alkyls from the

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[1] Shirley, Zietz, and Reedy, *J. Org. Chem.*, **18**, 378–381 (1953); Shirley and Reedy, *J. Am. Chem. Soc.*, **73**, 4885–4886 (1951); Shirley and Zietz, *J. Org. Chem.*, **18**, 1591–1593 (1953).

corresponding halides, and in many laboratory syntheses. The Grignard synthesis is particularly applicable for making mixed ethers:

$$C_2H_5MgCl + ClCH_2OCH_3 \rightarrow C_2H_5CH_2OCH_3 + MgCl_2$$

Alkylzinc halides, zinc dialkyls, and tetraethyllead are also occasionally employed as alkylating agents. Alkylzinc and alkylmagnesium halides are prepared by the action of the alkyl halide on the metal (or a copper-zinc alloy), usually suspended in a dry solvent such as ether, benzene, or toluene. Alkyl halides of less active metals are obtained from the metal halide by the action of alkylzinc or alkylmagnesium halide. Distillation of alkylzinc halides gives the zinc dialkyls (spontaneously flammable), which are very useful in difficult alkylations:

$$(CH_3)_3CCl + R_2Zn \rightarrow (CH_3)_3CR + RZnCl$$

Miscellaneous Alkylating Agents. Noller and Dutton have studied the trialkyl phosphates as alkylation agents.[1] They found that ethers are formed by using one equivalent of the trialkyl phosphate per mole of phenol. The yields of the ether in Table 14-1 are based on the amount of the alkyl radical available and hence are a measure of the relative alkylating ability of the various sulfate or phosphate esters. Dialkyl oxalates[2] and ethyl-ε-bromosorbate[3] have also been used to alkylate phenol and cresols.

TABLE 14-1. YIELDS OF PHOSPHATES AND PHENOL ETHERS

Ester	Phosphates		Phenol ethers	
	Yield, %	Bp, °C	Yield, %	Bp, °C
Ethyl sulfate	....	....	73.0	168–170
Ethyl phosphate	51.7	104–107 (16 mm)	21.6	167–170
n-Propyl phosphate	63.5	128–134 (15 mm)	Not run	
n-Butyl phosphate	74.0	160–162 (15 mm)	39.0	204–211
sec-Butyl phosphate	44.0	119–129 (8–12 mm)	18.7	188–198
n-Amyl phosphate	63.7	158–163 (6 mm)	15.0	125–128 (25 mm)

Alkylene Oxides. Various compounds are hydroxyalkylated, using various alkylene oxides. Ethylene oxide is the agent most frequently used, but propylene, butylene, and styrene oxides are also employed. These alkylene oxides will, under the proper circumstances, react with compounds containing —OH, =N—H, and —S—H groups to form carbon bonds

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[1] NOLLER and DUTTON, *J. Am. Chem. Soc.*, **55**, 424 (1933); *cf.* Consortium für Electrochem. Ind., Brit. 433,927 (1935).

[2] MATSUURA and SAKAKIBARA, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **73**, 367–368 (1952).

[3] UNGNADE and HOPKINS, *J. Am. Chem. Soc.*, **73**, 3091–3093 (1951).

between the oxygen, nitrogen, and sulfur, respectively. The hydrogen atom which is replaced forms a valence bond with the oxygen in the alkylene oxide. Compounds which have been obtained include diethylene glycol, triethylene glycol, Cellosolve, Carbitol, monothioethylene glycol, tertiary alkyl mercaptoalkanols, and ethanolamines. Side chains have also been added to nylons using ethylene oxide.[1]

IV. FACTORS CONTROLLING ALKYLATION

Thermodynamics

Various thermodynamic functions (latent heat of vaporization and $(F^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, and S° of the ideal gas at 1 atm) and physical properties (vapor pressure, viscosity, PVT relationship, etc.) have been tabulated in API Project 44[2] for the most important hydrocarbons including normal paraffins, isoparaffins, olefins, and aromatics. The heats of formation and the standard free energies of formation can be calculated for the ideal gaseous state using these data. Such information is reported[3] for several alkylbenzenes, as shown in Tables 14-2 and 14-3. The data of API Project 44 can also be used to calculate most of the equilibrium constants for the reactions occurring in commercial carbon-alkylation processes. In many cases, the reactions occurring during carbon alkyl-

TABLE 14-2. VALUES OF HEATS OF FORMATION AND OF STANDARD FREE ENERGY OF FORMATION FOR SEVERAL ALKYL BENZENES FOR THE IDEAL GASEOUS STATE*

(In Kg-Cal per Mole)

Compound (gas)	Temperature, °K							
	0		298.16		500		700	
	ΔH_f°	ΔF_f°	ΔH_f°	ΔF_f°	ΔH_f°	ΔF_f°	ΔH_f°	ΔF_f°
Benzene	24.000	24.00	19.820	30.989	17.536	39.242	16.040	48.211
Toluene	17.500	17.500	11.950	29.228	9.005	41.811	7.067	55.306
Ethylbenzene	13.917	13.917	7.120	31.208	3.699	48.554	1.529	66.921
o-Xylene	11.096	11.096	4.540	29.177	1.189	46.852	−1.076	65.548
m-Xylene	10.926	10.926	4.120	28.405	0.571	45.906	−1.792	64.482
p-Xylene	11.064	11.064	4.290	28.952	0.680	46.724	−1.751	65.604
n-Propylbenzene	9.810	9.810	1.870	32.810	−2.06	54.94	−4.52	78.22
Cumene	9.250	9.250	0.940	32.738	−3.01	55.46	−5.44	79.33

* These data have been tabulated from TAYLOR et al., "Heats, Equilibrium Constants, and Free Energies of Formation of the Alkylbenzenes," *J. Research Natl. Bur. Standards*, **37**, 109, 111 (1946). Data for 400 and 600°K also are given in this reference.

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[1] HAAS, COHEN, et al., *J. Polymer Sci.*, **15**, 427–446 (1955).

[2] ROSSINI (director), "Selected Values of Properties of Hydrocarbons and Related Compounds," API Project 44, Carnegie Institute of Technology, 1955.

[3] ROSSINI and KNOWLTON, *J. Research Natl. Bur. Standards*, **19**, 339–345 (1937); TAYLOR et al., *ibid.*, **37**, 95–122 (1945).

TABLE 14-3. VALUES OF EQUILIBRIUM CONSTANTS FOR SOME REACTIONS OF BENZENE ALKYLATION*

Reaction	Temperature, °K				
	298.16	500	800	1100	1500
C_6H_6 (*g*) + C_2H_4 (*g*) = C_8H_{10} (*g*) (ethylbenzene)	5.940×10^{11}	2.196×10^{4}	1.908	3.004×10^{-2}	1.712×10^{-3}
C_6H_6 (*g*) + C_3H_6 (*g*) = C_9H_{12} (*g*) (*n*-propylbenzene)	4.30×10^{9}	8.47×10^{2}	1.96×10^{-1}	4.99×10^{-3}	3.95×10^{-4}
C_6H_6 (*g*) + C_3H_6 (*g*) = C_9H_{12} (*g*) (isopropylbenzene)	4.85×10^{9}	4.99×10^{2}	8.16×10^{-2}	1.76×10^{-3}	1.29×10^{-4}
C_6H_6 (*g*) + C_nH_{2n} (1-alkene, *g*) = $C_nH_{2n+1}C_6H_5$(*n*-alkylbenzene, *g*) $n > 3$	9.12×10^{9}	1.17×10^{3}	0.209	4.64×10^{-3}	3.29×10^{-4}

* These data have been tabulated from TAYLOR et al., "Heats, Equilibrium Constants, and Free Energies of Formation of the Alkylbenzenes," *J. Research Natl. Bur. Standards*, **37**, 119 (1946).
(*g*) = gas.

ation are sufficiently slow so that equilibrium is not reached. The equilibrium constants are, however, of value for calculating the extent of a reaction possible for a given set of operating conditions.

Carbon alkylations are generally exothermic. The heat of reaction can be determined using the available thermodynamic and physical properties.[1] These heats are used in designing reactors and auxiliary heat exchangers.

Mechanisms of Reaction

Considerable research has been devoted to studies to elucidate the mechanism and characteristics of alkylation reactions. Although the present information is incomplete, the mechanisms of several commercial reactions have been determined with fair certainty. A knowledge of the mechanism is of value for developing kinetic equations applicable over wide ranges of operating conditions and also for planning research for process improvements and modifications.

Mechanisms for Liquid-phase Alkylations of Hydrocarbons. Either Friedel-Crafts or protonic acid catalysts are often used when liquid isoparaffins or aromatic hydrocarbons are alkylated with olefins. These catalysts are generally considered to be proton donators which form carbonium ions.[2] The basic reactions are probably similar for all catalysts, and the reaction temperatures are all relatively close to room temperature, about −40 to 30°C.

A typical alkylation may be represented by the following series of reactions:

$$CH_2{=}CH_2 + HCl + AlCl_3 \rightleftharpoons CH_3{-}CH_2^+ + AlCl_4^- \qquad (1)$$

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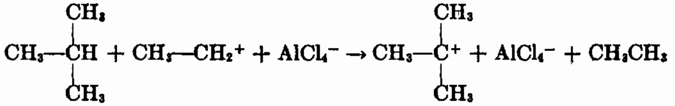
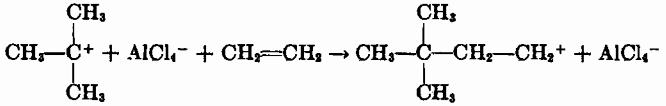
[1] ROSSINI, API Project 44, *op. cit.*

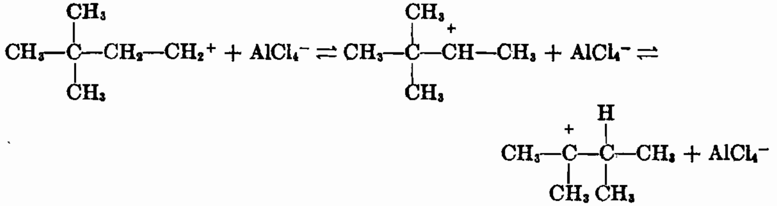
[2] BROOKS et al., *op. cit.*



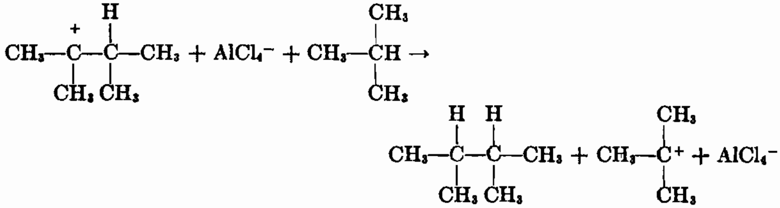
$$CH_3-\underset{CH_3}{\overset{CH_3}{CH}} + CH_3-CH_2^+ + AlCl_4^- \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + AlCl_4^- + CH_3CH_3 \qquad (2)$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + AlCl_4^- + CH_2{=}CH_2 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2^+ + AlCl_4^- \qquad (3)$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2^+ + AlCl_4^- \rightleftharpoons CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{C}H-CH_3 + AlCl_4^- \rightleftharpoons CH_3-\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 + AlCl_4^- \qquad (3a)$$



$$CH_3-\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 + AlCl_4^- + CH_3-\underset{CH_3}{\overset{CH_3}{CH}} \rightarrow CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 + CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + AlCl_4^- \qquad (4)$$

The *tert*-butyl ion formed in Eq. (4) starts another alkylation cycle, Eqs. (3), (3*a*), and (4). Although carbonium ions are presumably formed by all the usual catalysts (e.g., HF, H_2SO_4, $AlCl_3$), the anions will, of course, vary with the catalysts. The role of hydrogen chloride when used with aluminum chloride is to increase the acidity of the catalyst and hence make it more effective. The activity of boron trifluoride is similarly increased by trace quantities of water or hydrogen fluoride. When sulfuric acid is used as a catalyst, the concentration and the resulting acidity must be carefully controlled.

Side reactions such as polymerization, isomerization, hydrogen transfer, and destructive alkylation occur during the catalytic alkylation of isoparaffins and aromatics with olefins. All these reactions can be explained by means of the carbonium-ion theory.[1] In the case of polymerization, the carbonium ions such as formed in Eqs. (1) and (3) react with olefins, causing chain growth. Polymerization is minimized by using relatively large excesses of isoparaffins or aromatics. Normal paraffins are not generally alkylated satisfactorily using catalysts. The hydrogen atoms joined to primary or secondary carbon atoms are apparently not labilized so easily as that attached to the tertiary carbon of isobutane; polymeri-

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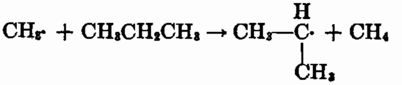
[1] *Ibid.*

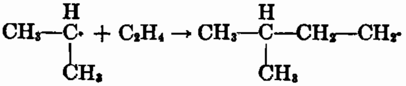
zation of the olefins, instead, is the main reaction. Certain side reactions also occur between the catalyst and the hydrocarbons. For example, sulfuric acid partially oxidizes hydrocarbons and releases sulfur dioxide, especially at high acid concentrations and at fairly high temperatures. As a result, sulfuric acid alkylations are generally operated at lower temperatures than other alkylations. When hydrofluoric acid is used as the catalyst, some alkyl fluorides are formed if the water content of the reactor becomes too high.

Mechanisms of Vapor-phase Alkylations of Hydrocarbons. Paraffins can be alkylated in the absence of catalysts at sufficiently high temperatures, about 500°C, so that a small amount of the paraffins will decompose into free radicals. A free-radical mechanism for the alkylation seems probable,[1] as is shown below for the reaction between propane and ethylene:

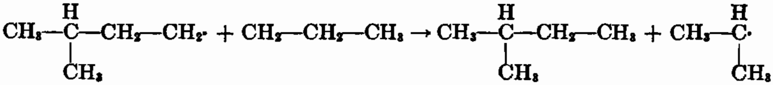
$$CH_3-CH_2-CH_3 \rightarrow CH_3\cdot + C_2H_5\cdot \qquad (1)$$



$$CH_3\cdot + CH_3CH_2CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{H}{C}}\cdot + CH_4 \qquad (2)$$



$$CH_3-\underset{CH_3}{\overset{H}{C}}\cdot + C_2H_4 \rightarrow CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-CH_2\cdot \qquad (3)$$



$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-CH_2\cdot + CH_3-CH_2-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-CH_3 + CH_3-\underset{CH_3}{\overset{H}{C}}\cdot \qquad (4)$$

The isopropyl radical formed in Eq. (4) starts a new alkylation cycle [see Eqs. (3) and (4)]. When propane reacts with free radicals as in Eqs. (2) and (4), *n*-propyl radicals are sometimes obtained; however, isopropyl radicals are formed predominantly. As a result, more isopentane is produced than *n*-pentane. Side reactions occurring include olefin polymerizations which also follow a free-radical path and produce higher-molecular-weight hydrocarbons. Polymerization is minimized by decreasing the olefin: paraffin ratio and hence reducing the probability of the free radicals formed in Eq. (3) reacting with more olefin molecules. Another side reaction occurs when two free radicals react with each other. For example, when two propyl radicals combine, a hexane will be formed. Such a reaction is favored by the presence of high concentrations of free radicals. Because of the relatively high temperatures used in thermal alkylation, some cracking, dehydrogenation, and isomerization of the hydrocarbons occur in most cases. The high pressures, about 2,500–4,000 psi, normally used for thermal alkylation processes tend to favor the alkylation steps and to suppress most of the side reactions.

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[1] *Ibid.*

When about 1–3 per cent of an aliphatic halogenated compound or a nitro compound is added to a paraffin-olefin mixture, the alkylation reaction proceeds at milder temperatures, about 300–400°C. The substances that are effective have a relatively low thermal stability and form free radicals at the reaction temperatures. The free radicals react similarly to those of Eqs. (3) and (4). The products obtained contain some chlorine atoms when a chlorinated initiator is used; otherwise the products are similar to those in which no initiators are used.

Mechanisms of Carbon-Oxygen Alkylations. Kinetic studies have been made[1] of reactions between chlorinated hydrocarbons and sodium or potassium alcoholates. The rate data indicate second-order equations between the reactants. Phenol and substituted phenols were alkylated using sulfonic acid esters.[2] The rates of the reactions depend on the substituent on the aromatic ring. The relative velocities were as follows: *p*-cresol, 1.58; 2-naphthol, 1.46; phenol, 1.0; salicyclic acid, about 0.3; *p*-chlorophenol, 0.16; and *o*-cresol, less than 0.12. Electronic considerations are probably the cause of the different reaction rates.

Catalysis. An apparent characteristic of many alkylation and dealkylation reactions is their initial slowness, and it has been necessary to resort to catalysis to make the reactions proceed at a rate that will be commercially feasible. Mineral acids, such as sulfuric, phosphoric, hydrochloric, and hydrofluoric, are widely employed as are aluminum chloride, ferric chloride, boron fluoride, etc. With a wide variety of catalysts and alkylating agents to choose from, the choice of agents to use will depend on the relative costs and the reaction rates which will result.

Concentration of Reactants. An excess of the methylating agent acts frequently to better the yield. This is particularly true when the less vigorous alkylating agents, such as the alcohols, are employed. In the preparation of dimethyl or diethylaniline, use of excess of the alcohol tends to lessen the formation of the monoalkyl derivatives. Diethylation of aniline is more difficult than dimethylation; consequently, the procedure is to separate the monoethylaniline from the diethylaniline by benzylating the monoethylaniline to benzylethylaniline and distilling. Since one of the two methyl groups in dimethyl sulfate acts more vigorously than the second, it is better to proportion the reactants to use only one methyl group in difficult alkylations.

For certain energetic alkylating agents, it is advantageous frequently to dilute them in order better to control the reaction. For dialkyl sulfates the addition of alkali speeds up the reaction, while for alkyl halides,

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[1] Simonetta and Favini, *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e. nat.*, **16**, 84–88 (1954); Manabe and Hiyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **37**, 164–166 (1954); De la Mare and Vernon, *J. Chem. Soc.*, **1952**, 3325–3331.

[2] Ogata and Ishikawa, *Science (Japan)*, **19**, 185–186 (1949).

alkaline media are often too fast; so here the alkylation is conducted in an acid medium to retard the reactants. In some cases, however, it may be necessary to maintain a low concentration of one of the reactants. In the manufacture of alkylate in the petroleum industry, where an isoparaffin is treated with an olefin, the olefin is diluted with the isoparaffin to lower its tendency to react with itself by polymerization, e.g., to keep butylene from forming diisobutylene.

In many instances, there is more than one place in the molecule where alkylation can take place. This is true in the methylation of morphine to codeine, where an alcoholic hydroxyl, a phenolic hydroxyl, and a tertiary nitrogen are present. In such cases, it is necessary that only the theoretical amount of the alkylating agent be used or that special conditions be employed (cf. Codeine).

Whenever possible and necessary, one of the reactants should be added as a solvent, since this not only brings in the mass-action effect but also simplifies the recovery, because of the absence of any extraneous substance. This principle is used in making alkylated benzene, dimethylaniline, and "alkylate." However, nonreacting solvents are sometimes used, such as nitrobenzene, carbon tetrachloride, and chloroform. As a rule, though not invariably, all solvents should be anhydrous. A solvent may also cause products or by-products to crystallize out. For instance, when dimethyl sulfate is employed for certain alkylations, it is dissolved in benzene and added to an alcoholic solution of the sodium phenoxide derivative to be alkylated. In the presence of these solvents, sodium methyl sulfate is very little soluble and is precipitated out. This procedure tends to give good yields. Similar conditions are applied to other alkylating agents.

Temperature. When such alkylating agents as methanol, ethyl alcohol, or the alkyl halides are employed, a much higher temperature is necessary than that required with dimethyl sulfate or diethyl sulfate or even methyl-*p*-toluenesulfonate. As described later, the methylation of aniline to dimethylaniline will take place at about 200°C. Alkylations that are carried on in the vapor phase call for much higher temperatures of about 400°C. When isoparaffins are alkylated with olefins, ordinary temperature is employed with HF catalyst, but refrigeration is required with H_2SO_4 catalyst to lessen tar formation. A number of alkylating reactions are exothermic as, for example, when aminoantipyrine is methylated with methyl bromide to give aminopyrine, and here cooling is advisable in the early stages of the methylation. Increased temperature frequently causes migration of alkyl groups to an aromatic nucleus. Dimethylaniline sulfate gives N-methyl-*p*-toluidine in this manner.

Pressure. In most alkylations, the number of molecules decreases during the course of the reaction; in these cases, according to the principle of Le Châtelier, pressure favors the alkylation product. Also in other cases, particularly those involving the lower members of the alkyl halides as alkylating agents, pressure is used to keep the reactants in the liquid phase.

Energy Requirements. In presenting the power requirement for any unit process, not merely the energy of the reaction should be considered but also any externally applied energy needed to bring about the reaction. If much electricity or steam is required for heating or power, it must necessarily be considered as part of the cost. Fundamentally, the energy of the chemical reaction must be known or determined, at least approximately, before the reaction is transferred to a commercial scale, in order that the equipment can be adequately designed. As a matter of experience, alkylations as a class are not large energy consumers, except those such as thermal alkylation, in which fairly high temperature and pressure are needed. This is one of the reasons why this process for the production of gasoline was unsuccessful in competition with similar catalytic alkylations (e.g., hydrogen fluoride) carried on at nearly atmospheric pressure and temperature.

V. EQUIPMENT FOR ALKYLATIONS

Materials of Construction. In a great many cases, steel is suitable for the construction of alkylating equipment, even in the presence of the strong acid catalysts, as their corrosive effect is greatly lessened by the formation of esters as catalytic intermediate products. In the petroleum industry, sulfuric acid and hydrogen fluoride are employed on a very large scale as alkylation catalysts; however, these must be substantially anhydrous to be effective; so steel equipment is satisfactory. Where conditions are not anhydrous, lead-lined, Monel-lined, or enamel-lined equipment is satisfactory. In a few cases, copper or tinned copper is still used, as in the manufacture of pharmaceutical and photographic products, to lessen contamination with metals.

Corrosion of Apparatus. Corrosion may be caused by the catalyst used in the alkylation or by the hydrogen halides formed by hydrolysis of alkyl halides. In the preparation of the N-alkyl compounds, the original amines or the alkylamines formed have an inhibiting action against corrosion. However, there are many cases in which the agents used in alkylation are corrosive. In the alkylation of aniline to diethylaniline by heating aniline and ethyl alcohol, sulfuric acid cannot be used, because it will form ether; consequently, hydrochloric acid is employed, but these conditions are so corrosive that the steel autoclaves used to resist the pressure must be fitted with replaceable enameled liners.

Certain other alkylations employing alkyl halides are carried out in an acidic medium. For example, hydrobromic acid is formed when methyl bromide is used. For such reactions, an autoclave with a replaceable enameled liner and a lead-coated cover is suitable.

Special attention must be given to moving parts and instruments to protect against fouling due to corrosion. If steel is to be used in parts under corrosive conditions, such as valves, the parts must be designed with ample clearance to allow for the corrosion and the deposits of iron-salt scale. To obviate this difficulty, pumps, valves, and instruments are often made from special alloys such as Monel.

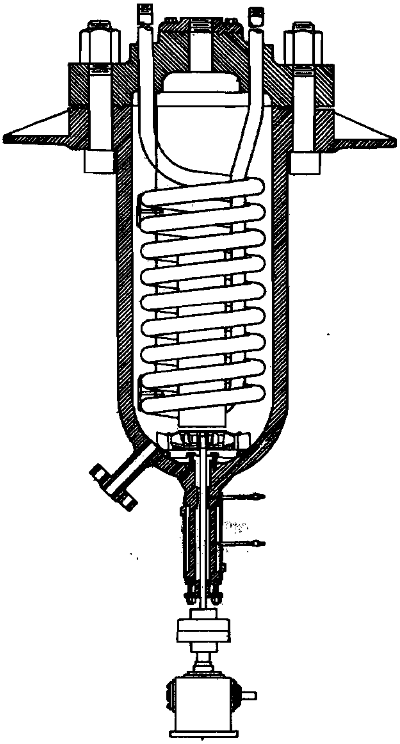

FIG. 14-2. Agitated internally heated autoclave.

Type of Equipment. A number of alkylations are carried out on a small scale where batch operation is more satisfactory. For this scale of operation, the reactor is usually an autoclave of any one of several designs, depending upon reaction conditions (see Figs. 14-2 and 14-10). These are generally constructed of steel, with or without an anticorrosion liner. In most instances, it is necessary to heat the autoclave, and this may be done for small autoclaves through the use of a jacket, although steel autoclaves have been directly heated in a suitably designed furnace using gas. When jackets are provided, the cleanest and cheapest source of heat is direct steam. For higher temperatures, superheated steam, Dowtherm, or hot oil is circulated through the jacket.

Autoclaves must be provided with inlet and outlet tubes, pressure gauge, thermometer well, and either a safety valve or, better, a safety disk (Fig. 14-3) that will yield before a dangerous pressure is reached. The safety disk is more certain to function than the safety valve, which may become corroded or clogged. Frequently it is not necessary to provide a stirring mechanism in the autoclave, because the heating generally causes sufficient homogeneity, but the charge should always be well stirred before it is run into the autoclave and the heating started. Figure 14-2 shows an excellent stirring mechanism for those alkylations where agitation is desired. This figure likewise depicts a cheaper and better method of applying heat or cold by means of an internal coil rather than by a jacket.

When dimethyl or diethyl sulfate can be used advantageously, a jacketed stirred kettle is generally used, and in these cases, the operation is carried on at lower temperatures. Such an apparatus is employed in the making of *p*-nitrophenetole from *p*-nitrochlorobenzene by heating with alcoholic potash in the presence of potassium sulfite at 50–80°C. Similarly, a lead-lined agitated jacketed kettle is suitable for the methylation of *p*-aminophenol with dimethyl sulfate to furnish Metol.

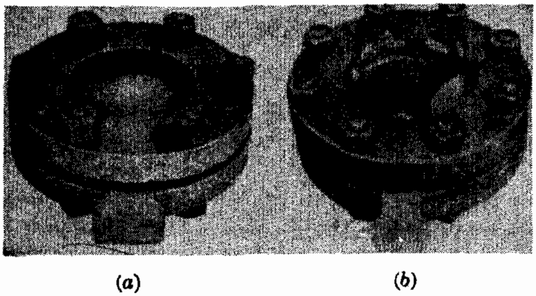
(*a*) (*b*)

FIG. 14-3. Safety diaphragm (frangible disk) for the relief of excessive autoclave pressures: (*a*) Before bursting and (*b*) After bursting.

Recovery of Alkylated Product. Wherever possible, rectification furnishes the most convenient and cheapest procedure. This technique is used extensively in the petroleum field. Even in those instances in which the boiling points are rather close together, as is true of the alkyl- and dialkylanilines, a separation can be effected by first benzylating the monoalkyl derivative and then distilling. Frequently such a distillation will furnish a finished material of quality sufficient to meet the demands of the market. If not, other means of purification may be necessary, such as crystallization or separation by means of solvents. The choice of a proper solvent will, in many instances, lead to the crystallization of the alkylated product and to its convenient recovery.

Safety. Alkylated products in themselves are not as a rule hazardous, although some of them, such as tetraethyllead, are toxic. However, some alkylating agents must be handled with considerable care, e.g., dimethyl sulfate. Among the catalysts, hydrogen fluoride is very toxic and hazardous, but the conditions for its safe handling have been worked out (see HF Alkylation), and consequently it may be employed without undue risk.

To ensure safety, in the control of autoclave procedures, the apparatus should be removed from use for periodic tests or inspection. In most cases, it is sufficient to apply a hydrostatic pressure 50 per cent higher than is used in practice. It is necessary to remove the safety disk and safety valve which are usually set to blow at lower than test pressure. Naturally, these instruments and all others must be frequently checked.

VI. EFFECT OF ALKYLATION

Although the effect of alkylation on the properties of organic compounds is sometimes contradictory, there are some general observations that are of value, particularly in the field of motor fuels, medicinals, dyes,[1] and solvents.

High-octane motor fuels are manufactured in large amounts by alkylation because the desired branched chains are thus economically obtained.

Schmiedeberg formulated a series of rules regarding the effect of alkyl groups on physiological activity, which May summarizes as follows.[2] In the first place, a close connection exists between "medical" action and the ordinary physical properties of volatility and solubility. In the aliphatic paraffin series, the lower members, which are more volatile, exhibit a narcotic effect that is absent in the insoluble, nonvolatile higher members.

Alkylation often causes very poisonous compounds to lose this effect; e.g., the nitriles (RCN) and isonitriles ($R—N\equiv C$) are poisonous only when HCN is split off. The action of alkyl radicals can be masked or inhibited by the presence of other radicals; this is illustrated by the behavior of methyl-, dimethyl-, and trimethylamine, which react like ammonia but have no narcotic effect. In this conduct, these amines follow Schmiedeberg's preceding rule and are less toxic than ammonia. The physiological action of alcohols and ethers is ascribed to the nature of the alkyl groups. For the ethers, single or mixed, the effect is due to the presence of the alkyls, each of which acts independently of the other.

One of the most interesting studies of the effect of various alkyl groups on physiological activity is illustrated by the alkyl derivatives of resorcinol, which are discussed under Hexylresorcinol. The bactericidal action at first increases with the length of the side chain and then diminishes because of decreased solubility of the alkylresorcinol. Coincident with this increase is found a decrease in toxicity.

Phenol was the first antiseptic used, and a thorough study of its derivatives has been made. The substitution of a methyl group for the hydrogen in the ring of phenol, forming the cresols, increases the antiseptic action.

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[1] GROGGINS, "Unit Processes in Organic Synthesis," 3d ed., pp. 583–584, McGraw-Hill Book Company, Inc., New York, 1947.

[2] MAY, "The Chemistry of Synthetic Drugs," 3d ed., Longmans, Green & Co., Inc., New York, 1921; *cf.* HARTUNG, *Chem. Rev.*, **9**, 389–465 (1931).

In the case of the dihydroxybenzenes, the alkyl derivatives of resorcinol have been carefully investigated, and it is found that the entrance of the methyl group into the ring, forming orcinol, depresses the bactericidal power. The influence of higher alkyl groups on the nucleus of the resorcinol molecule is considered under Hexylresorcinol (*q.v.*).

VII. TECHNICAL ALKYLATIONS

A few selected examples of technical alkylation are here given to illustrate various and typical procedures. These are chosen to illustrate the different linkages and are classified by the type of alkylation linkage.

Alkyl Bound to Carbon

Alkyl aryl Detergents. Alkyl aryl is used to designate the predominantly important class of aliphatic aromatic organic compounds which are sulfonated to manufacture detergents. Benzene is almost always the aromatic compound alkylated either with dodecene or with "keryl" chloride. The dodecene is normally a propene tetramer containing 12 carbon atoms and with a boiling range of 350–420°F. With keryl chloride, the benzene[1] is alkylated with the 10-14 carbon kerosene cut of relatively straight-chain hydrocarbons after chlorination. Both alkylations are catalyzed by $AlCl_3$, HF, or H_2SO_4.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\substack{\text{Dodecene}\\\text{("Propylene}\\\text{Tetramer")}}}{(C_3H_6)_4} \xrightarrow[115°F]{AlCl_3} \underset{\text{Dodecylbenzene}}{C_6H_5{\cdot}C_{12}H_{25}}$$

Figure 14-4 represents a continuous-flow diagram for manufacturing alkyl aryl detergents.[2] The benzene is alkylated with dodecene catalyzed by $AlCl_3$ continuously introduced. The temperature is kept at 115°F as a maximum, this being controlled by cooling coils or by circulating a part of the benzene alkylate through an external cooler and back to the agitated alkylator. The alkylator is followed by a continuous settler. The benzene is in excess to suppress the formation of isomers ("heavy" alkyl aryl hydrocarbons). After separation of the $AlCl_3$ sludge, the charge goes to a benzene fractionator where the excess benzene is distilled overhead and recycled. The bottoms from the benzene fractionator as shown in Fig. 14-4 are passed through the intermediate fractionator, furnishing as overhead a small quantity of a light alkyl aryl hydrocarbon, then to the dodecylbenzene

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[1] For other flow diagrams for alkylaryl detergents including keryl chloride, see SHREVE, "Chemical Process Industries," 2d ed., p. 633, McGraw-Hill Book Company, Inc., New York, 1956; BROOKS et al., *op. cit.*, vol. 3, pp. 599–601; SHARRAH and FEIGNER, *Ind. Eng. Chem.*, **46**, 248 (1954).

[2] *Petroleum Refiner*, **34** (12), 126 (1955).

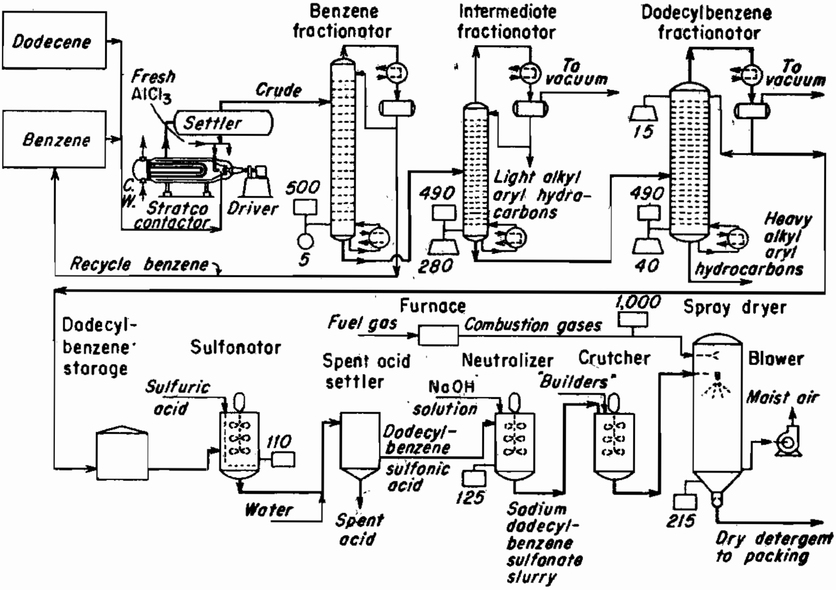

Fig. 14-4. Flow diagram for alkyl aryl sulfonates.

vacuum fractionator. The dodecylbenzene has a boiling range of 530–600°F and is a blend predominantly of monoalkylbenzenes with a saturated side chain averaging 12 carbons. See Chap. 7 for sulfonation of dodecylbenzene.

The solubilities of sodium alkylbenzenesulfonates were found[1] to decrease considerably with the length of the alkyl group. The surface tension showed a minimum value for the dodecyl group, however. Naphthalene and phenol and its homologues are also alkylated to produce synthetic detergents which have excellent properties but are more expensive than detergents produced from benzene.

Alkylate for the Petroleum Industry. The manufacture of the so-called "alkylate" has furnished an important constituent of high-quality motor and aviation fuels. This is made by the reaction of olefins with paraffins or isoparaffins and has been carried out commercially in several ways:

1. By thermal alkylation in the vapor phase.
2. By catalytic alkylation with hydrogen fluoride, sulfuric acid, or aluminum chloride–hydrocarbon complexes, all in the liquid phase.

In both of these methods it is necessary to keep the olefin in a low concentration, which suppresses the tendency of these hydrocarbons to polymerize, and the paraffin in a high concentration to favor the paraffin-

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[1] Ogawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **64**, 779–781 (1951).

olefin junction. About 3–8 moles of the isoparaffin is required for 1 mole of the olefin or olefins, and the excess isoparaffin is separated from the alkylation product and recycled.

In 1956 it was reported by S. R. Stiles[1] that, "There are 66 alkylation plants in the United States, including those under construction, ranging in size from 650 bbl per day to 12,500 bbl per day and having a total capacity of more than 258,000 bbl per day. Of these, 19 are HF alkylation plants rated at 54,000 bbl per day. Sulfuric units account for the other 47 with a capacity of 203,000 bbl per day."

Thermal Alkylation. Thermal alkylation has ceased to be a commercial process. Neohexane, the main product of the thermal process, has a research octane number of 104.8 with 3 ml tetraethyllead (TEL) per gal as determined by Phillips Petroleum Company (103.8 on new API scale), while the corresponding number for "diisopropyl" with 6–6.8 ml TEL is 118.7 (120 new API scale). The diisopropyl is obtained by catalytic alkylation. For this reason and because the thermal process operated under the extreme condition of 5,000 psi pressure and 950°F temperature, it is very doubtful if operations will be resumed.

HF *Alkylation.* Alkylation reactions of olefins with isoparaffins, catalyzed by anhydrous liquid hydrofluoric acid, are carried out on a large scale commercially. The highest quality of alkylate is produced by the reaction of isobutylene with isobutane to form mainly "isooctane" (2,2,4-trimethylpentane). The reaction produces a number of other products, including those having more or less than eight carbon atoms (see Table 14-4). To ensure useful reaction rates, it is necessary to provide agitation because the hydrocarbons are only slightly soluble in the catalyst, liquid hydrogen fluoride. Other olefins react similarly, but isobutane is the sole isoparaffin used. The best data available are for the alkylation of isobutane with a mixture of 80 per cent 2-butene and 20 per cent 1-butene.[2] The effect of increasing the isobutane:olefin ratio in the feedstock is to improve the yield of acceptable alkylate and to improve the octane number of that alkylate. The former effect is great until a ratio of 5 or 6:1 is reached, after which it is slight. A change of ratio from 4 to 14 improves the octane number about four units. The effect of acid:hydrocarbon ratio is not critical, but a ratio of 1:1 seems to be favorable, convenient, and economical.

Temperatures commonly obtainable with cooling water are satisfactory for this reaction. A high temperature lowers the quality of alkylate, but too high or too low a temperature results in excess organic fluoride for-

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[1] STILES, World Petroleum, Annual Refinery Review, 1956.

[2] An excellent book on hydrogen fluoride alkylation is "Hydrofluoric Alkylation," Phillips Petroleum Co., Bartlesville, Okla., 1946, which gives flow charts, operating data, and results. See also PETERS and ROGERS, *Petroleum Refiner*, **34** (9), 126 (1955), new flow diagram.

TABLE 14-4. SOME HYDROCARBONS FORMED IN HF ALKYLATION*

Hydrocarbons Produced	Approximate % Present in Total Alkylate
Alkylation of isobutane with propylene:	
2,4-Dimethylpentane	10–15
2,3-Dimethylpentane	40–50
Other hydrocarbons:	
Pentanes	Few % each
Hexanes	
2,2,4-Trimethylpentane and other isooctanes	
Isononanes, isodecanes, and isoundecanes	
Alkylation of isobutane with butylenes:	
2,2,4-Trimethylpentane	35–40
2,3,4-Trimethylpentane	20–30
2,3,3-Trimethylpentane	
Other hydrocarbons:	
Isopentane	Few % each
2,3-Dimethylbutane	
2,4-Dimethylpentane, 2,3-dimethylpentane	
Dimethylhexanes	
Isononanes (including 2,2,5-trimethylhexane)	
Isodecanes	
Isoundecanes	

* Phillips Petroleum Company.

mation. A temperature of 27°C results in alkylate about one octane unit better than that obtained at 46°C.

Contact times of over 5 min do not affect the yield, and the octane number is at a slight maximum at a contact time of 15 min. An acid strength of 87.5 per cent gives the maximum octane alkylate, but the balance of the acid phase should be organic. A water content of less than 2 per cent is not very harmful, but octanes are replaced by heavier and lower hydrocarbons as the water content builds up. Fluorine content and olefin content in the alkylate build up in the presence of excess water.

The alkylation reaction with hydrogen fluoride as the catalyst is complete in one cycle when it is run under the conditions indicated above. By dispensing with the bauxite defluorinizing towers, there results a consumption of 0.2 lb of hydrogen fluoride per barrel of alkylate. Hydrogen fluoride which is no longer suitable for alkylation is regenerated by a two-step distillation procedure. In the first distillation, hydrogen fluoride and water are flashed away from heavy acid-soluble oils which are next reboiled to split out combined hydrogen fluoride. The overhead from this operation is rectified to produce substantially pure hydrogen fluoride overhead and a maximum boiling water–hydrogen fluoride azeotrope containing about 35 per cent hydrogen fluoride as bottoms product which is discarded. For typical operating conditions and yields, see Table 14-7.

Sulfuric Acid Alkylation. Despite some disadvantages, such as acid-recovery expense and refrigeration to minimize oxidation, about four fifths of the alkylate produced for motor fuels is based on sulfuric acid as a catalyst. As with HF alkylation, isobutane is alkylated with olefins (other than ethylene), and a flow diagram for such a process is given in Fig. 14-5.

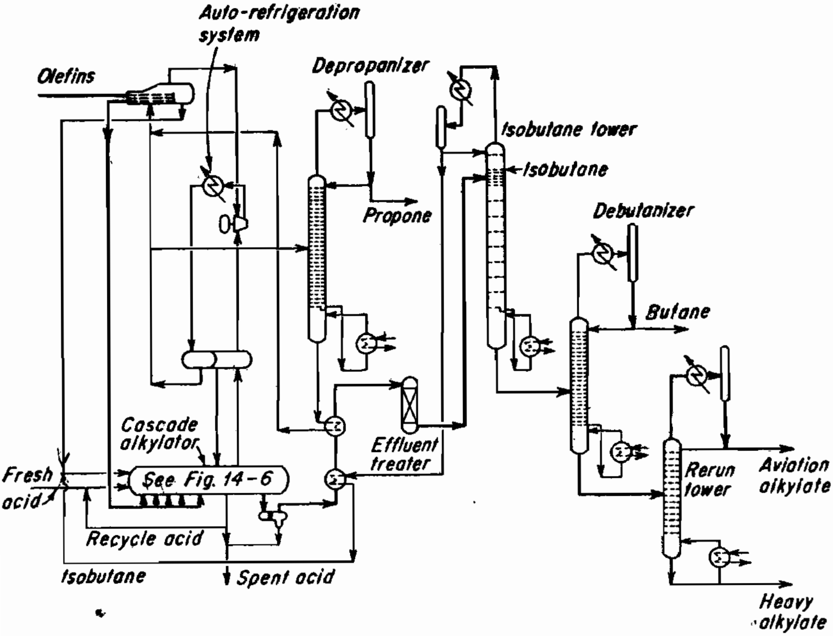

FIG. 14-5. Flow diagram of sulfuric acid alkylation for petroleum "alkylate."

The alkylation is exothermic, and means must be provided to control the temperature and to secure good contact with the reactants and the catalyst. This is done by having the sulfuric acid saturated with the isobutane and by feeding the olefins into the system in such a manner to provide the isobutane in excess. This procedure and keeping the temperature down minimize any polymerization of the olefins used. As practically employed (Fig. 14-5), an emulsion of the acid and the isobutane is circulated in large volume past the point of olefin injection.[1]

While alkylation reactors can employ indirect heat exchange, the one depicted in Fig. 14-5 and detailed in Fig. 14-6 employs autorefrigeration by

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[1] STILES, *op. cit.*

evaporation, outside condensation, and return of isobutane or other low boilers to maintain the temperature at 35–45°F. Isobutane is charged and is also returned from the deisobutanizer tower. The olefins are injected in small amounts in each of the five successive zones of the reactor, thus maintaining a high ratio of isobutane:olefin in the reaction zones with a low isobutane concentration in the effluent.

The right-hand or settling zone of this cascade reactor (Fig. 14-6) serves to separate isobutane vapors going to the refrigeration system from the spent and recycle acid, and the effluent. The effluent is fractionated in the series of four towers shown in the flow diagram, Fig. 14-5.

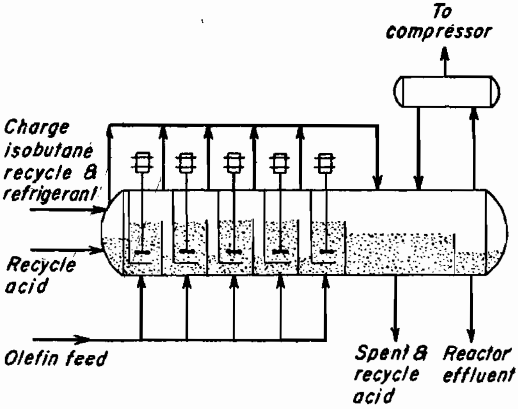

FIG. 14-6. Kellogg cascade alkylator.

Typical results are summarized[1] in Table 14-5. "The higher the isobutane concentration, isobutane to olefin ratio, acid to olefin ratio and acid strength, and the lower the reaction temperature, the higher the octane rating of the 338°F end-point material and the lower the acid consumption and the quantity of heavy polymer formed." As the sulfuric acid is contaminated, a portion is withdrawn and replaced by fresh acid. The effluent treater is to remove acidic material.

$AlCl_3$ *Complex Alkylation.* Another catalyst used for paraffin alkylation is a liquid complex made from aluminum chloride in a hydrocarbon solvent. The complex contains 55–62 per cent by weight aluminum chloride and is understood to be a kerosene selected for certain impurities which enhance the catalytic effect of the aluminum chloride.

Isobutane is alkylated with a mixture of ethylene and propylene, the ratio of the lighter to the heavier olefin being about 4:1. In commercial production, 70–90 lb of alkylate is produced per pound of aluminum

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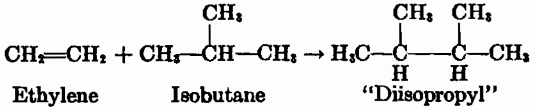
[1] ANON., Sulfuric Acid Alkylation, M. W. Kellogg Co., *Petroleum Refiner*, **35** (9), 251 (1956).

TABLE 14-5. TYPICAL SULFURIC ACID ALKYLATION YIELD DATA*

Olefin feed type	Propylene	40% C_3- 60% C_4-	Butylenes	Pentenes
Yield, bbl alkylate per bbl olefin	1.78	1.74	1.72	1.60
Isobutane consumption bbl iC_4 per bbl olefin	1.275	1.174	1.106	0.965
Acid consumption (avg): lb 98% H_2SO_4 per gal total alkylate	2.5–0.84	1.5–0.6	0.84–0.33	1.0–0.4
338 F end point alkylate quality:				
F-1 research octane No., clear	89–92	92–95	94–97	90–93
+3.0 cc TEL	101.5–103.0	103.5–105.0	104.2–106.3	103–103.6
F-2 ASTM octane No., clear	87–90	90–93	92–94	90–92
F-3 or 1-C performance No., 4.6 cc TEL	117–122	124–127	127–132	116–123
F-4 or 3-C performance No., 4.6 cc TEL	129–142	141.6–154	150–162	136–148

* *Petroleum Refiner*, **35** (9), 251 (1956).

chloride. Under proper conditions, 75–85 per cent of the ethylene reacts according to the following over-all reaction:



$$CH_2{=}CH_2 + CH_3{-}\overset{CH_3}{\overset{|}{C}}H{-}CH_3 \rightarrow H_3C{-}\underset{H}{\overset{CH_3}{\overset{|}{C}}}{-}\underset{H}{\overset{CH_3}{\overset{|}{C}}}{-}CH_3$$

The olefins for this alkylation are supplied from propane or *n*-butane cracking, being available for alkylation as a solution in isobutane. Recycle isobutane, olefin-containing isobutane, and catalyst are mixed and contacted in a mechanically stirred reactor. The catalyst is settled, and the hydrocarbon mixture is fractionated to remove propane, recycle isobutane, pentane, and heavy hydrocarbons. The product "diisopropyl alkylate" is a very high-quality ingredient for aviation fuels. Table 14-6 gives data on the composition of diisopropyl alkylate. As with the other alkylates, one compound makes up the major part of the product, other compounds being formed by side reactions. Typical operation and yields are indicated in Table 14-7. As in the other processes, variation of operating conditions and feedstocks causes considerable change in both yield and composition of the product.

Cumene. Cumene has long been an important constituent of aviation and high-quality motor fuels. However, recently it has become an im-

TABLE 14.6. SOME HYDROCARBONS FORMED IN $AlCl_3$-COMPLEX ALKYLATION*
Alkylation of Isobutane with Ethylene-Propylene Mixture

Hydrocarbons Produced	Approximate % in Total Alkylate
2,3-Dimethylbutane (diisopropyl)	55–70
Other hydrocarbons:	
Isopentane	Few % each
Methylpentanes	
2,4-Dimethylpentane and 2,3-dimethylpentane	
2,2,4-Trimethylpentane, 2,3,4- and 2,3,3-trimethylpentanes	
Isononanes	
Isodecanes	
Isoundecanes	

* Phillips Petroleum Company.

TABLE 14-7. TYPICAL OPERATIONS OF PARAFFIN-OLEFIN ALKYLATION PROCESSES*

Operating conditions	Thermal alkylation	HF alkylation	$AlCl_3$-complex alkylation
Molar isobutane:olefin ratio (feed)	2.7:1	4 to 8:1	3.5–8:1
Contact time, min	4.5	10–20	20
Reaction temperature, °F	930	70–115	100–130
Reaction pressure, psi	5,000	125–175	400
Catalyst:			
In reactor, vol. %	None	45–60	35–45
Acid strength, % HF	....	85–95	
$AlCl_3$ content, % by wt	....	....	55–62
Charge and yields:			
Hydrocarbons reacted	Ethylene Isobutane	Butylenes Amylenes Isobutane	Ethylene Propylene Isobutane
Total alkylate yield, lb per lb olefin reacted	1.3–1.4	1.5–2.0	2.6–2.8
Isobutane consumed, lb per lb olefin reacted	0.8	1.0–1.1	1.7–1.9
Conversion of olefin, %	95	100	95–98

* Phillips Petroleum Company.

portant step in the manufacture of phenol and acetone by oxidation (see Chap. 9).

$$\underset{\text{Propylene}}{C_3H_6} + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{H_3PO_4} \underset{\text{Isopropylbenzene}}{C_3H_7{\cdot}C_6H_5} + \underset{\text{Polyisopropylbenzene}}{(C_3H_7)_nC_6H_{6-n}}$$

Preparation. The formation of cumene or isopropylbenzene is frequently carried out[1] at about 250°F, using a phosphoric acid catalyst. The

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[1] Flow diagrams, quantities, and details are available: *Petroleum Refiner*, **34** (12), 139 (1954); BROOKS et al., *op. cit.*, vol 3, p. 589.

reaction is exothermic and also produces polyalkylated benzenes even with a high ratio of 5:1 for benzene to propylene. The polyalkylated benzenes can be used to an extent limited by their boiling points in motor fluids, or they can be dealkylated-realkylated.

Ethylbenzene. Ethylbenzene has been made in a very large quantity in recent years as a step in the manufacture of styrene for GR-S synthetic rubber and for plastics. The reactions involved are essentially

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5 \qquad \Delta H = -48{,}700 \text{ Btu per lb mole at } 95^\circ\text{C}$$

Preparation. Gaseous ethylene is passed into the liquid benzene in the presence of a metal chloride catalyst, such as aluminum chloride, at moderate temperatures (40–100°C). The reaction is promoted by hydrogen chloride.

A continuous process[1] for ethylbenzene is shown by Fig. 14-8. Anhydrous conditions must prevail; hence the 99+ per cent purity benzene is pumped through an azeotropic drying column from which benzene with less than 30 ppm water is withdrawn. This benzene is mixed with recirculated "catalyst complex" and fresh catalyst (anhydrous $AlCl_3$). The hydrogen chloride which serves as a promoter is furnished indirectly from the ethyl chloride previously mixed with the ethylene (90–95 mole per cent purity).

The catalyst complex consisting of heavy organics and solid anhydrous aluminum chloride is separated as shown in Fig. 14-8 and recycled after mixing with needed fresh $AlCl_3$. An approximate composition[2] is

	Per cent
$AlCl_3$ (combined with hydrocarbons)	26
$AlCl_3$ (free)	1
High-molecular-weight hydrocarbons	25
Benzene and ethylbenzene	46

In the alkylation, the benzene is converted to ethyl- and polyethylbenzenes (Fig. 14-7) at 200°F and a pressure slightly above atmospheric. As the reaction is exothermic, heat must be removed by evaporation or cooling. The crude alkylate is separated from the catalyst complex, cooled, and washed with water and then with caustic soda solution. This crude product contains 40–45 per cent benzene, 15–20 per cent polyethylbenzene, and a small amount of tar, the rest being ethylbenzene. Separation is effected as shown in Fig. 14-8 by a train of conventional columns,

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[1] ANON., *Petroleum Refiner*, **34** (12), 147 (1955). Other flow sheets and earlier references are given in GROGGINS, "Unit Processes in Organic Synthesis," 4th ed., pp. 838 and 889; SHREVE, "Chemical Process Industries," 2d ed., p. 811; MITCHELL, *Trans. Am. Inst. Chem. Eng.*, **42**, 293 (1946).

[2] BROOKS et al., *op. cit.*, pp. 583ff. for many details and references.

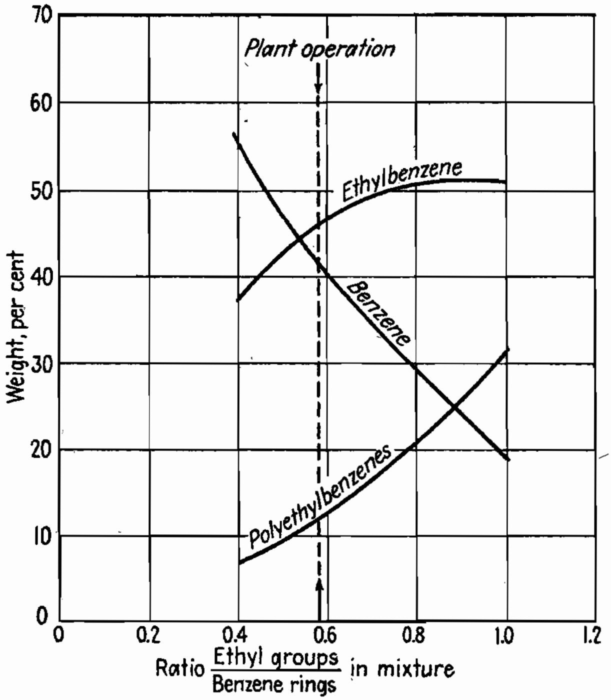


Fig. 14-7. Equilibrium relations in the ethylation of benzene at 95°C.

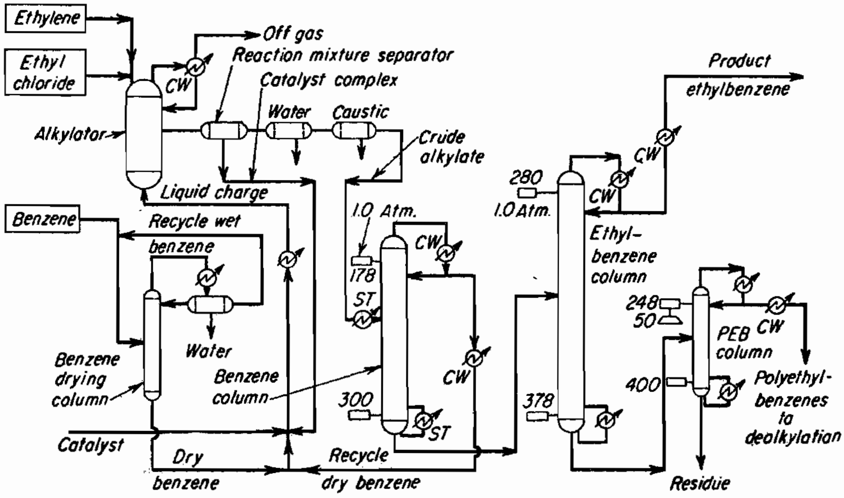
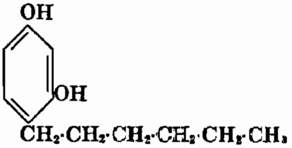


Fig. 14-8. Continuous flow diagram for ethylbenzene.

with the third one operated at a head pressure of about 50 mm Hg absolute, furnishing an overhead of the polyethylbenzenes which is charged to the dealkylator-realkylator (using $AlCl_3$ and excess benzene at higher temperature and different catalyst ratio). Ethylbenzene and dimethylbenzene result.

Hexylresorcinol. Caprokol.



The normal hexylresorcinol has been found to possess marked germicidal properties with a phenol coefficient of over 50. It is relatively nontoxic when administered by mouth and is partly excreted by the kidneys. A great number of acyl- and alkylresorcinols have been studied as regards their germicidal action.[1] The normal alkylresorcinols particularly have been found to be of value, a very pronounced increase being observed in the bactericidal power shown by these compounds up to normal hexylresorcinol. This action then decreases as the length of the chain increases because of the diminishing solubility of the alkylresorcinol. In Fig. 14-9 is shown the relationship between the atomic weight of the alkyl chain and the phenol coefficient (ratio of antibacterial power measured against *Eberthella typhosa* relative to that of phenol under the same conditions). Similar experiments with different strains of *Staphylococcus aureus* gave results shown in Table 14-8.[2]

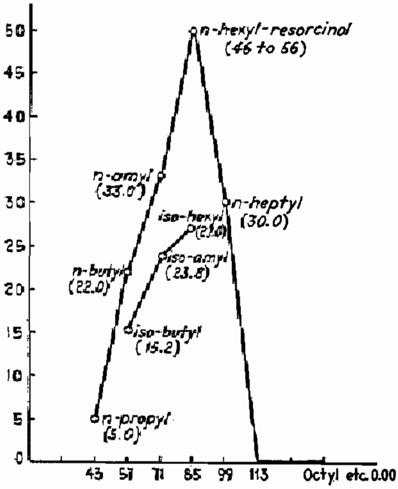


FIG. 14-9. Bacterial activity of the alkylresorcinols. The curve is obtained by plotting the phenol coefficients (U.S. Hygienic Laboratory technique) as ordinates against the sum of the atomic weights of the atoms in the alkyl chain as abscissas. (*According to Dohme, Cox, and Miller.*)

Preparation. According to various patents pertaining to the manufacture of hexylresorcinol, resorcinol and caproic acid are heated with a

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[1] DOHME, COX, and MILLER, *J. Am. Chem. Soc.*, **48**, 1688 (1926); SCHAFFER and TILLEY, *J. Bact.*, **14**, 259 (1927).

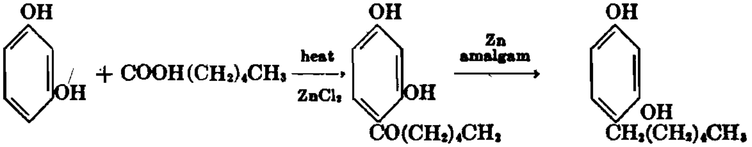
[2] SCHAFFER and TILLEY, *loc. cit.*

TABLE 14-8. COEFFICIENTS OF THE NORMAL RESORCINOLS WITH DIFFERENT STRAINS OF *Staphylococcus aureus*

Alkyl derivative	Phenol coefficients*		
	Strain 1	Strain 2	Strain 3
Ethyl	1.55	1.5	1.5
Propyl	3.9	3.7	3.7
Butyl	10.7	10	10.2
Amyl	30.2	30.2	30.6
Hexyl	97	98	98
Heptyl	295	280	280
Octyl	690	680	725
Nonyl	1,000	980	1,000

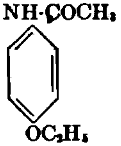
* At 25°C.

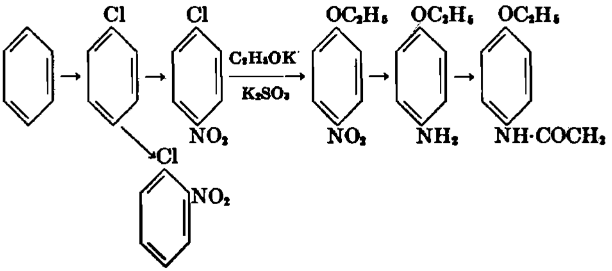
condensing agent, such as zinc chloride, whereby the intermediate ketone derivative is formed. This is purified by vacuum distillation. By reduction with zinc amalgam and hydrochloric acid, impure hexylresorcinol results which can be purified by vacuum distillation.



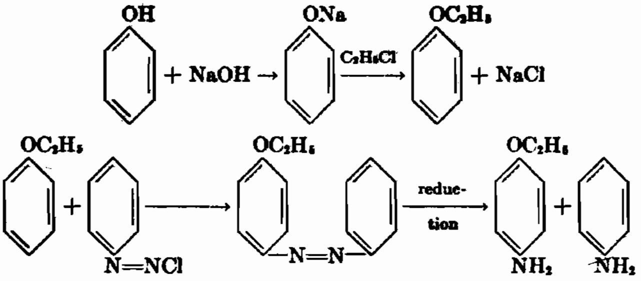
Alkyl Bound to Oxygen

Acetophenetidine. Phenacetin.





(1)



(2)

Acetophenetidine is an important analgesic and antipyretic that has attained widespread use in medicine. The principal series of reactions for its preparation are given above; the one involving the nitration of chlorobenzene is of most value technically. These reactions are intertwined with the preparation of other products; e.g., the ortho-nitration product of either chlorobenzene or of phenol is methylated to give *o*-nitroanisole, which is made into guaiacol or dianisidine. In general, the alkylation of nitrochlorobenzenes or of the nitrophenols is effected by use of either the alkyl halide or the alcohol—in both cases, in the presence of an alkali. Diethyl sulfate (or dimethyl sulfate) is also employed and can be handled more easily than the alkyl halide.

p-Nitrophenetole from p-Nitrochlorobenzene (Reaction 1). As Schwyzer points out, *p*-nitrochlorobenzene when heated with alcoholic potash yields but little of the *p*-nitrophenetole.[1] In the presence of sulfites, however, the reaction proceeds smoothly and without the formation of by-products.

First, 1,000 liters of 95 per cent alcohol and 63 kg of 94 per cent KOH are charged at 45°C to a stirred, jacketed iron kettle. Then, 5 kg of powdered K_2SO_3 and 157 kg of *p*-nitrochlorobenzene are added. The temperature is raised to 50°C and at 6-hr intervals is raised 5° until 80°C is reached, where the reaction mass should be kept for 12 hr. At each temperature increase, 1 kg of powdered K_2SO_3 is added. The hot precipitated potassium chloride is pressure-filtered, and the filtrate plus 7 kg of K_2SO_3 are returned to the reactor for 3 hr at 80°C. The filtration is repeated, and the combined filtrates constitute an almost theoretical yield of *p*-nitrophenetole. The product is isolated from the residuum after the alcohol distillation.

Phenetidine is obtained from *p*-nitrophenetole by reduction with iron and hydrochloric acid. It is then acetylated to *p*-acetophenetidine by heating with glacial acetic acid in a silver-lined still.

p-Phenetidine from p-Ethoxy-azobenzene[2] (Reaction 2). The Dow Chemi-

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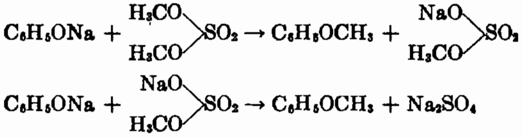
[1] SCHWYZER, "Die Fabrikation pharmaceutischer und chemischtechnischer Produkte," pp. 211–212. Springer-Verlag, Berlin, 1931.

[2] BARROWCLIFF and CARR, "Organic Medicinal Chemicals," pp. 116–117, Baillière, Tindall & Cox, London, 1921, describes a more complicated but similar procedure through 4-ethoxy-4′-hydroxyazobenzene.

cal Company's process is based on alkylating sodium phenoxide with ethyl chloride and coupling the alkoxy derivative with diazotized aniline, splitting the *p*-ethoxy-azobenzene by reduction, and recovering aniline—to be used over again—and the *p*-phenetidine. The latter is acetylated to acetophenetidine.

Anisole.

Outline of Reactions.



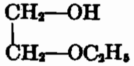
$$C_6H_5ONa + \begin{matrix} H_3CO \\ H_3CO \end{matrix}\!\!>\!SO_2 \rightarrow C_6H_5OCH_3 + \begin{matrix} NaO \\ H_3CO \end{matrix}\!\!>\!SO_2 \qquad (1)$$

$$C_6H_5ONa + \begin{matrix} NaO \\ H_3CO \end{matrix}\!\!>\!SO_2 \rightarrow C_6H_5OCH_3 + Na_2SO_4$$

$$C_6H_5ONa + CH_3Cl \rightarrow C_6H_5OCH_3 + NaCl \qquad (2)$$

Anisole is used directly in perfumery and is an intermediate for further synthesis. It is prepared by the action of methyl chloride or of dimethyl sulfate on phenol. When dimethyl sulfate is employed, both of its methyl groups can be made to react, yielding about 72–75 per cent of theory of the anisole. When only one of the methyl groups is caused to react, the yield is higher, being 85–95 per cent of theory, but it is usually more economical to use both of the available methyl groups.[1]

Cellosolve. Ethylene Glycol Ethyl Ether (2-Ethoxyethanol).



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OC_2H_5 \end{array}$$

Ethylene glycol ethyl ether belongs to three major chemical families: it contains an alcoholic group, —OH; a hydrocarbon group, $\overset{|}{C}H_2 \cdot \overset{|}{C}H_2$; and an ether group, —$CH_2$—$OC_2H_5$; and it is not surprising that this compound and its homologues have proved to be useful solvents.

Since the ethylene glycol ethers contain an ether as well as an alcohol group, they are very good solvents for cellulose esters. The ethylene glycol methyl ether is an excellent solvent for both nitro- and acetylcellulose, whereas the ethyl and the higher homologous ethers dissolve only the nitrocellulose.

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[1] For fuller description, see GROGGINS, "Unit Processes in Organic Synthesis," 3d ed., p. 588, 1945; ULLMANN, "Enzyklopädie der technischen Chemie," 2d ed., vol. I, p. 239, Urban & Schwarzenberg, Berlin, 1928–1932.

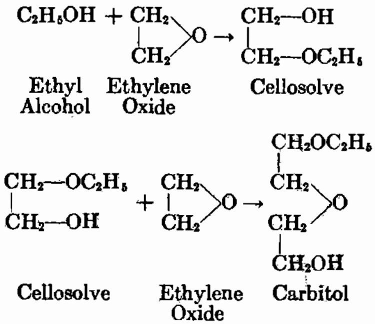
Because of the strong solvent action of the methyl ether of ethylene glycol, the so-called Methyl Cellosolve, it is used to seal cellophane-covered cigarette packages. Here, only 6 drops is needed per package, and yet Methyl Cellosolve is sold in carload quantities.

Carbitol. Diethylene Glycol Monoethyl Ether [2-(β-Ethoxyethoxy)-ethanol].

$$HOCH_2CH_2—O—CH_2CH_2—OC_2H_5$$

Polyethylene glycols as high as the octaethylene glycol have been prepared.[1] The ethers of these polyethylene glycols have attained commercial significance; and this is particularly true of the diethylene glycol ethyl ether, which is sold commercially under the name of Carbitol. This product is especially useful in the manufacture of laminated glass, wherein the celluloid interleaf is misted over with a spray of Carbitol, which increases the adhesion to the glass. In the printing and dyeing of textile fabrics, it makes possible more economical use of dyes. Carbitol is a solvent with a mild odor, a low rate of evaporation, and a boiling point of 201.9°C. It enters into the manufacture of wood stains and automobile polishes and is used as a lacquer solvent. However, it is particularly valuable in the cosmetic field, where it is employed for creams and hair tonics.

Preparation of Glycol Ethers (Cellosolve and Carbitol).



There is a large quantity of data available on the German process for the manufacture of glycol ethers.[2] The monomethyl, ethyl, and *n*-propyl ethers of ethylene glycol are manufactured by the continuous reaction of ethylene oxide with the anhydrous alcohol at about 200°C and at 25–45 atm pressure. One volume of ethylene oxide and 6 vol. of alcohol are fed

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[1] Lawrie, "Glycerol and Glycols," pp. 381ff., Reinhold Publishing Corporation, New York, 1928.

[2] Goldstein, et al., "Manufacture of the Monoalkyl Ethers of Ethylene Glycol and of Diethylene Glycol," *B.I.O.S. Final Rept.* 1618 (British Intelligence Objectives Subcommittee).

to a pressure tower packed with iron Raschig rings. Excess of alcohol is used to give the required high ratio of glycol ether:diglycol ether, to control the heat liberated in the reactor, and to avoid high concentrations of the ethylene oxide because of explosive possibilities. The reaction between ethylene oxide and alcohol is exothermic, about 20–25 kg-cal per g mole of ethylene oxide reacted. The reaction product emerges from the base of the pressure tower and is distilled semicontinuously. The alcohol is recycled; the pure glycol and diglycol ethers are isolated by batch fractionation. After removal of excess alcohol, the crude product contains about 85 per cent glycol ether, 10 per cent diglycol ether, and 2–3 per cent polyglycol ethers. The yield of ethers is about 90–95 per cent on ethylene oxide and alcohol consumed. The reaction is controlled to give complete conversion of ethylene oxide. Conditions in the pressure tower and feed ratios for methyl, ethyl, and *n*-propyl alcohols are given in Table 14-9. The contact time has been calculated on the assumption that the reactor capacity is 3.5 cu m.

TABLE 14-9. CONDITIONS FOR PREPARATION OF GLYCOL ETHERS*

Alcohol	Temp, °C	Pressure, atm	Rate, lb/hr		Contact time, hr
			Ethylene oxide	Alcohol	
Methyl	200	40	120	720	About 4
Ethyl	200–210	35	100	600	About 5
n-Propyl	220–230	25	80–90	450–540	About 6

* GOLDSTEIN et al., Manufacture of the Monoalkyl Ethers, of Ethylene Glycol, and of Diethylene Glycol, *B.I.O.S. Final Rept.* 1618.

Either acids or bases may be used as catalysts in the reaction between ethylene oxide and alcohol. However, acids are corrosive and must be neutralized before treating the crude reaction product, and alkalies lead to the formation of resins with the acetaldehyde present in the ethylene oxide. Because of the above reasons a noncatalytic process was developed. The Germans also developed a process using aqueous ethyl alcohol, but as this involves a difficult products separation, it is not preferred.

Ethylcellulose. The cellulose ethers obtained by the alkylation of cellulose are important plastic materials. They are more stable than the cellulose esters and are incapable of undergoing hydrolysis, which makes them more resistant to acid and alkalies. The alkyl ethers are, however, soluble to a considerable extent in water and alkalies, more so than benzylcellulose but less than cellulose acetate.

The data below show how the solubility of the alkyl ethers varies with the percentage of etherification.[1]

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[1] TRAILL, *Oil Colour Trades J.*, 1936, 1109.

Ether	Soluble in alkali	Soluble in water	Soluble in organic solvents
Methylcellulose	3–4% $-OCH_3$	33–36% $-OCH_3$	40% $-OCH_3$
Ethylcellulose	5% $-OC_2H_5$	27% $-OC_2H_5$	47% $-OC_2H_5$

The alkali-soluble compounds are of interest to the textile industry but are not suitable for the preparation of lacquers. Of the ethylcellulose now manufactured, about 70 per cent is consumed as plastics while about 30 per cent is compounded into protective coatings.

$$[C_6H_7O_2(ONa)_3]_n + 3nC_2H_5Cl \rightarrow [C_6H_7O_2(OC_2H_5)_3]_n + 3nNaCl$$

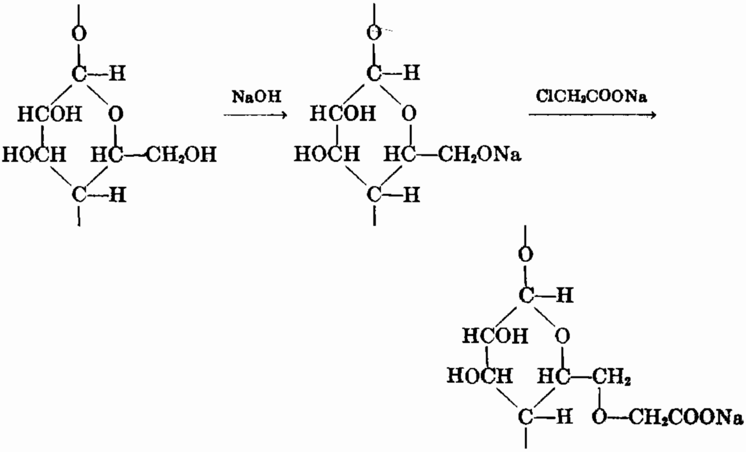
Preparation. The manufacture of ethylcellulose by the Hercules Powder Company[1] consists of treating the purified cellulose (sheeted chemical cotton or sulfite pulp) with an iron-free sodium hydroxide solution. The alkylator is then charged with the alkali cellulose and with ethyl chloride and the temperature raised to nearly 205°C, resulting in the formation of ethylcellulose, salt, ether, and alcohol. For every 100 lb of cellulose charged, 125 lb of ethylcellulose is produced. The sodium chloride solution is removed and electrolyzed to provide chlorine and caustic soda for the treatment of cotton linters. Some of the sodium chloride is used in making hydrogen chloride, which is employed to convert the ethyl alcohol and ethyl ether back to ethyl chloride. The ethyl alcohol and ethyl ether are obtained in the main reaction of cellulose with ethyl chloride in a basic solution. The storage tanks for the sulfuric and hydrochloric acids are glass-lined, the storage tanks for all the solvents are steel, and the ethyl chloride building has glass-lined pressure vessels with a concrete fire wall separating the reactor from the operator. The alkylators are steam-jacketed autoclaves of 4,500-gal capacity, tested to 700 psi, constructed of nickel-clad steel, and provided with solid nickel shafts and agitators.

The resulting highly-alkylated ethylcellulose is a powdery flocculent substance which is soluble in a number of organic solvents, e.g., chloroform and alcohol, and these solutions give clear, transparent, flexible, and water-resistant films when evaporated.

The aralkyl celluloses, e.g., benzylcellulose and phenylethylcellulose, are made in a similar manner. Their purification may be accomplished by treating the crude alkylation mass with a selective solvent, e.g., propanol or diamyl ether, which removes organic impurities. The granular precipitate is then washed with methanol and finally with water.

[1] ANON., *Chem. Met. Eng.*, **52** (9), 129 (1945) with pictured flow sheet; SHREVE, Alkylation, *Ind. Eng. Chem.*, **40**, 1566 (1948); ULLMANN, *op. cit.*, 3d ed., vol. 3, p. 176, 1954.

Sodium Carboxymethylcellulose (Sodium CMC) (Sodium Cellulose Glycolate).



Carboxymethylcellulose (CMC) is an alkylated compound that has achieved great commercial prominence in recent years. The sodium salt of CMC is the most important derivative. It is a white, granular, odorless, tasteless hygroscopic powder. The potassium salt resembles it in many of its properties and gives a similar solution in water.[1] The ammonium derivative is unstable, and certain metallic salts, such as lead, mercury, silver, aluminum, copper, nickel, and iron, are insoluble in water.

The dissociation constant of CMC is 5.0×10^{-5}, indicating that it is a moderately strong acid, comparable to acetic acid in this property. The molecular weight, as determined by osmotic-pressure determinations, is 6,400 ± 1,000.[2] It is insoluble in water in the acid form, which accounts for its use as a salt. Sodium CMC is supplied commercially in several grades, depending upon viscosity and purity.

The useful property of sodium CMC is its ability to increase the viscosity of mixtures to which it is added. At 25°C, water has a viscosity of slightly less than 1 centipoise. A 1 per cent solution of high-viscosity sodium CMC at the same temperature has a viscosity approximately 2,000 times as great. Thus it finds application as a thickener in textile printing pastes, latex dispersions, lubricants, and the like. As a stabilizer for emulsions and suspensions, sodium CMC is an important ingredient in synthetic detergents to prevent redeposition of soil and is helpful in creams, lotions, tooth pastes, and in many types of oil-in-water emulsions. Its

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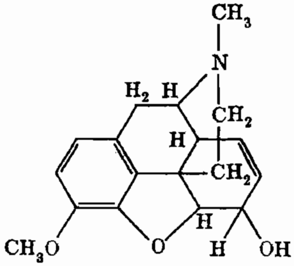
[1] BROWN and HOUGHTON, *J. Soc. Chem. Ind.*, **60**, 254–258 (1941).

[2] SHAW, *Proc. S. Dakota Acad. Sci.*, **25**, 57–61 (1945); HADER, *Ind. Eng. Chem.*, **44**, 2808 (1952); ULLMANN, *op. cit.*, 3d. ed., vol 3, p. 172.

film-forming properties are employed in emulsion paints and lacquers, greaseproofing paperboard, and sizing paper and textiles. It also is used in ice cream, ices, etc., and in the paper, leather, detergent, and ceramic industries.

Preparation. The following German[1] process was developed during World War II: shredded and aged alkali cellulose is reacted with sodium chloroacetate in a jacketed reactor. Before the product is discharged, enough sodium bicarbonate is added to neutralize the excess alkali. The material is then treated with methanol containing a little water, and the by-product sodium salts (chloride, carbonate, glycolate) are extracted to the desired product purity. The excess methanol is pressed out, and the sodium CMC is dried. The methanol used in the extraction process is purified by rectification, and the by-product sodium salts are discarded. For some uses, the impurities are not objectionable, and the unpurified sodium CMC is shipped to consumers without drying.

Codeine. Codeine, $CH_3O(C_{17}H_{17}ON)OH$, occurs naturally in opium and is extracted industrially along with morphine. It is derived from morphine, $HO(C_{17}H_{17}ON)OH$, by methylation of the phenolic hydroxyl. Because the demand for codeine for many years has exceeded the quantities that were naturally available by extraction from opium, a great deal of work has been done on the synthesis of codeine from morphine.[2]



In this and similar methylations, it is particularly difficult to secure the excellent yields that are necessay for the economic handling of such high-priced materials. In the morphine and codeine molecules, a tertiary nitrogen is present that can be alkylated to a "pentavalent" condition by the simple addition of methyl iodide or similar alkylating agents, whereupon the ring system is quite liable to be destroyed, following the reaction known as Hofman's exhaustive methylation. Consequently, the treatment of morphine with the ordinary simple methylating compounds results in low

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[1] ANON., *Chem. Inds.*, **60**, 236 (1947).

[2] SMALL, "Chemistry of the Opium Alkaloids," Supplement 103 to Public Health Reports, pp. 147, 175–176, 188, U.S. Government Printing Office, Washington, D.C., 1932.

yields of codeine and considerable destruction of the molecule. This applies to the treatment of the anhydrous solution of sodium morphinate with the ordinary alkylating agents, such as a methyl halide or dimethyl sulfate.[1]

On the other hand, as has been described by Boehringer,[2] Rodionov,[3] Schwyzer,[4] and Small,[5] high yields are obtained if a quaternary methylating agent is employed. With a quaternary ammonium base having nitrogen in the pentavalent condition, there is little or no tendency to form a pentavalent nitrogen derivative on the morphine nitrogen with consequent destruction of the morphine-ring system. Hence, the methylation proceeds almost exclusively on the phenolic hydroxyl, resulting in excellent yields of the methyl ether, codeine.

Methylation Reactions with Quaternary Nitrogen Methyl Derivatives.[6]

$$C_6H_5N(CH_3)_2 + CH_3Cl \rightarrow C_6H_5N(CH_3)_3Cl \qquad (1)$$

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$$

$$\underset{\text{Morphine}}{HO(C_{17}H_{17}ON)OH} + \underset{\substack{\text{Phenyl-}\\\text{trimethyl-}\\\text{ammonium}\\\text{Chloride}}}{C_6H_5N(CH_3)_3Cl} + \underset{\text{Sodium Ethylate}}{C_2H_5ONa} \rightarrow$$

$$\underset{\text{Codeine}}{CH_3O(C_{17}H_{17}ON)OH} + \underset{\text{Dimethylaniline}}{C_6H_5N(CH_3)_2} + \underset{\text{Ethanol}}{C_2H_5OH} + NaCl$$

$$C_6H_5SO_3H + ClSO_2OH \rightarrow C_6H_5SO_2Cl + H_2SO_4 \qquad (2)$$

$$C_6H_5SO_2Cl + CH_3OH + NaOH \rightarrow C_6H_5SO_2OCH_3 + NaCl + H_2O$$

$$C_6H_5SO_2OCH_3 + C_6H_5N(CH_3)_2 \rightarrow C_6H_5N(CH_3)_3OSO_2C_6H_5$$

$$C_6H_5N(CH_3)_3OSO_2C_6H_5 + NaOH \rightarrow C_6H_5N(CH_3)_3OH + NaOSO_2C_6H_5$$

$$C_6H_5N(CH_3)_3OH + HO(C_{17}H_{17}ON)OH \rightarrow CH_3O(C_{17}H_{17}ON)OH + C_6H_5N(CH_3)_2 + H_2O$$

$$p\text{-}CH_3C_6H_4SO_2OCH_3 + C_6H_5N(CH_3)_2 \rightarrow C_6H_5N(CH_3)_3OSO_2C_6H_4CH_3 \qquad (3)$$

$$HO(C_{17}H_{17}ON)OH + C_6H_5N(CH_3)_3OSO_2C_6H_4CH_3 + C_2H_5ONa \rightarrow CH_3O(C_{17}H_{17}ON)OH + C_6H_5N(CH_3)_2 + NaOSO_2C_6H_4CH_3 + C_2H_5OH$$

Methylation According to Reaction (1). Phenyltrimethylammonium chloride is an excellent methylating compound not only for morphine but for a number of other compounds such as antipyrine and theobromine. It is prepared and used according to the method of Schwyzer by warming dimethylaniline with methyl chloride in absolute alcohol in a 100-liter stirred autoclave provided with an enameled liner.[7] The sodium ethylate is prepared by dissolving metallic sodium in absolute alcohol. Schwyzer

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[1] BARROWCLIFF and CARR, *op. cit.*, pp. 55–57.

[2] Boehringer and Söhne, Ger. 247,180 (1909).

[3] RODIONOV, *Bull. soc. chim.*, 39, 305–325 (1926); 45, 109–121 (1928).

[4] SCHWYZER, *op. cit.*, pp. 374, 392.

[5] *Ibid.*

[6] It is clear that the formation of phenyltrimethylammonium chloride exemplifies alkyl bound to pentavalent nitrogen.

[7] SCHWYZER, *op. cit.*, pp. 388–390.

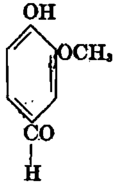
directs that 96 per cent alcohol be used, but other workers prefer absolute alcohol.

When this methylating compound is used, it is necessary to conduct the operation in an autoclave which should be charged with 10 kg of anhydrous morphine alkaloid, 7 kg of absolute alcohol, and 14.1 liters of sodium ethylate solution of such strength that 25 cc will neutralize 60 cc normal hydrochloric acid. The autoclave contents are carefully mixed, 6.5 kg of phenyltrimethylammonium chloride are then introduced, and the autoclave is closed and slowly warmed to a pressure of 60 lb. The vapors are blown off, and the autoclave allowed to cool overnight.

The contents of the autoclave are dissolved in 20 liters of water, and the alcohol is distilled off, after which the product is made acid to litmus with dilute sulfuric acid, 60 liters of water is added, and the dimethylaniline is distilled off. Codeine is separated from the small amount of unaltered morphine by extraction with 40 liters of benzene after being made alkaline with caustic soda. The benzene-codeine extraction is repeated twice. About 500–700 g of unaltered morphine can be recovered by acidifying the alkaline aqueous liquor and adding ammonia. Codeine is obtained usually by treating the benzene extracts with 40 liters of 10 per cent sulfuric acid. The yield is 91–93 per cent.

Methylation According to Reactions (2) *and* (3).[1] These methods depend on the preparation of an alcoholic solution of the phenyltrimethylammonium hydroxide directly [reaction (2)] or indirectly [reaction (3)] with the sodium salt either of the benzenesulfonate or of the toluenesulfonate being thrown out of solution. The alcoholic solution of the alkylating agent is then reacted with the compound to be methylated.

Vanillin. (3-Methoxy-4-hydroxybenzaldehyde).



The chemical transformation of a closely related, naturally occurring product into vanillin has long been the important source of supply. Among such available materials, oil of cloves is used most extensively, the eugenol being converted into isoeugenol and then into vanillin. In this case, the methoxy group found in vanillin is present in the original eugenol. Vanillin is also being made on a large scale by caustic soda treatment of lignin.

A great amount of work has been done on the synthesis of vanillin from

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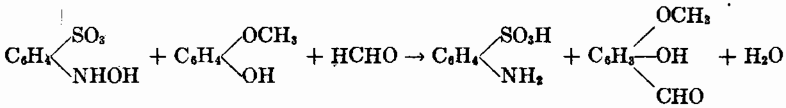
[1] See Groggins, op. cit., 2d ed., for details on Rodionov and Small.

cheap organic compounds. Several processes have been made to compete, probably the most important being that which introduces the formaldehyde group into guaiacol by the reaction of guaiacol with formaldehyde and



$$C_6H_4\begin{cases}SO_3\\NHOH\end{cases} + C_6H_4\begin{cases}OCH_3\\OH\end{cases} + HCHO \rightarrow C_6H_4\begin{cases}SO_3H\\NH_2\end{cases} + C_6H_3\begin{cases}OCH_3\\OH\\CHO\end{cases} + H_2O$$

phenylhydroxylaminesulfonic acid.

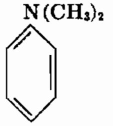
Alkyl Bound to Trivalent Nitrogen

Diethylamine. $(C_2H_5)_2NH$.

Diethylamine finds extensive use in the preparation of wetting and dispersing agents and enters into many syntheses. Through its employment, the alkyl groups are introduced into procaine. Its preparation from ethanol and ammonia by ammonolysis is described in Chap. 8. Schwyzer[1] also describes the synthesis from ethyl chloride and ammonia:

$$2C_2H_5Cl + 3NH_3 \rightarrow 2NH_4Cl + NH(C_2H_5)_2$$

Dimethylaniline.



Dimethylaniline is widely used as an intermediate in the manufacture of dyes, rubber accelerators, explosives, and some medical products. Such important dyes as auramine, malachite green, methyl violet, crystal violet, and methylene blue are derived from dimethylaniline. This compound also finds application in the preparation of quaternary alkylating compounds, such as are described under Codeine. The explosive tetryl, which is trinitrophenylmethylnitramine, is manufactured by the nitration of dimethylaniline.

The present technical preparation of dimethylaniline depends upon heating aniline, excess methanol, and an acid in an autoclave.

$$C_6H_5NH_2 + 2CH_3OH \xrightarrow{H_2SO_4} C_6H_5N(CH_3)_2 + 2H_2O$$

Although the literature states that either hydrochloric or sulfuric acid can be used, technically only the sulfuric is employed, as the hydrochloric acid is too corrosive.

The technical preparation of dimethylaniline proceeds along these lines: 200 lb of aniline is mixed with 220 lb of methanol, and 20 lb of 66°Bé

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[1] SCHWYZER, *op. cit.*, pp. 230–233. See GROGGINS, *op. cit.*, 3d ed., pp. 596–597.

sulfuric acid is added. The mixture becomes warm, and considerable aniline sulfate separates out; this is well stirred and then pumped into a steel autoclave of sufficient capacity to allow for expansion of the charge when hot. The autoclave is heated during the course of 2 hr to around 205°C and then maintained at 205°C or slightly higher for 5 or 6 hr, the pressure rising to around 525 psi or sometimes 550 psi. The autoclave either can be allowed to cool or can be discharged while still hot, through a cooling condenser into a neutralizing vessel. Here the acid is neutralized with caustic soda, after which the products of the reaction are subjected to vacuum distillation for the recovery of the excess methanol and the purification of the dimethylaniline produced. A yield of around 95 per cent, based on aniline used, is obtained; the net yield, based on the methanol, is somewhat smaller. When the reaction is carried to completion, the dimethylaniline should not contain more than 0.4 per cent of monomethylaniline.

An unlined steel autoclave can be used very satisfactorily for this purpose (see Fig. 14-10), although periodic hydraulic tests should be made on the apparatus at 500 psi in excess of working pressure, to ensure its continued safe condition. An occasional inspection should be made, at least of the upper section at the vapor line where corrosion is most likely to occur. Various heating mediums have been employed, such as direct fire, circulated hot oil, or superheated steam. For the last, which is certainly the cleanest and most convenient heating medium, 200–250°F superheat should be given to the ordinary steam at 100 psi.

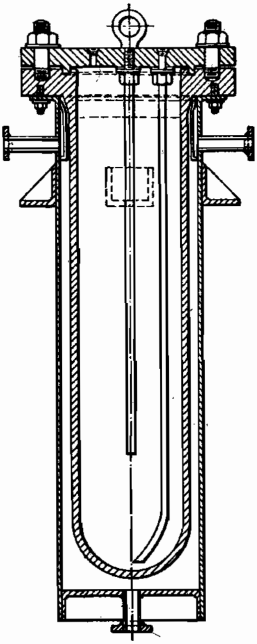

FIG. 14-10. Autoclave.

It is necessary that dimethylaniline be free from all except a few tenths of 1 per cent of monomethylaniline; consequently, great care must be taken in conducting the initial reaction, as monomethylaniline is difficult to separate by distillation because of the small boiling-point difference between the two. Benzylation of the monomethylaniline yields benzylmethylaniline, and this derivative can be separated easily from the dimethylaniline by fractionation. The formation of similar derivatives of monomethylaniline with toluenesulfonyl chloride or with phthalic acid[1] removes this by-product more completely.

In this methylation, a number of side reactions occur to a small extent. The quaternary ammonium salt, $C_6H_5N(CH_3)_3{\cdot}HSO_4$, is formed and is

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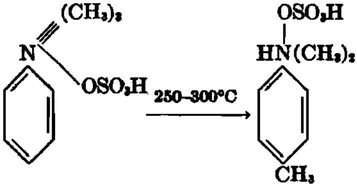
[1] Britton and Holmes, U.S. 1,890,246 (1932).

quite stable, being decomposed by heating with concentrated caustic soda only when the temperature is elevated considerably (170–180°C). There are some nuclear methylated products which are very probably formed from the quaternary compound. Nuclear methylation is more pronounced at temperatures of around 250°C and is one of the reasons for avoiding such high temperatures or local overheating. In case the reaction does not go to completion, the heating period rather than the temperature should be increased. Excessive sulfuric acid also appears to lead to formation of nuclear products. Nuclear methylation can be carried far enough, for example, by heating under pressure at a temperature of 300–350°C, to form mesidine (2,4,6-trimethylaniline) as well as *p*- and *o*-toluidine, *m*-xylidine, etc. However, it is unlikely that the conditions in the manufacture of dimethylaniline ever go beyond the following reaction:



In the technical manufacture of dimethylaniline, the formation of some substituted diphenylmethanes is observed. Here, undoubtedly part of the methyl alcohol is oxidized to formaldehyde, causing this condensation. Much of the loss of methanol is due to the formation of methyl ether, which is usually lost in the blowoff at the end of the run.

Alkyl Bound to Lead and Sulfur

Tetraethyllead[1] **(TEL)** [$Pb(C_2H_5)_4$]. Tetraethyllead is widely used for the prevention of knocking in high-compression gasoline engines, 0.04 per cent TEL being as efficient in this respect as 25 per cent benzene. In order to prevent the deposition of lead in the exhaust sections of the engine, 3 parts by volume of TEL are mixed with 2 parts of ethylene bromide (CH_2BrCH_2Br) or a mixture of ethylene bromide and ethylene chloride. The ethylene halide converts the lead oxide formed during the combustion into the volatile lead halide.

Preparation. The mechanism of reaction is not known but the following is a simplified representation of the main reaction.

$$4PbNa + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

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[1] See GROGGINS, *op. cit.*, 4th ed., p. 841, for earlier patents. The following are some issued within the past few years which pertain to the manufacture of TEL: Shapiro et al., U.S. 2,635,106 (1953); Rudy, U.S. 2,723,227 (1955); Wall, U.S. 2,723,913 (1955); Madden, U.S. 2,727,052 (1955); Neher, U.S. 2,728,656 (1955); Hobbs, U.S. 2,739,526 (1956); Mattison, U.S. 2,744,126 (1956).

In the commercial production of tetraethyllead, lead-monosodium alloy is placed in a jacketed autoclave equipped with an agitator, nitrogen and ethyl chloride are then added. As the reaction between the ethyl chloride and the alloy begins, heat is evolved and the pressure of the system begins to rise because of the vapor pressure of the ethyl chloride. At optimum reaction conditions, about 65–75°C and about 50–65 psi, a cooling medium is introduced to the autoclave jacket and condenser. About this time the autoclave, condenser, liquid-gas separator, and connecting pipes are filled with ethyl chloride vapor. The ethyl chloride in the condenser is condensed and flows back into the autoclave (see Fig. 14-11). This condensation causes a decrease in pressure, drawing more vapors into the condenser so that the side reaction gases may be removed. As the ethyl chloride is added, the pressure should be about 60–75 psi and should not rise over 80 psi. This is done by regulating the feed rate. When all the ethyl chloride is added, the pressure will decrease rapidly to 50 psi. At this point, the flow of the cooling media is stopped and the reaction is permitted to go to completion.[1]

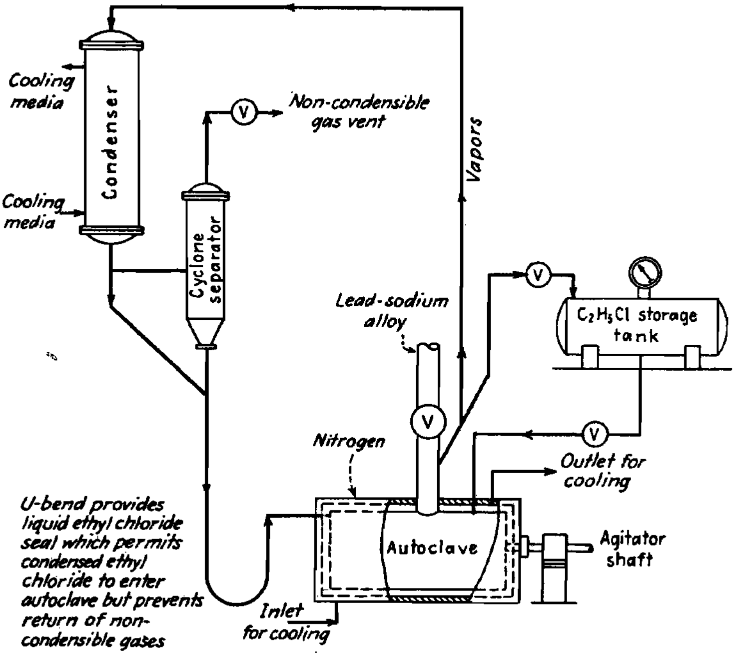

FIG. 14-11. Flow diagram for the preparation of tetraethyllead. Yield is 85 to 90 per cent on Na with 10 per cent of the Na causing side reactions leading to C_2H_6, C_2H_4, and C_4H_{10}.

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[1] Mitchell et al., U.S. 2,411,453 (1946).

The product from the autoclave reactor is discharged to a batch-type steam still, partly filled with water, where the ethyl chloride and the TEL are distilled off and fractionated from the solution of NaCl and the unreacted lead. The yield of TEL is 85–90 per cent based on sodium used; approximately 10 per cent of the sodium is involved in side reactions, leading to the formation of C_2H_6, C_2H_4, and C_4H_{10}.

Lauryl Mercaptan. Lauryl mercaptan, n-$C_{12}H_{25}SH$, also named dodecyl mercaptan and 1-dodecanethiol, is commercially important as a modifier in the polymerization of synthetic rubber and is of interest because of its potentialities as an intermediate in the manufacture of detergents, flotation agents, insecticides, etc.[1] Pure lauryl mercaptan is a clear water-white liquid which boils in the range 133–135°C at 7 mm pressure. The commercial lauryl mercaptan is more of a gray color with a relatively wide boiling range (135°C ± 25°). Most recipes for synthetic GR-S polymerized at 50°C (122°F) specify lauryl mercaptan, while recipes for use at 5°C (41°F) mostly use mixed tertiary mercaptans.

The commercial lauryl mercaptan is made from the lauric acid fraction of coconut oil. The acids are reduced either catalytically with hydrogen or with sodium metal to alcohols (Lorol), which are converted to the chlorides. The chlorides are reacted with sodium acid sulfide.[2] The alkylation takes place in a stainless-steel agitated autoclave suitable for pressures up to 250 psi. The sequence of operations and the operating procedure are substantially the following: 1,345 lb lauryl chloride, 600 lb commercial sodium acid sulfide, 600 lb methanol, and 10 lb zinc dust are charged to an autoclave. The autoclave is pressured to 50 psig with carbon dioxide, heated to 150–155°C, and held at this temperature for 6 hr with agitation. The mixture is run to a settling tank after cooling. The maximum pressure on the autoclave is 240 psig. The mercaptan is water-washed and finally purified by vacuum fractionation. The conversion is 84.5 per cent, or 1,100 lb of lauryl mercaptan is obtained. A small amount of unreacted lauryl chloride is recovered.[3]

Since polymerization at lower temperatures results in a superior synthetic GR-S (cold rubber), the tertiary modifiers have an opportunity to play an important role in this process. The tertiary mercaptans are a mixture of mercaptans having 11–13 carbon atoms with an average molecular weight corresponding to about 12 carbon atoms, as compared to commercial lauryl mercaptan which is 60 per cent normal lauryl and the balance normal mercaptans having 10, 14, and 16 carbon atoms.[4] Tertiary

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[1] GILMAN, "Organic Chemistry," Vol. I, pp. 839–852, John Wiley & Sons, Inc., New York, 1943; U.S. 2,376,675 (1945); 2,404,613; 2,402,614; 2,402,642; 2,402,643 (1946).

[2] U.S. 2,085,452 (1937); 2,395,240 (1946).

[3] U.S. 2,395,240 (1946).

[4] KOLTHOFF and HARRIS, *J. Polymer Sci.*, **2**, 49 (1947).

mercaptans are made by adding hydrogen sulfide to olefins of petroleum origin.[1] The olefins are polymerization products of isobutylene, isobutylene-propylene mixture, propylene, or a narrow cut of highly olefinic, catalytically cracked gasoline. The hydrogen sulfide is a by-product of a Girbitol unit employed to remove hydrogen sulfide from sour natural gas.

The liquid scrubbed hydrogen sulfide is mixed with the olefinic material (usually a 165–200°C fraction of propylene-isobutylene polymer) in a molar ratio of 1.5:1 and passed into a catalyst chamber in the liquid phase. The residence time in the catalyst case is 1 hr with the temperature under 150°C. The conversion is about 35 per cent or better with a very active catalyst, and yields vary from 60–80 per cent based on olefin charged. The product is purified by vacuum fractionation after the recycle hydrogen sulfide is stripped at about 50 lb pressure. The olefin is taken overhead in one column and the mercaptan in a second. The final material contains 90 plus per cent isomeric mercaptans.

TABLE 14-10. PHYSICAL AND CHEMICAL PROPERTIES OF SOME LONG-CHAIN TERTIARY ALKYL MERCAPTANS*

Mercaptan product	Olefin feedstock		Sp gr 60°F/60°F	Mercaptan sulfur, wt %	Avg. mol. wt	Apparent mercaptan purity
	Source	Boiling range, °F				
tert-Dodecyl	C_3H_6-C_4H_8 polymer	320–380	0.8713	15.9	194	97.0
tert-Tetradecyl	C_3H_6-C_4H_8 polymer	400–450	0.8770	11.9	230	85.6
tert-Hexadecyl	C_3H_6-C_4H_8 polymer	450–500	0.8830	10.3	249	80.0
tert-Tetradecyl	C_3H_6-C_4H_8 polymer	400–450	0.8821	14.1	226	99.2
tert-Dodecyl	Hexene dimer	372–405	0.8945	15.6	203	99.3

* SCHULZE et al., *Ind. Eng. Chem.*, **40**, 2313 (1948).

Commercial-scale production of the high-molecular-weight tertiary mercaptans has yielded a number of products identified as tertiary dodecyl, tetradecyl, and hexadecyl mercaptans. Typical properties of these products are listed in Table 14-10. These tertiary mercaptans as a class undergo metal salt formation, oxidation to disulfides, and other known reactions of the sulfhydryl group.

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[1] SCHULZE et al., *Ind. Eng. Chem.*, **40**, 2308–2313 (1948); "Summary of Technical and Patent Assets," Phillips Petroleum Company, 1946.

CHAPTER 15

POLYMERIZATION

W. PETER HOHENSTEIN[1] AND ROBERT ULLMAN[1]

Part 1. Principles of Polymer Chemistry

I. INTRODUCTION

Among the substances with which the chemist and the chemical engineer deal either in the laboratory or in industrial production is a group of materials which, although differing greatly in physical and mechanical behavior among themselves, show certain common characteristics and thus can be distinguished clearly from other chemical compounds. These substances, which can be characterized as rubbers, fibers, resins, or plastics, consist of molecules of high individual molecular weights which may vary from a few thousands up to the tens of millions. Thus, the over-all molecular weight of each of these materials can be expressed only as a statistical average of the total of the molecular species of which it consists. The molecules of each of these high-molecular-weight substances consist of a sequence of one or more basic units which are linked together in chains or networks of covalent bonds. The basic unit or units are called monomers, and the corresponding network or chain of linked monomers is known as a polymer.

While the primary emphasis in this chapter will be directed toward man-made polymers, it is important to remember that many natural products are polymeric. One of the most important of these is rubber, a form of polyisoprene with distinctive elastic properties from which its practical importance is derived. Other important natural polymers are silk, wool, gutta-percha, cellulose, starch, and all the natural proteins. It is a curious and interesting fact that natural polymers have not been obtained synthetically (with the possible exception of a recently prepared polyisoprene which has a structure similar to the natural one), even though the experimental conditions which can be employed in the laboratory may be varied and controlled to a much greater degree than the actual conditions under which these polymers are formed in nature.

One of the outstanding characteristics of low-molecular-weight ma-

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terials is a sharp melting point. Polymers, however, have a more or less extended melting range[1] during which they pass through several stages, changing from a rigid solid to a rubber and then almost imperceptibly to a highly viscous liquid as the temperature is raised.

The reason that polymers do not possess a sharp melting point is twofold. First of all, the polymer is not made up of molecules of identical molecular weight, but contains a mixture of homologues of various degrees of polymerization.[2] Secondly, even if the polymer were of uniform molecular weight, the very size of its large molecules would prevent them from forming the perfect sharp melting crystals which are found in many low-molecular-weight materials.

Of the various types of physical measurements which can be employed to characterize nonpolymeric molecules, certain ones are of primary importance. Among these are freezing-point depressions, vapor pressures, boiling points, and crystal structure. These measurements are suitable only to a limited extent for the characterization of polymeric materials, and other physical methods have to be employed to obtain satisfactory results. Of particular usefulness are studies of polymer solutions, which yield data on their viscosity, osmotic pressure, light scattering, and sedimentation in the ultracentrifuge. The experimental results gathered from these investigations provide much useful information about the polymers themselves.

The reason that methods conventional for low-molecular-weight compounds prove unsatisfactory for polymers arises from the fact that the polymer molecule is so much larger than the monomer. Such measurements as freezing-point depressions, for example, which are easy to carry out for molecules of a molecular weight of 500 or less, and which give satisfactory results, show only an insufficient magnitude of the effect for high polymers and do not allow exact determinations. Contrariwise, ultracentrifugation, for example, is applicable only for materials where the individual molecules are sufficiently large, and diffusion is not accentuated by too active Brownian motion.

X-ray and electron-diffraction analysis of high-polymeric materials show that the molecules in some of them are arranged in a state of complete disorder (amorphous state); others exhibit a high degree of order (crystalline and oriented states). In most cases the diffraction diagrams indicate the simultaneous existence of ordered and disordered domains. Intensive studies relating the properties of high polymers to the spatial arrangement of their molecules show this to be one of the major factors which determine their physical and chemical behavior.

[1] Certain proteins have been found which form nearly perfect crystals, and some of these melt sharply under appropriate conditions.

[2] Again certain proteins are exceptional.

Other contributing factors are the average molecular weight, the molecular-weight distribution function, the chemical composition of the polymer, and the spatial arrangement of substituents along the molecular chain.

Among the most important of the properties of polymers from a practical and industrial point of view are their high-temperature and low-temperature behaviors. Some of them soften upon heating and regain their original hardness upon subsequent cooling, whereby the heating and cooling cycle can be repeated at will. These materials are called *thermoplastics*. Others become insoluble and infusable after the first heating and decompose on further increase in temperature. These are called *thermosetting materials*. Many polymers tend to become brittle and unworkable at low temperatures; on the other hand, softening ranges of other polymers are often too low and inadequate for specific industrial application. Therefore the improvement of softening temperatures for thermoplastics, the resistance of thermosettings to high temperatures without charring and decomposition, and, finally, the avoidance of brittleness and stiffness of rubbery and flexible polymeric materials at low temperatures have been the subject of most intensive research by industrial polymer chemists.

The science of high polymers has developed as a branch of chemistry somewhat separately from other related subject matter, though the basic laws of chemistry are the same for both high- and low-molecular-weight substances. By investigating closely the molecular structure of polymeric materials and by studying the relationships between this structure and the performance of the polymer, the industrial scientist has been able to prepare new materials with improved properties. He has also succeeded in creating polymeric systems which possess certain advantages for industrial manufacturing purposes by applying the specific principles of polymer chemistry. Finally, it has been possible to devise and manufacture polymers with highly specific properties suitable for special applications, where they perform better than other working materials which were previously used. All these developments have caused the present yearly production of synthetic polymers to be higher by an order of magnitude than it was ten years ago, and every indication points to a further comparable increase.

II. CHEMISTRY OF POLYMERIZATION REACTIONS

Functionality

Large molecular complexes can be built up in two possible ways: either by an association of small molecules by means of secondary bonds (van der Waals forces, etc.) or by continuous chemical reactions between small molecules, thus establishing strong chemical bonds between them. In the first case, those molecular associations which exist, for instance, in water, alcohols, and organic acids are extremely sensitive to disturbances of physical or chemical nature, since the forces binding the molecules are relatively weak (3,000–6,000 cal per mole); the dissociation energy of primary chemical bonds, however, has an entirely different order of magnitude (50,000–100,000 cal per mole). Natural and synthetic high polymers consist of large molecules built up by chemical bonds of the latter type.

The conception of low-molecular-weight organic molecules linking up to give a polymer molecule poses the question of the nature of the reactions that produce such polymers and the types of molecules that are capable of undergoing these reactions. The number of polymeric substances found in nature and produced artificially, and especially the variety of properties exhibited by them, seemed at first to indicate an almost unlimited number of possibilities in both respects. In later investigations, however, and primarily through the brilliant contributions of Carothers,[1] it was shown that two basic principles determine whether polymerization will occur at all. The first of these establishes the concept of *polyfunctionality* of a molecule as a requirement for the formation of polymer; the second divides all polymerization reactions into two distinct types: "addition" and "condensation" polymerizations. Later on though, some polymerization reactions were discovered which show characteristics of both types simultaneously. With the aid of these two principles, it becomes possible to choose from the set of presently available molecules those which possess the structure necessary for the formation of macromolecules by either one of the two typical reactions.

A molecule is called bi- or polyfunctional if two or more reactive or functional groups either are present at the beginning of the reaction or appear in the course of it. A monofunctional material can react at one point, a bifunctional material at two points, and a polyfunctional material at many points. Simple examples of bi- or polyfunctional molecules are hydroxy or amino acids, di- or polyalcohols, -amines, or -acids. These molecules interact with each other through their chemically active groups; but since two or more of them are located on each molecule, the reaction continues in two or three directions and linear or tridimensional molecules are formed. Figure 15-1 illustrates schematically the reaction between two monofunctional molecules, which does not produce macromolecules (*a*), whereas bifunctional monomers lead to linear-chain molecules (*b*), and the reaction of trifunctional molecules produces complicated networklike structures (*c*).

Another type of bifunctionality is exhibited by a large group of molecules containing double or triple bonds. Under the influence of heat or light energy, or if subjected to other forms of radiation, the two second-

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[1] CAROTHERS, *Chem. Revs.*, **8**, 353 (1931); MARK and WHITBY, "Collected Papers of W. H. Carothers," Interscience Publishers, Inc., New York, 1940.

order (or π) electrons of the double bond may go into an excited state and may thus become available for a bifunctional reaction of the molecule. The over-all reaction may be expressed as

$$nH_2C{=}CH_2 \rightarrow R{-}CH_2{-}CH_2{-}(CH_2{-}CH_2)_{n-2}{-}CH_2{-}CH_2{-}\cdots$$

Another way to induce bifunctionality in a double-bond molecule is to create high polarity in its originally neutral or only slightly polar structure.

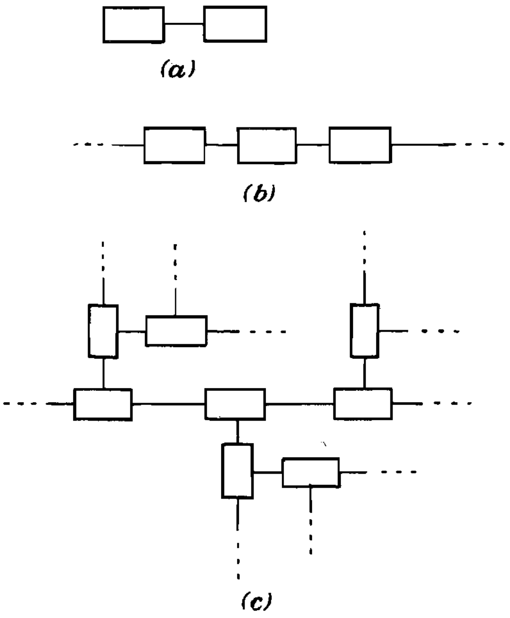


FIG. 15-1. Reactions of (a) monofunctional, (b) bifunctional, and (c) polyfunctional molecules.

This can be achieved by introducing a highly polar molecule such as, for instance, boron trifluoride, BF_3, into the reaction mixture under appropriate reaction conditions. It has been found that ionic polymerizations of this type require the presence of a small amount of a cocatalyst such as, for instance, water, which forms a highly polar molecular compound with the main catalyst. If such a highly polar compound approaches a monomer molecule containing a double bond, a charge separation may take place in the latter by a displacement of the two π electrons. These electrons will now be located at one specific site of the molecule, causing it to be negatively charged there and resulting in the formation of a positive charge at an opposite site. Figure 15-2a illustrates the charge separation in a schematic form and shows also how the new "bifunctional" molecule can be the beginning of a polymer chain.

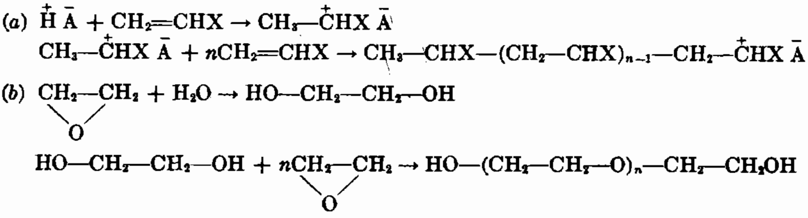
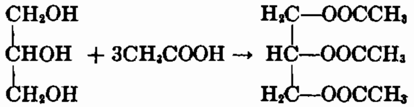


FIG. 15-2. Examples of polymer chain initiation by bifunctional molecules.

Bifunctional molecules may result from the opening of three—or more—membered rings, as for instance in the case of the formation of polymer molecules from ethylene oxide or tetrahydrofuran. An illustration of the over-all reaction scheme is given in Fig. 15-2*b*.

It must be emphasized again that polymer formation can be achieved only in a reaction where *all* participating molecules are bi- or polyfunctional. Monofunctional groups reacting with bi- or polyfunctional groups do not lead to polymer formation as can be seen from the reaction of glycerine with acetic acid:



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3CH_3COOH \rightarrow \begin{array}{l} H_2C—OOCCH_3 \\ \quad | \\ HC—OOCCH_3 \\ \quad | \\ H_2C—OOCCH_3 \end{array}$$

The influence of the functionality concept in determining polymer structure is decisive. In any reaction where the average functionality of the product is less than the average functionality of the reactants, polymerization does not take place. If it is equal in the product to that of the reactants, a polymer is formed; it is linear in structure and grows to a finite size. If, however, the average functionality of the product is greater than that of the reactants, then the reaction, if carried far enough, produces a tridimensional network polymer. The tridimensional and the linear polymers differ sharply in many of their physical and chemical characteristics, particularly in their solution properties and their fusibility. In general, linear polymers are thermoplastic; they are fusible and soluble in appropriate solvents. Tridimensional network polymers are thermosetting; they may imbibe solvents and swell, forming a gel-like material, but they will not dissolve. They do not melt but, upon continuous heating, decompose and break down chemically.

Polymerization Reactions

Polymerization reactions are either *condensation* reactions or *addition* reactions. The polymer formation in condensation polymerization proceeds stepwise, the various intermediates, dimer, trimer, etc., existing as stable molecules until the next reaction step. Small molecules, usually water, are split off at each step of the reaction.

Addition polymerization is characterized by the fact that the reaction from monomer to polymer occurs without elimination of by-products. During the addition reaction, no stable compounds are formed because the intermediates are comparatively short-lived radicals or ions. The formation of the polymer chain is usually accomplished in a fraction of a second and in one single sweep. Polymerization at the double bond is a typical addition reaction of this type. Certain addition reactions, which proceed by first opening the ring of a cyclic compound, follow a stepwise procedure. Thus they occupy a position in between the two reaction types, showing certain similarities to each.

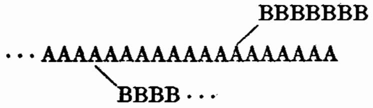
A form of addition polymerization is that of copolymerization in which two or more different monomers are linked together, either at random or alternating, to form one single copolymer chain or network:

· · · AABABBBBABABBAAABBBAB · · · random
· · · ABABABABABABABAB · · · alternating

Recently two special types of copolymerization have been investigated intensely and have shown promise for use in large-scale industrial production. They are called block polymerization and graft polymerization, respectively. In block polymerization, sequences of one type of monomer are prepolymerized and then joined to the prepolymerized sequences of another monomer:

$$\cdots \underbrace{\mathrm{AAAAAAAA}}_{\mathrm{A}}\ \underbrace{\mathrm{BBB}}_{\mathrm{B}}\ \underbrace{\mathrm{AAAAA}}_{\mathrm{A}}\ \underbrace{\mathrm{BBBBBBBB}}_{\mathrm{B}}\ \underbrace{\mathrm{AAA}}_{\mathrm{A}} \cdots$$

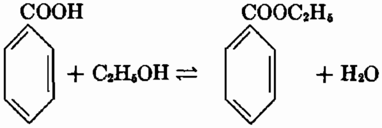
A typical example of graft polymerization is one in which sequences of monomer B are grafted onto the main chain consisting of A units:



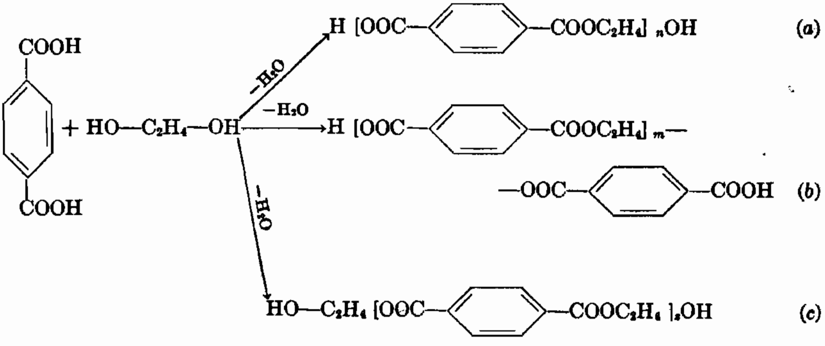
Finally a type of addition polymerization calling for the employment of stereospecific catalysts has recently aroused much interest in the laboratory as well as in industry. With the aid of such catalysts, an addition polymerization yields certain polymers in which the main chain as well as the chemical substituents are situated in a highly ordered spatial pattern. Polymers of physical and chemical characteristics are thus obtained which contrast markedly from those formed in normal polymerizations.

POLYCONDENSATION

Polycondensation proceeds fundamentally in the same manner as condensations between low-molecular-weight substances. For instance, the energy of activation for polyesterifications and for polyamide formations lies between 15,000 and 30,000 cal per mole. These data come fairly close to the energy of activation for esterification and amidation of monofunctional molecules. The same acidic or basic catalysts are effective in the formation of a condensation-polymer molecule and of a low-molecular-weight condensation product. The mechanism of the polyreaction presents all characteristics of a step reaction; i.e., the chains grow proportionally to the reaction time, and each of the chain molecules is stable at any stage of the propagation process. Condensations between low-molecular-weight compounds are equilibrium reactions. In polycondensations the same principles hold true, though certain complications do arise. Consider, for instance, the esterification of benzoic acid with ethyl alcohol:

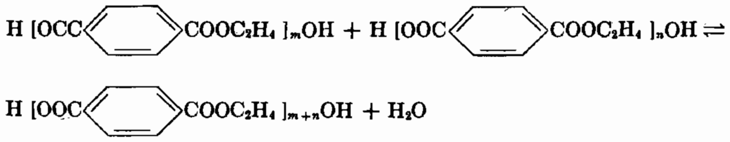


Under given conditions of temperature, pressure, and initial reactant concentration, the reaction will proceed at a certain measurable rate and reach an equilibrium. In a polycondensation, employing bifunctional reactants of a similar character, i.e., terephthalic acid and ethylene glycol, three types



of polymer molecules are formed. Type *a* is a polymer with one terminal carboxyl and one terminal hydroxyl, *b* is a polymer with two terminal carboxyls, and *c* is a polymer with two terminal hydroxyls. The prevalence of each type is critically dependent on the initial concentrations of the reactants. Molecules of type *a* appear in appreciable amounts only when the molar ratio of reactants is unity. An excess of acid causes all the polymer to be of type *b*, and an excess of glycol leads to molecules of type *c*. The quantity *n* or *m* or *z* in the above formulas is called the degree of polymerization $\overline{DP}$ and depends in part on reactant concentration. If all the acid molecules are used up, the polymerization does not proceed further. If there is a molar excess of glycol, this may occur at a time when the $\overline{DP}$ is not very large.

The conditions of esterification are such that there is a certain tendency of the polymerized molecule to hydrolyze and thus to depolymerize. In the reaction



the possibility of hydrolysis is very great. There are only two places where the ester bond may form, but there are $m + n$ sites at which the ester bond may be hydrolyzed. As a result, even though the tendency toward esterification as opposed to hydrolysis may be very high, let us say 200:1, the reaction proceeds no further after a certain $\overline{DP}$ is attained, because the number of places at which hydrolysis may take place is so large.

This leads to serious problems in the industrial production of polyesters and polyamides where it is essential to remove the last traces of water during polymerization in order to attain a molecular weight high enough for the polymer to form a useful material. Figure 15-3 illustrates the relationship between the amount of water present at a certain stage of a polyester

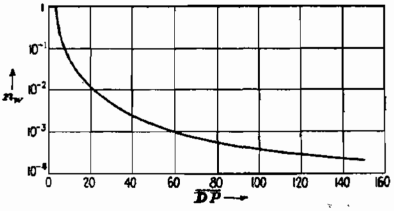
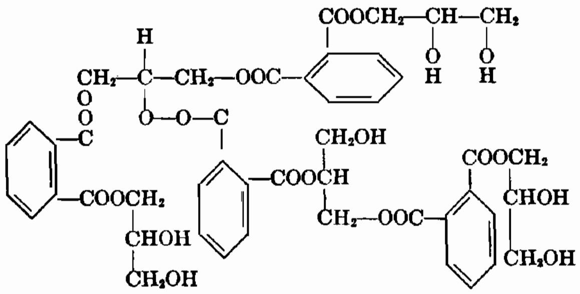


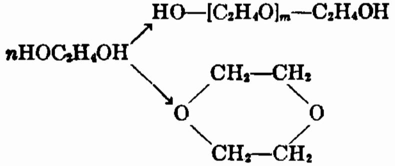
FIG. 15-3. Relationship between water content (mole fractions) and average polymerization degree in polyesters.

reaction and the average degree of polymerization of the polymer at that stage.

While systems of sufficiently high functionality usually lead to gelation and consequently to the formation of infusible and insoluble materials, this gelation may be prevented by including an adequate excess of one of the reacting components. For example, a stoichiometric reaction between glycerine and phthalic acid yields a large tridimensional network polymer, while in a reaction involving a molar excess of glycerine only a limited and considerably less extensive network is formed in which all the remaining end groups are hydroxyl. The excess glycerine serves to esterify all the acid groups before the critical infinite network forms. Such a molecule is pictured below.



Another reaction which may interfere with the polycondensation of difunctional molecules is the formation of cylic compounds. In the self-condensation of alcohols to form polyethers, for example, either of the following products may be formed:

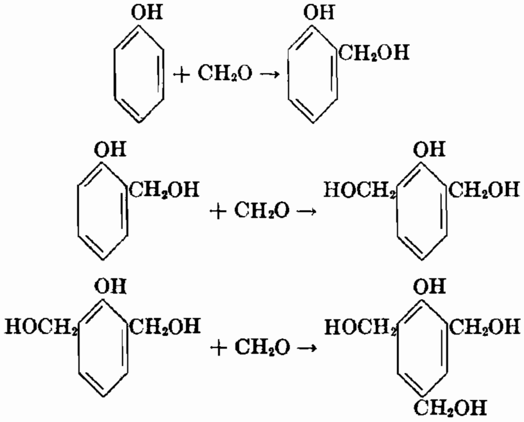


Whether or not the cyclization reaction competes seriously with the formation of a linear polymer depends on the ease of formation of the ring compound. Five- to seven-membered rings are quite easily formed, and larger ones containing up to 12 atoms occur to a lesser but still appreciable amount. When such a possibility exists, the formation of a cyclic low-molecular-weight compound may seriously interfere with polymerization. Likewise, if cyclization is possible at the active end of a growing polymer chain, then the chances of growth of this chain may be greatly impaired, resulting again in the formation of an excessive amount of relatively low-molecular-weight species. If, however, the only possible ring structures contain less than 5 or more than 12 carbon atoms, then the concentration of cyclic material formed is negligible. For example, in the case of the reaction between hexamethylenediamine and adipic acid leading to the formation of nylon 66 polymer the smallest possible ring structure contains 16

$$n\mathrm{H_2N(CH_2)_6NH_2} + n\mathrm{HOOC(CH_2)_4COOH} \xrightarrow{-\mathrm{H_2O}} \mathrm{H_2N{-}[(CH_2)_6NHOC(CH_2)_4CO]_{\mathit{n}}OH}$$

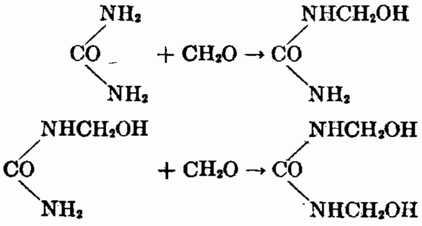
atoms, and very little, if any, of this is formed under ordinary polymerization conditions. However, ω-caprolactam which polymerizes to form another polyamide (nylon 6) is a seven-membered ring, and up to 10 per cent of low-molecular-weight specimen can be detected in the polymer under certain reaction conditions.

Some polycondensations are preceded by an addition reaction which first creates reactive groups on the monomer molecules. These groups interact then by polycondensation with one another and form large molecules. An example is the reaction of phenol and formaldhyde in aqueous solution, resulting in the formation of mono-, di-, or trimethylol phenols:



In the different stages of this reaction the formaldehyde adds to one or two or to all three functional positions of the phenol molecule, and a new carbon-carbon bond is established. Once the phenol alcohols are formed, polycondensation sets in, and by splitting out water and later formaldehyde, large chain and network molecules are built up.

A similar mechanism is encountered if urea and formaldehyde interact in an aqueous medium. The four functional positions on the two nitrogen atoms of urea may be occupied partly or completely by methylol groups:



It must be emphasized that in both cases the products of the initial addition reaction are of low molecular weight; the reaction serves only to prepare monomeric units with two or more functional groups in the molecule.

Linear polycondensation leads to molecules with a regular succession of the monomer units along the chains; there are two functional groups at the chain ends still unreacted. In many cases it is possible to determine the number of unreacted end groups analytically and to compute from them the number average molecular weight of the polymer.

ADDITION POLYMERIZATION

Two types of addition polymerization exist that differ in their reaction mechanism and their kinetic behavior from each other and from polycondensations. The first proceeds as a step reaction, whereas the second one shows all characteristics of a chain reaction. The step-reaction type of addition polymerization may be exemplified by the polymerization of ethylene oxide in the presence of traces of water (see Fig. 15-2*b*). The chains grow proportionally to the reaction time, and each intermediate product is a stable, saturated molecule. The main difference between this reaction and a polycondensation is the absence of any reaction product that is split off during the process. On the other hand, it differs distinctly from the second type of addition polymerization in which the polymer chain is built up instantly after an initiator has been formed and where the intermediates are unstable species. Some addition polymers of the step-reaction type have become industrially important. Foremost among them are polysiloxanes, polyethylene oxides, and polyurethanes.

Of particular interest, however, are those addition polymerizations which proceed as a chain reaction and which mostly involve molecules possessing aliphatic double or triple bonds. The reaction consists of a number of separate phases which follow each other consecutively and rapidly until the polymer attains its final molecular weight, which does not change thereafter.[1]

The polymerization begins with a slow initiation step in which an unstable species is first formed, possessing either unpaired electrons or bearing electrical charges. The chain propagation is the next phase in which this unstable active center attacks a monomer, creating a new unstable intermediate capable of attacking and adding other monomers. The propagation step is very rapid and occurs a great many times before one of various possible termination reactions stops the growth of the chain. During the polymerization another process, chain transfer, may occur; this is a process by which the activity of a growing chain is transferred, by collision, to either a "dead" chain, i.e., a chain which has been terminated, or to a monomer.

Whether or not an active center can be formed, i.e., whether or not an unsaturated molecule is suitable for addition polymerizations depends on a number of factors. In the first place, the energy necessary to open one of the two links of an aliphatic double bond depends upon the nature of the

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[1] Because of chain transfer, certain exceptions to this statement will be encountered. These do not invalidate the general principles discussed here.

two atoms that are linked together by it, for instance, C═C or C═O. The electronic configurations of each of these atoms and the distances between them influence the dissociation energy of the double or triple bond. In Table 15-1, the approximate values of a number of dissociation energies of the more common types of unsaturated molecules are listed.

TABLE 15-1. DISSOCIATION ENERGIES OF CERTAIN BONDS

	Total dissociation energy, cal per mole
C—C aliphatic	70,000
C═C aliphatic	100,000
C≡C	123,000
C—N	49,000
C═N	94,000
C≡N	150,000
C—O	70,000
C═O aldehyde	149,000
C═O ketone	152,000
C—S	54,000
C═S	103,000

These data show that it takes 70,000 cal per mole to break a single bond (σ electrons) between carbon and carbon atoms and only 30,000 cal per mole more to break also the second link (π electrons) of the double bond. If one examines the bond strengths between carbon and other atoms, such as nitrogen, sulfur, and oxygen, it becomes apparent that the dissociation energy for carbon-oxygen double bonds is comparatively high, as is the case with a carbon-nitrogen triple bond. It is known, indeed, that substances containing such bonds are difficult to polymerize, whereas polymerization reactions involving the carbon-carbon triple bond and the carbon-nitrogen double bond and the carbon-sulfur double bond are easier to accomplish.

Besides being dependent upon the atoms constituting the double or triple bond, the energy required to activate the bond is influenced by two more factors: (1) the substituents on the atoms which form the multiple bond and (2) the presence of conjugated or cumulated multiple bonds.

It can be generally stated that substitution decreases the energy necessary for activation of the bond, especially so if it is unsymmetric, i.e., if one or both hydrogen atoms on only *one* carbon atom of the double bond are replaced. If substitution in the vicinity of the double bond becomes too heavy, the tendency to polymerize decreases rapidly, presumably because of steric hindrance or resonance stabilization.

Also of importance for the reactivity of the double bond is the nature of the substituents. The following examples illustrate these empirical rules: if the usual free-radical type of catalysts are used, ethylene, $CH_2{=}CH_2$, polymerizes only under high pressure and high temperatures, whereas most of the monosubstituted ethylenes, the so-called vinyl derivatives $CH_2{=}CHX$, polymerize under very much milder conditions. Only if the substituent is very bulky, such as in vinylanthracene or vinylfluorene, a decrease in the tendency to polymerize can be observed. If the number of substituents is raised to two, it turns out that asymmetrically substituted monomers, such as vinylidene chloride, $CH_2{=}CCl_2$, polymerize much more easily than symmetrically substituted compounds, such as 1,2-dichloroethylene, $ClHC{=}CHCl$. Further increase in the number of substituents augments markedly the difficulties in forcing a polymerization reaction, and monomers like trichloroethylene, $Cl_2C{=}CHCl$, or maleic acid esters polymerize only under drastic conditions.

Examples of the influence of the *nature* of the substituent on the ease of polymerization are propylene and vinyl chloride. Propylene is much more difficult to polymerize than vinyl chloride. A possible explanation can be found in the fact that the polar nature of the chlorine-containing monomer accounts already for a partial shift of the π electrons of the double bond.

As far as conjugated and cumulated systems are concerned, it has been generally found that the ease of polymerization increases with the amount of unsaturation and that conjugation or cumulation of double bonds increases their reactivity. To support this general rule, Table 15-2 shows a comparison of the rates of polymerization of hydrocarbons that differ only in their unsaturation.

TABLE 15-2. COMPARISON OF THE RATES OF POLYMERIZATION OF HYDROCARBONS DIFFERING ONLY IN THE AMOUNT OF UNSATURATION

Compound	*% conversion under given conditions*
Butene-1, $CH_2{=}CH{-}CH_2{-}CH_3$	39.6% in 52.5 sec at 750°C. Stable at 200°C
Butadiene-1,3, $CH_2{=}CH{-}CH{=}CH_2$	10 days at 150°C in sealed tube, "all" polymerized. 70% polymerized in 1 hr at 350°C
Vinylacetylene, $CH{\equiv}C{-}CH{=}CH_2$	Explosive polymerization on contact with sulfuric acid or upon heating. Under pressure readily polymerized to a solid. Homologues form viscous sirups upon standing for 2 or 3 months

While Table 15-2 shows the influence of the amount of unsaturation, Table 15-3 indicates the importance of the relative position of the double and triple bonds on the tendency of a molecule to polymerize.

Other interesting relationships exist for double bonds located in five- or six-membered rings. Benzene and related aromatic compounds without additional side-chain aliphatic unsaturation do not polymerize. Cyclopentadiene can be readily polymerized, and combinations of five- and

TABLE 15-3. INFLUENCE OF CONJUGATION ON POLYMERIZATION

Substance	Formula	Polymerization
Diacetylene	$CH\equiv C—C\equiv CH$	Polymerizes extremely rapidly
Divinylacetylene	$CH_2=CH—C\equiv C—CH=CH_2$	Polymerizes rapidly
Vinylacetylene	$CH\equiv C—CH=CH_2$	Polymerizes very readily
Butadiene-1,3	$CH_2=CH—CH=CH_2$	Polymerizes readily
Pentadiene-1,4	$CH_2=CH—CH_2—CH=CH_2$	Rearranges into the conjugated system and polymerizes readily
Hexadiene-1,5	$CH_2=CH—CH_2—CH_2—CH=CH_2$	Polymerizes slowly

six-membered rings containing conjugated double bonds, such as coumarone and indene, exhibit a strong tendency to polymerize.

So far, only the energy requirements have been considered which are necessary to rupture that bond in a C=C double bond which can be attributed to the π electrons. However, there is still another factor which is responsible for the success or failure of a polymerization reaction. It concerns the stability of the active centers formed; if they are highly resonance-stabilized, they may not react with the monomer and no propagation will take place. On the other hand, if they are too unstable, they may be subject to internal rearrangement or to side reactions which also may interfere with the propagation of a polymer chain. If the circumstances are unfavorable for the formation of large molecules, very drastic reaction conditions must be employed to promote polymerization, even if all energy requirements are fulfilled.

The energy for the activation of the double bond can be supplied in the form of heat or by irradiation with photons, β and γ rays, or accelerated α particles. As in almost any other chemical process, a considerable increase in rate can be obtained by the use of a catalyst.

It is hard to perform an uncatalyzed or "thermal" polymerization, as traces of air or impurities in the monomer may already have a catalytic or retarding effect on the reaction. Some investigators have measured thermal polymerizations with great precaution and have calculated the energy of activation for the over-all reaction as well as for each of the three basic reaction steps. The activation energy can be calculated from the temperature dependence of the over-all reaction rate, in accordance with the Arrhenius equation:

$$k = Ae^{-E/RT}$$

Measurements of the temperature dependence of the over-all reaction rate, together with direct determinations of the rates of the individual reaction steps, have yielded data which allow the drawing of conclusions as to the magnitude of the various activation energies. As an example, the data for the uncatalyzed polymerization of styrene are given below.

Reaction	*Activation energy, cal per mole*
Initiation	~30,000
Propagation	~7000
Termination	~2800

The energy of activation varies of course considerably with the monomer used, and as an example the activation energies for the initiation of thermal polymerization for three monomers are shown in Table 15-4.

TABLE 15-4. CALCULATED ENERGY OF ACTIVATION FOR INITIATION OF SOME POLYMERIZATIONS

Compound	Temp range, °C	Activation energy, cal per mole
Styrene	79.5–131.5	~30,000
Vinyl acetate	81.8–110.9	~23,100
Methyl methacrylate	100–210	~16,000

There is no general agreement on the mechanism of thermal polymerization. The formation of a biradical from the monomer

$$CH_2{=}CHX \rightarrow \overset{*}{C}H_2{-}\overset{*}{C}HX$$

seems improbable. The formation of a biradical as a result of the collision of two energy-rich monomer molecules

$$CH_2{=}CHX + CH_2{=}CHX \rightarrow \overset{*}{C}H_2{-}CHX{-}CH_2{-}\overset{*}{C}HX$$

seems more likely from energy considerations, and it is also in fair agreement with experimental results which indicate a second-order reaction rate. On the other hand, the growth of a biradical to a long-chain molecule by addition of monomers on both ends is unlikely on the basis of configurational considerations, because self-termination and formation of cyclic compounds should set in already in the dimeric and trimeric stage. So far, no plausible theory of a reaction mechanism has been proposed which would satisfactorily explain the formation of monoradicals and still uphold the experimental findings of a second-order reaction rate.

The vast majority of the theoretically and practically important addition polymerizations are done in the presence of catalysts or, as they perhaps better may be called, initiators, and most of the studies have been concentrated on this type of reaction.

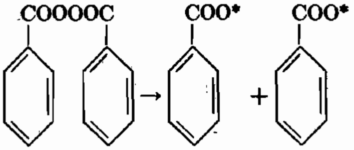
Initiators, or initiating systems, generate three distinct types of active centers and unstable intermediates: (1), free radicals, (2), carbonium ions, (3), carbanions. Consequently one distinguishes between "free radical polymerization" and "ionic polymerization," the latter being initiated either by carbonium ions or by carbanions. In the following sections the general characteristics of these two types of addition polymerization will be considered separately.

Free Radical Polymerization. The four principal steps of an addition polymerization chain reaction can be represented by the following scheme:

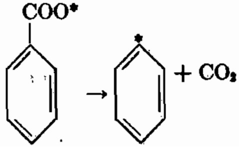
Initiation:	$C \to C^*$	
Propagation:	$C^* + M \to M^*$ $M^* + M \to MM^*$ $MM^* + M \to MMM^* \cdots \to M_n^*$	
Termination:	$2M_n^* \to M_{2n}$	Coupling
	$M_n^* + M_m^* \to M_n + M_m$	Disproportionation
Chain transfer:	$M_n^* + M \to M_n + M^*$	With monomer
	$M_n^* + M_m \to M_n + M_m^*$	With polymer
	$M_n^* + I \to M_n + I^*$	With any other molecule

in which C denotes any source of radicals, as represented by C^*; M denotes monomer and M^* the activated monomer species; M_n^* and M_m^* are growing chains containing n and m monomer units, respectively; M_n is a polymer molecule of n monomer units; and I may be an impurity, a solvent molecule, or in general any molecular species to which the activity of the growing chain M_n^* may be transferred.

Initiation. Any material which decomposes spontaneously or under external stimulus into free radicals may be used as an initiator for polymerization at the double bond. A variety of peroxides satisfy this condition, such as, for instance, benzoyl peroxide and tertiary butylhydroperoxide in systems where the initiator is dissolved in the monomer itself or in a monomer solution; also hydrogen peroxide and potassium persulfate in emulsion polymerizations where the initiator is dissolved in an aqueous medium. Benzoyl peroxide decomposition occurs by unimolecular reaction:

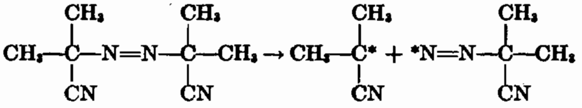


Some of the free radicals decompose further, liberating CO_2 to form phenyl radicals and CO_2:



The decomposition of benzoyl peroxide occurs at a sufficient rate between 60 and 90°C to be useful in polymerization.

Another common class of initiators are symmetric azonitriles which also decompose at 60 to 70°C to form radicals having structures like the one indicated below:

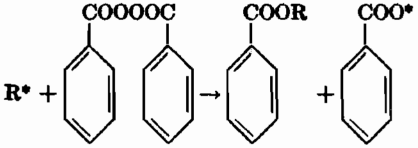


$$CH_3-\overset{CH_3}{\underset{CN}{C}}-N{=}N-\overset{CH_3}{\underset{CN}{C}}-CH_3 \rightarrow CH_3-\overset{CH_3}{\underset{CN}{C^*}} + {}^*N{=}N-\overset{CH_3}{\underset{CN}{C}}-CH_3$$

The azonitriles may also be used as initiators in photopolymerizations, in which case free radicals are formed at temperatures in the neighborhood of 0°C upon irradiation with rays of short wavelength in the visible or near-ultraviolet region.

It is now generally assumed that remnants of the initiator are permanently attached to the first link of the polymer chains. This view has been substantiated by experiments showing that fragments of halogenated benzoyl peroxide or other initiators can be found even in the most thoroughly purified polymers.[1]

One of the problems in polymer kinetics is that the rate as well as the order of the reaction of initiator decomposition may be changed by the presence of free radicals (R^*) in the polymerization mixture. These may be initiator fragments themselves, polymerizing chains, or solvent radicals formed by chain transfer; usually R^* denotes a growing polymer chain. They may attack undissociated initiator molecules in a reaction exemplified by



As a consequence, only one radical per initiator molecule is available for the initiation of a polymerization, the other one being terminated by the attacking radical.

This reaction occurs in addition to the spontaneous unimolecular decomposition of the initiator and is referred to as "induced" decomposition. Its net effect is to reduce initiator efficiency since fewer radicals are available to initiate polymerization than in an unhampered unimolecular reaction. The degree to which induced decomposition can influence the over-all rate of the polymerization depends on the susceptibility of the un-

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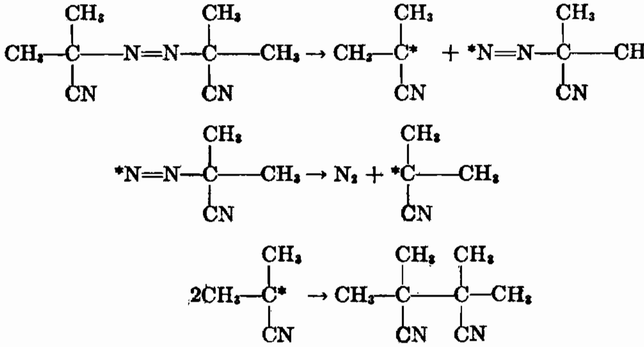
[1] Pfann, Salley, and Mark, *J. Am. Chem. Soc.*, **66**, 983 (1944); Price, Kell, and Krebs, *ibid.*, **64**, 1103 (1942); Price and Tate, *ibid.*, **65**, 517 (1943); Price and Durham, *ibid.*, **64**, 2508 (1942); Bartlett and Altschul, *ibid.*, **67**, 812, 816 (1945).

dissociated initiator molecule to undergo reactions with any radicals which may be present.

Another side reaction which is said to occur with certain initiators is a recombination of the radicals, forming a stable molecule. For example, the following formulas show how an azo-type initiator may undergo a decomposition into radicals which then reform a stable dicyanide molecule:



$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \rightarrow CH_3-\underset{CN}{\overset{CH_3}{C}}{}^{*} + {}^{*}N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3$$

$${}^{*}N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \rightarrow N_2 + {}^{*}\underset{CN}{\overset{CH_3}{C}}-CH_3$$

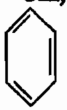
$$2CH_3-\underset{CN}{\overset{CH_3}{C}}{}^{*} \rightarrow CH_3-\underset{CN}{\overset{CH_3}{C}}-\underset{CN}{\overset{CH_3}{C}}-CH_3$$

Once the initiator fragments separate far enough, such a recombination reaction is very unlikely. However, the mobility of molecules or radicals in a solvent is limited. The neighboring solvent molecules form a "cage" about the initiator fragments from which they can escape only after a certain time. During this period collisions between the fragments occur frequently, and since apparently the nitrogen liberation occurs sufficiently rapidly some of the isobutyronitrile radicals can recombine before leaving each other's reaction sphere.

The magnitude of the cage effect depends among other factors upon the type of monomer and initiator, the nature of the solvent present, and the temperature. These factors influence the rate of diffusion of the radical and thus determine the probability of separation beyond the distance within which recombination may occur.

Propagation. Once an active center has been formed, it reacts with an inactive monomer to produce a new radical. The activation energy of this process has been found to be only about 7000 cal per mole, and consequently many collisions between activated chain ends and inactive monomer molecules are successful. Hence, the sequence of additions is very rapid. The total number of individual propagation steps in one molecule is equal to its degree of polymerization.

The mechanism of a propagation step is in effect the mechanism of the reaction of a radical M^* with its own monomer M. The reactivity of this radical-monomer system is largely governed by two factors. The first of these is related to the respective resonance stabilizations of the radical and the monomer, and these quantities, in turn, are dependent on the substituents on the carbon atoms adjacent to or in the neighborhood of the double bond in both reactant species. If this substituent contains unsaturation conjugated with that of the double bond as exemplified in styrene, $CH_2{=}CH$, then stabilization by resonance may be considerable. In such a case the monomer will have a relatively higher reactivity than will the radical formed from it, $R{-}CH_2{-}CH^*$. In most cases a more reactive monomer will produce a less reactive radical, and vice versa. Thus the propagation rate of a reactive monomer such as styrene, reacting with its less reactive radical, may be smaller than those of less reactive monomers such as, for instance, vinyl acetate or methyl methacrylate, reacting with their highly active radicals.



The second factor which influences the propagation step concerns that ratio of successful to unsuccessful collisions between the radical and the monomer which can be attributed to the geometrical structure of the two reactants. The location of a substituent on the molecule and the radical, the actual size and bulk of this substituent, and its electrical charge characteristic can greatly reduce the number of successful collisions simply because the unpaired electron of the radical is often unable to get within reacting distance to the π electrons of the monomer. This "steric hindrance" is particularly effective in cases of large and bulky substituents or with disubstituted monomers.

The addition of a new monomer to an existing radical M^* will occur almost exclusively in such a way that the unpaired electron is situated on the carbon atom with the substituent:

$$M^* + CH_2{=}CHX \rightarrow M{-}CH_2{-}CHX^*$$

Continuous addition of new monomer in this manner will finally produce a polymer chain in which the substituents are located on alternate carbon atoms. Though this structure, which is called a "head-to-tail" arrangement, is preferentially maintained in most polymerization, some monomers, for instance vinyl acetate, may yield small amounts (1–2 per cent) of "head-to-head" structures:

$$\cdots{-}CH_2{-}CHX{-}CH_2{-}CHX{-}CH_2{-}CHX{-}\cdots$$

Head-to-tail Structure

$$\cdots{-}CH_2{-}CHX{-}CHX{-}CH_2{-}CH_2{-}CHX{-}CHX{-}CH_2{-}\cdots$$

Head-to-head Structure

Termination. The most common termination or cessation processes are collisions (1) between two growing chains, (2) of a growing chain with an initiator radical, (3) of a growing chain with impurities or with the walls of the reaction vessel.

The effect of a collision between two growing chains can be twofold: either the two free valences unite to a single bond in a coupling reaction

$$\begin{gathered}\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots + \cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots\\ \downarrow\\ \cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots\end{gathered}$$

or a disproportionation of the two colliding chain molecules takes place

$$\begin{gathered}\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots + \cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots\\ \downarrow\\ \cdots\text{—CH}_2\text{—CHX—CH=CHX} + \text{CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots\end{gathered}$$

producing an unsaturated and a saturated terminal link on the two chains, respectively. The first possibility tends to increase the average molecular weight, since by the coupling of two chains one large molecule is formed, whereas disproportionation leads to products of lower average molecular weight.

In principle, it should be possible to determine the relative magnitude of the two termination processes by an analysis of the unsaturation in the reaction mixture. In practice, however, this is not easy if the molecular weight is very high. For example, if a polymer has a $\overline{DP}$ of 1,000, the double-bond content would be one-half of 0.1 per cent of the total number of carbon-carbon linkages if all termination occurred by disproportionation. In order to find the degree to which disproportionation has taken place, it would be necessary that the double-bond determination be accurate to one-tenth of the above, at least, or to 0.005 per cent of the entire sample. A better procedure to ascertain the extent of disproportionation depends on the fact that there are two initiator fragments per molecule if chain termination occurs by recombination and only one fragment per molecule if termination occurs by disproportionation. By using a radioactive initiator, it has been shown that the reaction between styryl radicals is predominantly a coupling, while methyl methacrylate radical reactions result mostly in disproportion.

The probability of collisions between activated chain ends and initiator fragments increases proportionally to the concentration of the initiator in the system. Whereas a high initiator concentration effectively accelerates the polymerization by producing a comparatively large number of active centers, it provides, on the other hand, for chain breakers and prevents the development of long chains. In practice, therefore, some speed of polymerization has to be sacrificed if high-molecular-weight material is desired, and the initiator concentration must be kept within limits.

The fact that active centers lose their activity upon collision with certain molecules has been industrially exploited in cases where polymerization of a given monomer is undesirable at a certain time. The production of the monomer itself often involves distillations or other operations at elevated temperatures during which polymerization must be avoided. Storing and shipping of monomers are other occasions when they must be kept stable for a considerable length of time. This is achieved by deliberately adding to the monomer small amounts of so-called *inhibitors*, the function of which is to stop any chain growth, preferably immediately after the initiation has occurred.

Chain Transfer. Besides the three reactions mentioned so far in which the radical R^* participates, namely, induced decomposition of initiator, propagation, and termination, R^* may react with a solvent molecule, a monomer, or a polymer molecule. This reaction, known as chain transfer, may be written generally as

$$R^* + Z \rightarrow P + Z^*$$

where Z may be monomer, polymer, or solvent molecule and P is the now terminated former radical. In chain transfer, one radical or a growing chain is terminated and another started, without any reduction in the number of *free* radicals. If Z is a solvent molecule or a monomer, the chain-transfer reaction tends to lower the average molecular weight of the resulting polymeric material by prematurely terminating some of the growing chains.

Certain solvents, such as CCl_4, are very effective chain-transfer agents and serve as moderators in polymerization in order to keep the average molecular weight purposely low.

$$\mathrm{R{-}CH_2{-}CHX{-}CH_2{-}CHX^* + CCl_4 \rightarrow R{-}CH_2{-}CHX{-}CH_2{-}CHXCl + CCl_3^*}$$

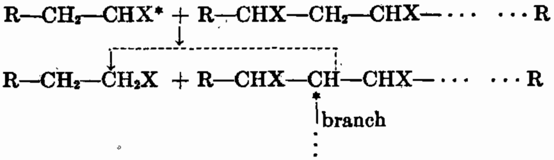
Chain transfer with a monomer occurs, for instance, in the early stages of a vinyl acetate polymerization:

$$\mathrm{R{-}CH_2{-}CHX^* + CH_2{=}CHX \rightarrow R{-}CH_2{-}CH_2X + CH_2{=}CX^*}$$

or

$$\mathrm{R{-}CH_2{-}CHX^* + CH_2{=}CHX \rightarrow R{-}CH{=}CHX + CH_3{-}CHX^*}$$

On the other hand, chain-transfer reactions between a growing chain and a dead chain may lead to increases in average molecular weight because of the formation of long branches, originating at that link of the dead chain from which the hydrogen had been abstracted.

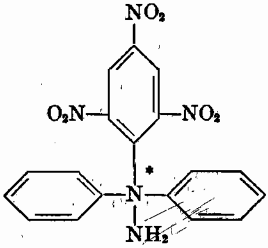


$$\mathrm{R{-}CH_2{-}CHX^* + R{-}CHX{-}CH_2{-}CHX{-}\cdots\ \cdots R}$$
$$\downarrow$$
$$\mathrm{R{-}CH_2{-}CH_2X + R{-}CHX{-}\underset{\overset{|}{\text{branch}}}{\overset{}{C}H^*}{-}CHX{-}\cdots\ \cdots R}$$

The formation of branched chains seems to occur quite often in polymerization reactions, particularly if they are carried out at elevated temperatures. The frequency of branch formation in one individual reaction increases with conversion, i.e., as more dead polymer chains are formed, the chances of chain transfer between them and radicals or growing chains increases.

Inhibition and Retardation. Certain substances, when introduced into a polymerization system, will slow down or stop the reaction; they are called *retarders* or *inhibitors*, respectively. Both operate by the same reaction mechanism, the distinction being that inhibitors are more effective in their action. Both react with active chain ends in such a way that either nonactive reaction products are formed or a radical of such low reactivity is produced that no further reaction with monomer can take place.

As an example of an inhibitor which is very effective, 2,2-diphenyl-1-pierylhydrazyl may be cited. This compound by itself is a radical:

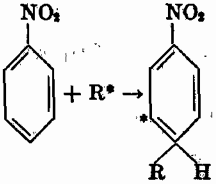


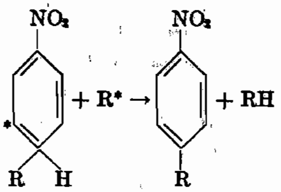
It has such low reactivity, however, that it cannot initiate a polymerization though it can easily and speedily react with an active chain end to form a stable compound:

$$R^* + I^* \rightarrow RI$$

Inhibitors and retarders which are not radicals themselves act in a more complicated way. For instance, quinones are very good inhibitors. There are several mechanisms proposed to explain their action; all of them are based on the idea that the reaction of quinones with chain radicals yields other radicals of such low activity that they are unable to enter into a propagation reaction with monomer.

As an illustration of a reaction mechanism for retardation, the one suggested by C. C. Price for aromatic nitro compounds is given below:





Oxygen acts as a retarder by complexing with a radical of high reactivity to form one of lower reactivity.

$$R^* + O_2 \rightarrow ROO^*$$

This peroxidic radical, though of low reactivity, may still add monomer to form a polymer chain containing peroxidic links. However, these peroxides are rather unstable, and in the further course of the polymerization they may decompose

$$ROOR \rightarrow RO^* + RO^*$$

thereby creating new radicals which then can accelerate the reaction. Thus, a polymerization in the presence of limited amounts of oxygen may show two phases: (1) an induction period, which lasts until all oxygen is used up, and during which polymerization proceeds at a lower rate than it would in a reaction in the absence of oxygen; and (2) the phase in which the peroxidic links in the polymer chain decompose, causing the reaction to proceed faster than a comparative one in the absence of oxygen. The length of this phase depends of course on the amount of peroxide formed.

Autoacceleration (*Gel Effect*). Autoacceleration occurs in the bulk polymerization of some monomers, particularly of the type $CH_2{=}CHX$. Experimentally, one notices that after a certain amount of polymerization has taken place (e.g., about 15 per cent in methyl methacrylate polymerization) the reaction rate increases considerably. The reason for this acceleration seems to be the following: the viscosity of the polymerizing liquid increases very rapidly as polymer is produced. The rate of diffusion is roughly inversely proportional to the viscosity, and the termination reaction, which depends on the collision of two radicals, is governed by the diffusion rate. As a consequence, the termination steps occur less frequently, the concentration of free radicals increases, and an increased reaction rate is observed after a certain amount of polymer is formed.

Ionic Polymerization. This important class of addition polymerizations proceeds according to a general reaction scheme which is similar to free-radical polymerization, i.e., initiation, propagation, and termination. It differs, however, significantly from it in that the active ends of the growing chains, the unstable intermediates, bear either a negative or a positive charge (anionic or cationic).

Cationic Polymerization. The initiators in cationic polymerization are acidic; among them are listed aluminum chloride, boron trifluoride, certain activated clays, and sulphuric acid. These compounds are all strong electron acceptors and are particularly effective when the monomer is an electron donor. The polymerizations proceed rapidly at low temperatures; for instance, isobutylene polymerizes immediately at −100°C in the presence of aluminum chloride.

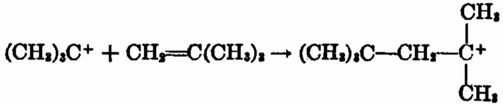
It has been found that the initiating action of metal halides in ionic polymerizations is dependent on the presence of small amounts of a promoter or cocatalyst for their effectiveness. The cocatalyst may be a proton-releasing substance such as water, chloroacetic acid, or tertiary butanol. It has been reported also that certain alkali halides which produce carbonium ions in the presence of metal halides can act as cocatalysts.

An example of the possible mechanism by which a cocatalyst may act is shown in the polymerization of isobutylene by boron trifluoride:

Initiation:

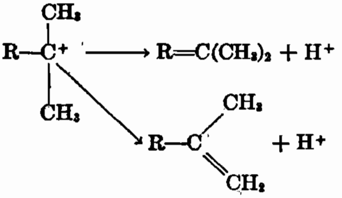
$$BF_3 + H_2O \rightleftharpoons F_3BOH^- + H^+$$
$$H^+ + CH_2{=}C(CH_3)_2 \rightarrow (CH_3)_3C^+$$

Propagation:



$$(CH_3)_3C^+ + CH_2{=}C(CH_3)_2 \rightarrow (CH_3)_3C{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C^+}}$$

Termination:



The need for the cocatalyst in the boron trifluoride–isobutylene system has been demonstrated by the fact that no polymerization takes place if water is rigorously excluded. Similar results have been obtained with other polymerizing mixtures.

In some reactions, polymerization can be initiated directly by the carbonium ion by a mechanism which is essentially the same as the polymerization by hydrogen ions:

Initiation: $SnCl_4 + XCl \rightarrow X^+ + SnCl_5^-$

Propagation: $X^+ + M \rightarrow R^+$

Termination: $R^+ \rightarrow P + H^+$

where X indicates any compound capable of forming a carbonium ion, M is the monomer, R the growing chain, and P the final, terminated, and inactive polymer.

While the role of the negative ion has been deemphasized in the above schemes, the requirement of electric neutrality will force the propagating positive ion and the negative counter-ion to remain in the same immediate neighborhood. The degree to which these may separate depends on the nature of the initiator as well as on the dielectric constant of the medium. The latter particularly will to a considerable extent affect the various reaction steps. The rate of initiation will be increased by media of higher dielectric constant because this is the step where charge separation of ion and counter-ion occurs. For the same reason the termination rate will be decreased owing to the decreased incidence of ion and counter-ion reaction. The over-all effect is an increase in polymerization rate and also in the degree of polymerization with an increase in the dielectric strength of the media.

Anionic Polymerization. Polymerization of olefins by metallic sodium, sodium ethoxide, and aqueous alkalies has been known for some time. The mechanism of this polymerization is still open to question though the present evidence indicates that the mechanism is similar to that of cationic polymerization, except that a polymeric anion is formed and the counter-ion is a cation. For example, potassium in liquid ammonia forms potassium amide, the amide ion attacks the monomer, forming a negative ion. This negative ion attacks another monomer, and so on, until termination occurs.

Initiation:

$$\mathrm{K} + \mathrm{NH_3} \rightarrow \mathrm{K^+} + \mathrm{NH_2^-} + \tfrac{1}{2}\mathrm{H_2}$$

$$M + \mathrm{NH_2^-} \rightarrow \mathrm{MNH_2^-}$$

Propagation:

$$\mathrm{MNH_2^-} + M \rightarrow \mathrm{RNH_2^-}$$

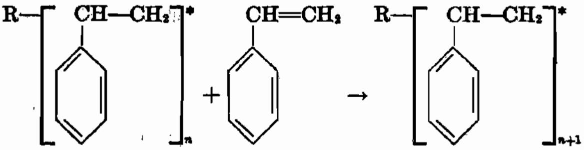
Termination:

$$\mathrm{RNH_2^-} \rightarrow P + \mathrm{NH_2^-}$$

$$\mathrm{RNH_2^-} + \mathrm{NH_3} \rightarrow P + \mathrm{NH_2^-}$$

Copolymerization. The physical properties of a given polymer depend, among other factors, on its molecular weight and on the chemical structure of the chain. One material may be very tough, another elastic, a third one very brittle. In the preparation of a polymer for a particular purpose, it would be desirable to combine some of the properties of one polymer with the properties of another. A mixture or solution of one polymer in another might appear to be a solution of the problem, but very often the polymers do not mix well, demix on aging, or are mutually insoluble. However, the simultaneous polymerization of two or more monomers, yielding a polymer molecule which contains both monomers linked in one chain, has proved satisfactory in a number of cases. This process is called *copolymerization,* and the production of copolymers of different composition (in contradistinction to a "homopolymer" which designates a polymer formed from one monomer only) enormously increases the variety of materials which may be synthesized. Copolymers of styrene and butadiene (GR-S rubber), styrene and acrylonitrile, vinyl chloride and vinyl acetate, isobutylene and isoprene, and many others have been prepared and widely used.

In dealing with the propagation reaction of a homopolymer, only one process must be considered, namely, the reaction of a radical with its own monomer. In the polymerization of polystyrene, for example, this may be written



Symbolically, this would be represented by

$$M_n^* + M \xrightarrow{k_p} M_{n+1}^*$$

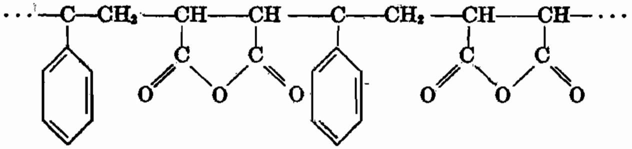
Where two monomers, M_1 and M_2, are involved, four reactions may occur in place of the single one above:

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$$
$$M_1^* + \longrightarrow_2 \overset{k_{12}}{M} \rightarrow M_2^*$$
$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$$
$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$$

Qualitatively it is easy to see how the polymer structure will depend on the reaction rates of these competing reactions. Suppose that k_{12} is much greater than k_{11} and that k_{21} is much greater than k_{22}. This means that a radical of monomer 1 will preferentially react with a molecule of monomer 2, and vice versa. The resultant polymer will contain both monomer units linked alternately in the following type of structure:

$$—M_1—M_2—M_1—M_2—M_1—M_2—M_1—M_2$$

This is presumably what occurs in the copolymerization of styrene and maleic anhydride. The proposed structure is indicated below:



In another case k_{11} may be greater than k_{12} and k_{22} greater than k_{21}. Under these conditions the radical prefers its own monomer and the copolymer structure is given by

$$—M_1—M_1—M_1—M_1—M_1—M_1—M_2—M_2—M_2—M_2—M_2—M_2—M_2—M_2—M_1—M_1—$$

with long blocks containing one monomer and only occasional alternations. If the ratios k_{11}/k_{12} and k_{22}/k_{21} are very large, the reaction $M_1^* + M_2^*$ and the reaction $M_2^* + M_1$ almost never occurs, and a mixture of the two homopolymers is formed.

A third case arises when both M_1^* and M_2^* react more readily with M_1 than with M_2. In such a mixture very little copolymer is formed at first, and the analysis of the polymer shows almost 100 per cent M_1 homopolymer. After M_1 is mostly consumed, some copolymer is formed. Eventually, M_2 homopolymer will be synthesized, but only after all M_1 is gone. This is true of vinyl acetate–styrene copolymerization, where the styrene monomer is much more reactive than vinyl acetate. As a result, a copolymer of styrene and vinyl acetate containing appreciable amounts of the latter can be made only if the polymerization mixture contains a large excess of vinyl acetate.

In many copolymerizations, though, the four reaction rates are not very different from each other, i.e., neither of the two radicals M_1^* and M_2^* has any particular preference for either monomer M_1 or M_2. In this case the two monomers will enter the copolymerization chain at random, as is illustrated below:

$$—M_1—M_2—M_2—M_1—M_1—M_1—M_2—M_2—M_2—M_2—M_1—M_2—M_1—$$

The two measurable quantities in a copolymerization are the over-all rate of the reaction and the composition of the copolymer at the various stages of the reaction. It is particularly the latter characteristic of the copolymer which is most valuable for the understanding of the mechanism and the kinetics of the propagation reaction in copolymerization.

The composition of a copolymer is directly dependent upon the *ratio* in which the two monomers enter the copolymer chain. If this quantity is brought into a definite relationship with the known concentrations of the two monomers at the beginning of the reaction, then the composition of the copolymer can be predicted from the original monomer concentration.

This is possible by using an equation which was arrived at by calculating the ratios of the reaction rates, basing the calculation on the steady-state assumption (see p. 908). The ratio between the rates of addition of M_1 and M_2 is given by the equation

$$\frac{dM_1}{dM_2} = \frac{[M_1]k_{21}(k_{11}[M_1] + k_{12}[M_2])}{[M_2]k_{12}(k_{22}[M_2] + k_{21}[M_1])} \tag{1}$$

Define $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. Then this equation can be simplified to

$$\frac{dM_1}{dM_2} = \frac{[M_1]}{[M_2]}\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \tag{2}$$

The composition of the copolymer, expressed in the ratio of moles M_1 to moles M_2 can be predicted from the original concentrations $[M_1]$ and $[M_2]$

and from the relative reactivities r_1 and r_2. These relative reactivities can be easily determined experimentally, and once they are known for a certain monomer pair, the composition of copolymers obtained from all possible combinations of original concentrations of the two comonomers can be predicted.

An attempt to organize the vast amount of copolymerization data in a coherent manner was made by Alfrey and Price in terms of the "Q and e" scheme. Q is a factor which can be correlated with the specific reactivity of a monomer as determined by resonance effects, and e is a measure of the electron-donating or electron-accepting nature of the radical formed. The relationships between the rate constants of the copolymerization propagation reactions and the Q and e values are given by

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} \exp[-e_1(e_2 - e_1)] \tag{3}$$

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] \tag{4}$$

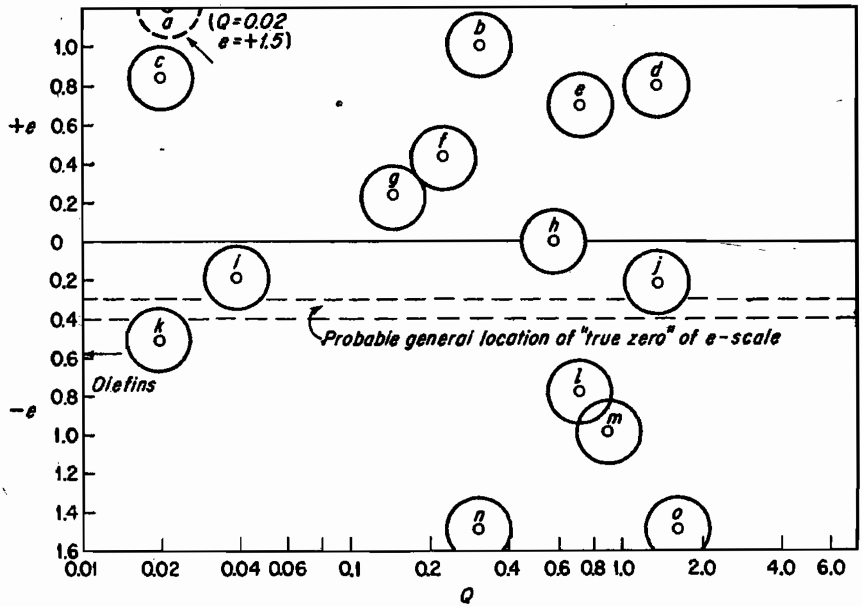


FIG. 15-4. Q-e map for a number of important monomers; the full horizontal line indicates the present choice for the scale of the polarities e; the band between the two broken lines represents the location of a more rational e scale: (*a*) chlorotrifluoroethylene, (*b*) acrylonitrile, (*c*) allyl chloride, (*d*) α-chloroacrylate, (*e*) methacrylonitrile, (*f*) methyl acrylate, (*g*) vinylidene chloride, (*h*) methyl methacrylate, (*i*) vinyl chloride, (*j*) chloroprene, (*k*) vinyl acetate, (*l*) butadiene, (*m*) styrene, (*n*) isobutylene, (*o*) *p*-methoxystyrene. (*Alfrey, Bohrer and Mark, "Copolymerization," p. 82, Interscience Publishers, Inc., New York,* 1952.)

This relationship is only semiquantitative at best, but it does provide a rough basis for correlation of the available copolymerization data and makes it possible to predict the probable success of the copolymerization characteristics of new and untried monomers. The Q and e values of such monomers can be obtained from the above equations via experimental determinations of the r_1 and r_2 ratios in copolymerizations with one or two reference monomers. These values for the new monomer can then be inserted in a "Q-e map" (Fig. 15-4) in which Q is plotted on a logarithmic scale along the abscissa and e is plotted along the ordinate. The intercept of these two plots determines the location which this new monomer occupies on the map and permits at least approximate predictions as to its copolymerization reactivity with respect to all the other monomers on the map. Not only will it permit certain assumptions to be made as to the ease with which the new monomer will copolymerize with any of the other ones, but it also will give a clue as to the probable structure of the copolymer chain, i.e., whether it will consist of regularly alternating M_1 and M_2 units, or have frequent alternation of random sequences of M_1 and M_2, or have infrequent alternations between M_1 and M_2 sequences, etc.

The above copolymerization schemes are concerned with free-radical polymerization, and in Table 15-5 relative reaction rates for a few representative monomer pairs are given. When initiators which form ions are used, the relative rates of copolymerization may be entirely different than those shown in this table.

TABLE 15-5. RELATIVE REACTION RATES FOR MONOMER PAIRS*

M_1	M_2	r_1	r_2	T,°C
Acrylonitrile...............	Methylstyrene	0.06 ±0.02	0.01 ±0.02	75
	Vinyl chloride	3.28 ±0.06	0.02 ±0.02	60
Methyl methacrylate......	Vinyl acetate	20 ±3	0.015±0.015	60
	p-Chlorostyrene	0.415±0.02	0.89 ±0.05	60
Styrene..................	Butadiene	0.78 ±0.01	1.39 ±0.03	60†
	Butadiene	0.23 ±0.07	1.48 ±0.08	50†
	Butadiene	0.5 ±0.1	1.4 ±0.2	50†
	Butadiene	0.6 ±0.1	1.8 ±0.4	45†
Vinyl chloride............	Isobutylene	2.05 ±0.3	0.08 ±0.1	60
	Vinyl acetate	2.1	0.3	68

* From Alfrey, Bohrer, and Mark, "Copolymerization," Table III, pp. 32–40, Interscience Publishers, Inc., New York, 1952.

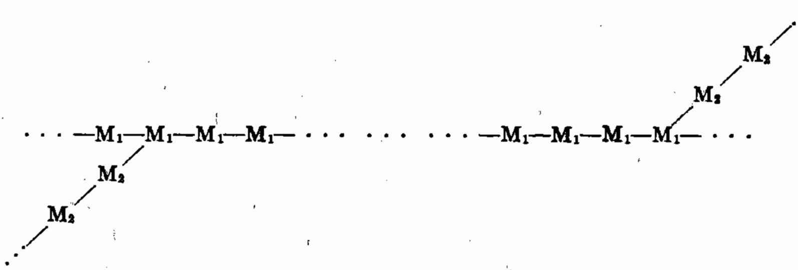
† Measurements carried out by different investigators.

Block and Graft Polymerization. These two types of polymerization have one feature in common, namely, that more or less extended sequences of monomer M_1 are joined to prepolymerized sequences of monomer M_2.

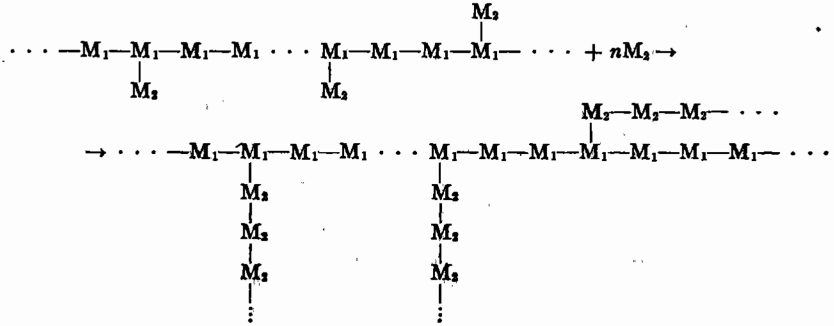
However, the structural characteristics of the two resulting copolymers are different. In block polymerization the sequences are joined end-to-end fashion

$$\cdots M_1 \cdots M_1{-}M_2 \cdots M_2{-}M_1 \cdots M_1{-}M_2 \cdots M_2 \cdots$$

while in graft polymerization either a prepolymerized section is grafted anywhere onto the main chain

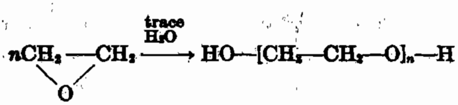


or a polymerizable monomer M_2 is by some means attached to one of the links of the main chain of M_1; this monomer is then able to polymerize *in situ* and forms a "grafted-on" section.



There are several methods available in the laboratory for the preparation of block polymers. The one which is primarily used, and which also has found industrial application, employs the reaction between active end groups of the individual M_1 and M_2 sequences. Consider, for example, the following reactions:

1. The self-addition of ethylene oxide leads to the formation of polyethylene glycol:



$$n\,\underset{\diagdown\,O\,\diagup}{CH_2{-}CH_2} \xrightarrow{\text{trace } H_2O} HO{-}[CH_2{-}CH_2{-}O]_n{-}H$$

2. The reaction product of adipic acid and propylene glycol prepared with a slight excess of glycol is given by the following formula:

$$\mathrm{HO{-}CH_2CH_2CH_2[{-}OOC{-}(CH_2)_4{-}COO{-}CH_2CH_2CH_2{-}O]_m{-}H}$$

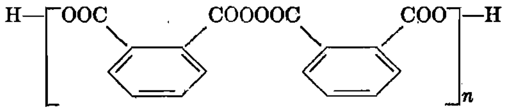
3. The reaction between diisocyanate and dialcohols yielding polyurethanes may be written schematically

$$\cdots\mathrm{{-}RNCO + HOR_1{-}}\cdots \rightarrow \cdots\mathrm{{-}RNHCOOR_1{-}}\cdots$$

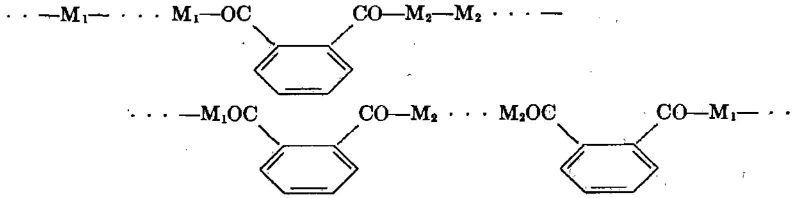
Note that the terminal groups on the polymers prepared in reactions 1 and 2 are free hydroxyls. Thus, if a diisocyanate is reacted with a mixture of these two polymers the adipic acid–propylene glycol ester polymer may be linked to the polyethylene glycol. The final polymer contains blocks of ester and polyglycol joined by a urethane linkage and is known as a "block polymer." It is interesting to note that only a small amount of isocyanate is required since the number of free hydroxyls is very few.

This principle of forming block polymers may be extended to a variety of systems and many different types of end groups such as, for instance, NH_2, COCl, or MgBr might be used to link the individual sequences to long linear chains.

An interesting technique for making block polymers in free-radical reactions depends on the use of a polymeric peroxide as initiator. Phthalyl peroxide is polymeric and may be written



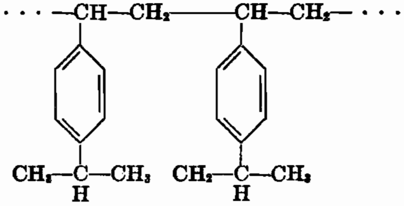
If this is used to initiate a vinyl polymerization with monomer 1, a polymer is formed which contains peroxide units as well as sections of polymer made from monomer 1. This reaction could be carried to completion or might be stopped when a certain fraction of the initiator is consumed. If this polymer is separated from the polymerizing mixture at a time when there is still an appreciable fraction of peroxide groups remaining in the polymer, polymerization may be carried out further by adding a second monomer. If then the reaction is continued until all the initiator is consumed, the resulting polymer is a block containing sequences of monomer 1 and monomer 2 along the chain, connected to each other by means of a phthalyl group.



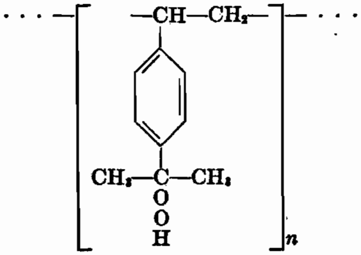
Block copolymers of styrene–methyl methacrylate and vinyl acetate–styrene have been prepared in this way.

In order to obtain a polymer by the grafting of an existing polymer onto a main polymer chain, reactive groups or radicals must be created on the main chain and/or on the grafted section. An example is the grafting of rubber onto a polystyrene chain. By means of β or γ radiation, radicals can be formed on the polystyrene or on the rubber chain, which then may react with each other or with existing double bonds in the rubber polymer chain.

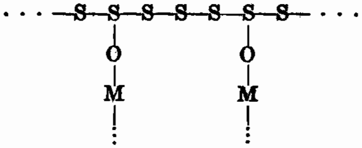
A more promising approach, though, is to make graft polymers by creating active groups or radicals on the main chain and let them react with a suitable monomer. For instance, a methyl methacrylate graft on a polystyrene-type polymer has been prepared in this manner. The starting monomer of *p*-isopropylstyrene is polymerized, forming a substituted polystyrene:



This polymer possesses a reactive tertiary carbon on the isopropyl group which may be selectively oxidized to form a hydroperoxide with the following structure:

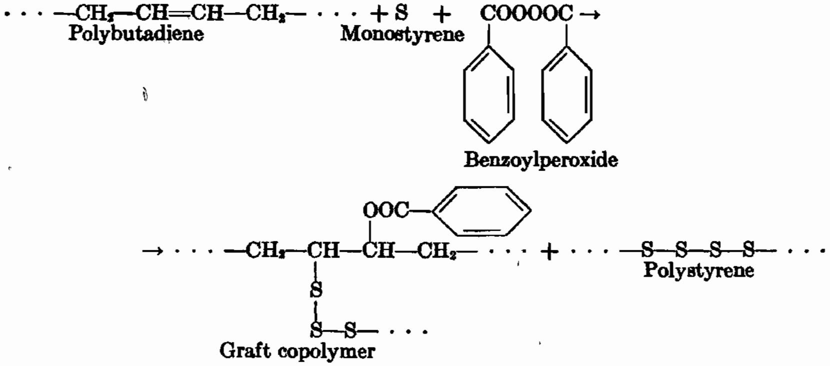


Hydroperoxide groups initiate polymerization, and by adding methyl methacrylate monomer to the oxidized polymer, a certain number of methyl methacrylate polymeric chains hook directly onto the hydroperoxide. The resultant material is a typical graft polymer with polymethyl methacrylate grafted onto a polystyrene backbone, with an oxygen atom as the connecting link. Its molecular structure is indicated below, where the isopropylstyrene is symbolized by S, the methyl methacrylate by M, and O is oxygen.



$$\cdots\text{—S—}\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{M}\\ |\\ \vdots}}{\mathrm{S}}\text{—S—S—S—}\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{M}\\ |\\ \vdots}}{\mathrm{S}}\text{—S—}\cdots$$

An interesting butadiene-styrene graft polymer can be obtained by adding a radical-type initiator to a reaction mixture containing polybutadiene and monostyrene. The polybutadiene contains a residual double bond which, when attacked by a radical under certain conditions, may open up and provide the initiating site for a polystyrene polymerization. This reaction can be schematically illustrated as follows:



This graft polymer cannot be obtained in a pure state since large amounts of pure polystyrene also are present. The previous reaction in which methyl methacrylate was grafted onto a substituted polystyrene was much more clearcut in that the only possible product was the graft copolymer.

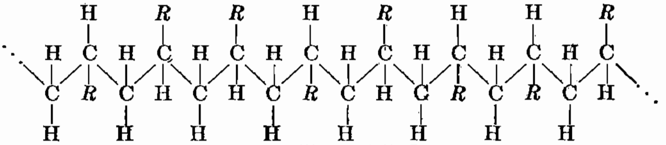
The use of γ radiation or electrons for the formation of radicals which then initiate polymerization has made it possible to create a great variety of graft polymers. An example of a polymer prepared in this way is the grafting of styrene onto polyethylene using γ radiation from an atomic pile. The γ rays bombard the molecules with high energy, creating a trail of free radicals in their wake. In the presence of a vinyl monomer, polymerization of the latter takes place. If polyethylene is immersed in styrene monomer and irradiated with γ rays, the final products are some of the original polyethylene, some pure polystyrene, and a graft of polystyrene on the polyethylene backbone. The various substances may be separated by their different solubility characteristics.

The scientific and technological aspects of block and graft polymerization are now being intensively investigated because these methods permit the preparation of specific types of copolymers having an orderly and well-regulated structure.

Stereospecific Polymerization. One of the more exciting recent developments in polymerization chemistry is the preparation and the study of "isotactic" polymers. Isotactic polymers are prepared from well-known monomers with new types of catalysts. The resultant products are polymers of the same chemical composition and configuration as those prepared with conventional radical-type or ionic catalysts, but of higher crystallinity, higher density, higher melting points, and improved mechanical properties. In order to understand how this can be achieved, it is necessary to introduce the concept of conformation of the polymer chain, as well as of its configuration.

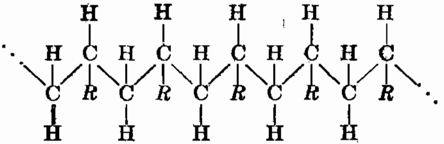
Consider a vinyl polymer in solution. This polymer contains only one substituted hydrogen on each monomer and has a structure which looks like · · · $—CH_2—CHR—CH_2CHR—CH_2—CHR—$ · · ·, where *R* may be a phenyl group (polystyrene), or a methyl group (polyisopropylene), or some other substituent.

This chain is coiled in space because of the free or partially free rotation of the substituents about the carbon-carbon bond, and the stereochemical structure of the chain does not depend on the position of the H and *R* groups with respect to the carbon atom Suppose that this polymer is solidified, and assume further that, in order to fit in a crystalline pattern, the chain must *conform* to a certain shape. For purposes of illustration it will also be assumed that this shape is a line in a plane. The molecular chains will then have the following appearance:



Nonisotactic ("Atactic") Polymer

Notice that in this nonisotactic polymer the substituted groups *R* are either above or below the chain in a *random* arrangement; they do not *conform* to a certain shape and thus do not easily fit into a crystalline pattern. In contrast to this picture of an ordinary polymer, the isotactic polymers, when arranged in a crystal pattern, presumably have all the *R* groups on the same side of the carbon chain when this chain has the conformation required by the crystal, as shown below:

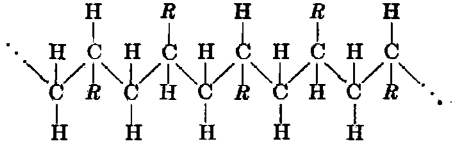


Isotactic Polymer

Because of the more symmetric arrangement of the chain in this case, the molecules fit better into a crystal lattice and the polymers generally are highly crystalline. The best estimate at the present time based on x-ray data is that these molecules are arranged in slightly twisted helices rather than in the straight chains indicated above.

This is a new type of specificity in spatial arrangement in which isotactic and atactic polymers have the same sort of molecular *configuration* in free space but do differ in the arrangement of the substituent groups *R* when the *conformation* of the molecule is such as to fit into a crystal lattice.

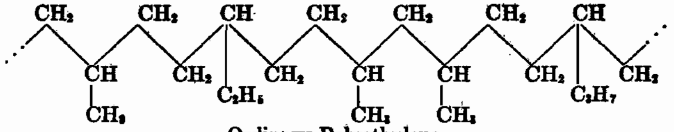
A similar situation is encountered in the case of syndiotactic polymers. Here the conformation required is that successive substituents are located on opposite sides of the chain:



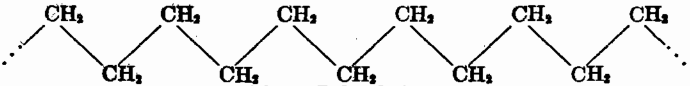
Syndiotactic Polymer

Success in carrying out a stereospecific polymerization depends on the choice of one of the recently developed initiator systems. One system which has been used in the synthesis of stereospecific polymers is a mixture of titanium tetrachloride and aluminum trialkyl. The tetrachloride is reduced to a black powder containing di- and trivalent titanium compounds. It is assumed that the polymerization takes place on the solid surface of the initiator, which might explain the stereospecific arrangement of the substituent group *R* with respect to the C atoms of the chain and which would allow for the conformation of the growing chain. Other initiator systems have been developed; one of them is based on lithium compounds, another one uses as an active agent a hexavalent chromium salt deposited on a silica-gel base. The mechanism of these polymerizations is being actively investigated in a number of laboratories, but at the present writing there is no general agreement in the interpretation of the experimental results.

A curious aspect of these new types of reactions is that polyethylene, which cannot be stereospecific because it has no substituents on the C atoms, also shows increased crystallinity, higher density and melting point, and better physical characteristics when prepared with the same initiation systems as used for isotactic polymers. In this case the improved properties are attributed to the fact that this polyethylene is a truly linear molecule, while ordinary polyethylene contains short side chains which inhibit crystallization.



Ordinary Polyethylene



Linear Polyethylene

The further development of these new polymer systems may be the single most important problem in polymerization chemistry today. The total effect of this work on polymer science is yet to be evaluated, though the outlook seems to be very promising.

III. METHODS OF POLYMERIZATION

Polycondensation Methods

The preparation of polycondensation products in the laboratory as well as on an industrial scale roughly follows procedures employed for low-molecular condensations. The reactants are brought together in appropriate reaction vessels and mixed with the catalyst. The polycondensation is started by heating the reaction mixture, and the reaction is continued under close temperature control until the desired degree of polymerization is reached. Reaction conditions have to be adjusted in such a way that premature gel formation is avoided. Likewise, stoichiometric proportions of the reactants have to be chosen carefully, or monofunctional additives have to be introduced, so as to assure that the desired extent of the reaction is reached. Finally, provisions have to be made to eliminate reaction product D in the general scheme of the polycondensation equilibrium reaction

$$A + B \rightleftharpoons C + D$$

to assure that the desired molecular weight of the polycondensate C is reached. This often presents some difficulties in technical operations, for instance, when a gaseous reaction product D is entrapped in a viscous reaction mixture.

Polycondensations can be carried out in an aqueous or a solvent medium, or they can be performed while the reactions are in a liquid or in a molten state. In industry, reactions of polyfunctional monomers leading ultimately to the tridimensional-network molecules of thermosetting resins are usually interrupted at a stage where the polymers still are soluble and fusible. They then are shipped to the fabricators, who convert them by heat "curing" processes into the final thermosetting product.

Addition Polymerization Methods

The simplest way to carry out an addition polymerization reaction of a vinyl-type monomer, $CH_2{=}CHX$, is to let it stand at room temperature over prolonged periods of time. However, not only is this procedure economically unfavorable if attempted on an industrial scale, but the reaction itself is exothermic and may get out of hand if spontaneous polymerization starts in large masses. Technical polymerizations are, therefore, always carried out under controlled heat and catalyst conditions which are closely followed throughout the course of the reaction.

There are, in principle, two ways in which addition polymerization can be carried out:

1. In a *homogeneous phase,* in which the monomer is a gas, a liquid, or a solid (bulk polymerization) or in which the monomer is completely dissolved in a solvent (solution polymerization).
2. In a *heterogeneous phase,* in which the monomer is emulsified in an aqueous medium (emulsion polymerization) or is suspended in an aqueous or any other medium (suspension polymerization).

POLYMERIZATION IN A HOMOGENEOUS PHASE

Bulk (Mass) Polymerization. This type of polymerization is accomplished by subjecting the liquid or gaseous monomer to polymerizing conditions. Although in recent years solid monomers also have been successfully converted into polymers, so far these reactions are rare and only of theoretical interest. Gas-phase polymerizations, on the other hand, have reached industrial importance in the case of ethylene polymerization, either under high pressure and temperature or in the presence of stereospecific initiator systems. Gas-phase polymerizations of propylene, butadiene, and other unsaturated gases, using stereospecific catalysts, are now being investigated extensively but have not as yet reached the industrial stage. On the other hand, the polymerization of isobutylene at low temperatures in the presence of ionic initiators is a large-scale industrial process.

However, most of the bulk polymerizations in the laboratory and in industry are carried out with liquid monomers. The main problem in this procedure is the efficient dissipation of the heat of the reaction (in most cases between 10,000 and 20,000 cal per mole), a matter that becomes increasingly difficult to achieve as the polymerization proceeds and the increased viscosity of the reaction mass renders agitation more and more difficult. On the other hand, the advantage of bulk polymerization lies in the fact that, with proper precautions, optically clear polymers free of air bubbles and impurities and without the tiny cracks and crevices that often impart a haze to otherwise clear materials can be obtained. Thus, it has proved valuable for the preparation of lenses and other optical products. It also is employed for the casting of sheets and plates and of limited quantities of objects of intricate design, when molding operations would be too costly.

Bulk polymerization is used in some cases for large-scale production of molding powders, though the method has certain technical and economical disadvantages. For instance, there is the difficulty of heat control of the reaction; also the product obtained has a relatively wide spread of the molecular-weight distribution curve. This characteristic is detrimental to the mechanical properties of the bulk-polymerized material and is a result of local overheating inside the polymerizing mass because significant temperature gradients can hardly be prevented in large batch operations.

For economic reasons, it is often advantageous to employ continuous processes instead of polymerization in batches. This has been accomplished for the polymerization of styrene by the use of towers into which prepolymerized monomer-polymer mixtures are fed at the top at temperatures of 120°C and which continue to polymerize during their passage down through the tower, leaving it at the bottom at a temperature of 180°C. A further continuous method consists in spraying prepolymerized monomer-polymer mixes into a room filled with inert gases at high temperature. The final polymerization is completed in a few seconds, and the polymer appears in granular form.

Solution Polymerization. The disadvantage of a continuous and elaborate heat control, which is necessary in bulk polymerization, is completely overcome if the monomers are dissolved in suitable solvents and the polymerizations carried out in solution. The heat created during the reaction is now dissipated over the whole solvent-solute system, and the upper temperature limit is governed by the boiling point of the solvent medium. This eliminates overheating and ensures a smooth course of the reaction. The limited temperature range, however, allows only a certain speed of reaction. The reaction is also slowed down by the solvation of the monomer molecules, which considerably decreases the number of possible collisions of monomers per unit of time. Thus the nature of the solvent and the concentration of the monomer are the determining factors for the progress of the polymerization at a certain temperature, which progress, however, never reaches the speed of a bulk polymerization.

The resulting polymers are of relatively low average molecular weight and cannot be completely freed of traces of the solvent. Again, the nature of the solvent may influence the molecular weight of the polymerization product, since solvents may act as chain breakers or chain-transfer agents for specific monomers. For instance, it is possible to obtain products of relatively high average molecular weight by polymerizing styrene in toluene. When, however, carbon tetrachloride is used as a solvent for styrene, then the polymerization yields considerably lower average-molecular-weight material.

In comparison with other methods, the solution polymerization is, therefore, at a certain disadvantage, yielding in a slow reaction a low-average-molecular-weight product that cannot be completely freed of traces of the solvent. This limits its use for industrial operations, and the quantity of polymers produced in this way is indeed small. The procedure itself is simple and consists of heating the solution of monomer and catalyst until the desired degree of conversion is reached. The remaining monomer and the solvent can be removed either by steam distillation or the application of vacuum. The polymer can also be separated from the solvent by the addition of liquids acting as a precipitant for the polymer. A continuous process can be achieved by passing the monomer solution under pressure through heated tubes.

A slight modification of the solution-polymerization method is of greater industrial importance. According to this procedure the monomer is mixed with a liquid that, while being a solvent for the monomer, precipitates the polymer from the solution. The polymer can be removed from the reaction mixture, and with the addition of new monomer, the process can be made continuous.

POLYMERIZATION IN A HETEROGENEOUS PHASE

Emulsion Polymerization. The disadvantages encountered in the two previously discussed methods, viz., difficult heat control in bulk polymerization, low-molecular-weight products, slow reaction, and presence of traces of solvents in solution polymerization, are all successfully overcome by polymerization of one or more monomers in an emulsified phase. The liquid or liquefied monomers are brought into the emulsified state by any of the customary emulsifiers and appear in the emulsion as spherical particles of sizes ranging between 1–10 μ (Fig. 15-5). During polymerization under the influence of heat and appropriate catalysts, the average particle size decreases to about one-tenth of its starting size, and the polymer is usually obtained in the form of a very stable emulsion called a *latex*. Recently, latices of very uniform particle size have been produced commercially.

The temperature of the process is easily controlled, since the heat of the reaction is immediately taken up by the aqueous medium; any overheating is thus effectively prevented. The reaction proceeds very rapidly as compared with bulk and solution polymerizations, and the average molecular weight of the resulting polymer is considerably higher than that of a product obtained under similar conditions by either one of the two other methods. For these reasons, the emulsion-polymerization method has become of outstanding technical importance, and a large part of industrial processes are now carried out in this manner.

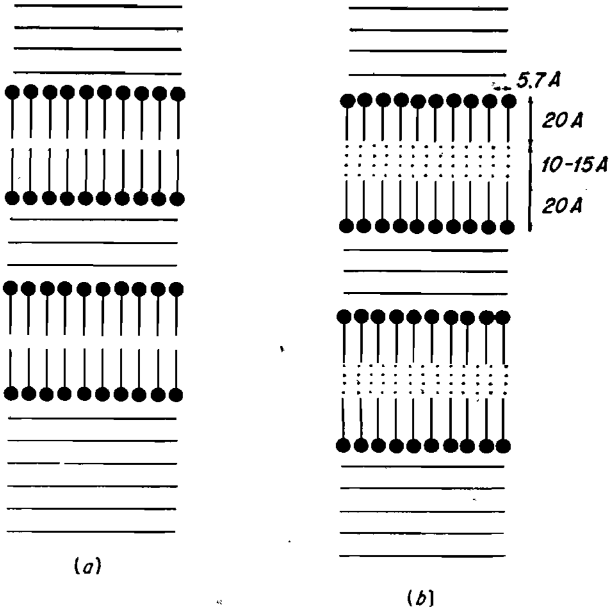


FIG. 15-5. Structure of soap micelles; (*a*) without and (*b*) with solubilized monomer. (*From Burnett, "Mechanism of Polymer Reactions," p.* 350, *Interscience Publishers, Inc., New York,* 1954.)

In spite of its widespread technical use, the fundamental principles and the mechanism of this type of polymerization are still not completely understood. This is due partly to the complexity of the heterogeneous system of an emulsion itself, which only in recent years has been sufficiently cleared up to allow an investigation of polymerizations taking place in such systems. Although a considerable number of patents pertain to empirical rules and conditions of emulsion polymerization and date back as far as 1912, it was only around 1936 that an explanation of the mechanism of the reaction was attempted.

The reaction scheme of polymerization in a heterogeneous phase differs in principle from that of a homogeneous-phase polymerization, in that the question of *where* the various reaction steps take place in the heterogeneous system has to be added to the question of *how* the reaction proceeds. Consider first the status of the various components of an emulsion polymerization system before the polymerization starts. There is, in the first place, the aqueous phase which contains the surface-active emulsifying agents (in most cases soap or synthetic emulsifiers), the catalyst, and small amounts of modifiying and pH-controlling ingredients. In the second place, there is the monomer phase, which may contain some catalyst and modifying ingredients. What happens, then, if the water-insoluble monomer is dispersed in the soap solution?

McBain[1] and Harkins,[2] who studied concentrated soap solutions (20–30 per cent) with the aid of x-ray diffraction, suggest that lamellar micelles are formed by soap molecules in such a way that the hydrocarbon chains of these molecules line up parallel to each other and form double layers, as shown in Fig. 15-5*a*. The hydrophilic ends of the soap molecules face outward, and each double layer is separated from the next one by a zone of water. If a hydrocarbon is now added to a strong soap solution, it is solubilized by locating in the hydrocarbonic part of the micelles, Fig. 15-5*b*. It is assumed that a similar solubilization occurs when a hydrocarbon monomer is added to a dilute soap solution (0.5–2 per cent), as used in emulsion polymerizations. In this case though, the aqueous zone between the layers is assumed to be much wider than in concentrated soap solutions.

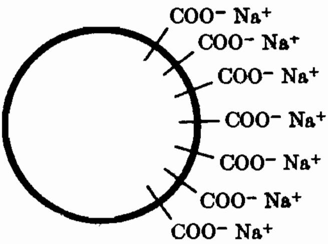


FIG. 15-6. Schematic representation of the surface of a monomer droplet covered with ionized soap molecules.

It can be said, then, that at the beginning of the polymerization the monomer is present (1) in the form of finely dispersed droplets covered with a layer of ionized soap (Fig. 15-6); or (2) it is solubilized in the micelles; or (3) it is dissolved in the aqueous phase to a very small amount. The catalyst is dissolved in the aqueous phase, and thus molecules of it are present in the aqueous zone of the micelles between the two hydrocarbon layers. If the catalyst is partly hydrocarbon soluble, a certain amount of it may also be found in the droplet and in the hydrocarbonic layer of the micelles.

When polymerization starts, active centers are being formed in the aqueous medium, which may migrate into the micelles, or in the micelles themselves. Thus propagation can start in the micelles and continue until

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[1] McBAIN, "Advances in Colloid Chemistry," vol. I, p. 142, Interscience Publishers, Inc., New York, 1942.

[2] HARKINS, *J. Chem. Phys.*, **13**, 381 (1945); **14**, 47 (1946).

the growing chain has attained a size which the micelle is unable to accommodate. The growing chain aggregate now looks like a polymer particle which as soap adsorbed on its surface. Monomer, which had diffused from the original droplet into the aqueous medium and through it, diffuses now into this newly formed polymer particle, and also radicals, formed in the aqueous medium, can enter it. Thus propagation and termination take place inside this monomer-polymer particle until all the monomer from the droplet reservoirs has been used up.

According to this theory, the initiation occurs in the micelles by radicals formed possibly in the aqueous phase, while the monomer-polymer particles are the loci of the propagation and the termination reaction. Since the newly formed particles readily adsorb soap on their surface and constantly grow in size, the number of soap micelles diminishes rapidly, and already early in the reaction they will have completely disappeared. Thus virtually all initiation has ceased, and the number of particles remains almost constant throughout most of the polymerization. The only reactions from this early stage on until most of the monomer is consumed are the growth and the termination of chains inside the monomer-polymer particles.

In large-scale industrial applications, emulsion polymerization is carried out in kettles that have adequate means of agitation and are equipped with reflux condensers. If one of the monomers is a gas or a low-boiling liquid, the polymerization is performed in a closed system capable of sustaining the pressure developed as a consequence of the increased temperature. An interesting method to control the temperature is to start with only a part of the batch in the kettle; after the reaction has started and the liberated heat of the reaction has caused an increase of the temperature of the kettle content, additional cold monomer emulsion or water is gradually added to keep the temperature at the desired level.

The duration of the polymerization process depends on the temperature employed and the degree of conversion desired and is, for instance, between 18 and 30 hr at 45–70°C. Emulsion polymerization recipes have also been developed which allow the reaction to proceed at temperatures as low as 0°C, and at much shorter reaction times than those cited before. This is achieved by the use of so-called "redox," reduction-activation, systems.

Whereas in bulk and in solution polymerization only catalysts and solvents are present besides the monomers, an emulsion polymerization requires a number of additional ingredients for a successful operation. There is first the emulsifying agent, which serves to produce the finely dispersed monomer particles of the emulsion. A large patent literature describes substances that show specific advantages for certain monomers under prevailing reaction conditions. Commonly used are the water-soluble soaps of long-chain fatty acids, sulfated long-chain alcohols, and salts of aliphatic and aromatic sulfonic acids. More recently, aliphatic amines having at least six C atoms or acid salts thereof, and certain synthetic and natural high polymers have been suggested as emulsifiers. Examples of polymeric emulsifiers are polyvinyl alcohol, polyacrylamides and polyacrylates, water-soluble polyvinyl ethers, phenolic and urea resins, reaction products of aliphatic alcohols or alkylated phenols with ethylene oxide, methyl cellulose, cholesterin, and saponin.

The reaction is efficiently catalyzed by water-soluble peroxidic compounds, of which hydrogen peroxide, urea peroxide, potassium persulfate, and sodium perborate are widely employed. Cumene hydroperoxide also has proved to be a most interesting and useful catalyst, particularly in the production of synthetic rubber GR-S, because of its particular solubility characteristics in both the aqueous and the hydrocarbon phase.

As mentioned before, outstanding results can be achieved in emulsion polymerizations by using a redox system. The reason can be explained as follows: it has been proved experimentally that in an emulsion polymerization the initiation step is the rate-determining quantity. In turn, this step depends on the rate of radical generation by the catalyst. The latter is a temperature-controlled reaction, and with a nonredox type of emulsion polymerization catalyst a temperature range of 45–70°C is necessary to obtain a suitable rate of radical formation.

Reactions occurring in reduction-oxidation systems furnish radicals at a considerably lower energy expenditure than that of a decomposition of a peroxide or a hydroperoxide. In the following equations, a redox reaction is exemplified by the oxidation of a divalent ferrous ion to a trivalent ferric ion:

$$\mathrm{Fe^{++} + H_2O_2 \rightarrow Fe^{+++} + OH^- + OH^*}$$
$$\mathrm{HO^* + C{=}C \rightarrow HO{-}C{-}C^*}$$

The hydrogen peroxide itself undergoes a reduction to hydroxyl ion and hydroxyl radical, the latter being able to initiate a polymerization reaction, as schematically indicated in the second part of the equation. Certain redox systems require a comparatively low activation energy, and if such a system is employed in an emulsion polymerization, the reaction can proceed at a temperature of, for instance, 0°C with a satisfactory rate.

Many emulsions of monomers are not too stable and break during the course of the reaction. In order to prevent this, stabilizers and buffering agents must be added. Natural or synthetic protective colloids (e.g., casein, glue, albumin, starch, methyl celluloses, and polyvinyl alcohol) act as stabilizers, and normal buffering agents (e.g., phosphates and carbonates) keep the pH of the emulsion within the desired range. To impart specific properties to the polymer, modifiers may be added to the emulsion before the polymerization is started. It is sometimes necessary to avoid cross-linking or branching of the polymer, especially if dienes are polymerized or copolymerized. It has been found that chlorinated hydrocarbon, mercaptans, diazo-aminoaryl compounds, disulfides, and dixanthates will achieve this purpose. Many of these compounds not only act as regulators and modifiers but also influence the rate of the reaction, whereas mercaptans with more than six C atoms exert only a regulating effect on the thermal and solubility properties of the polymer.

After the emulsion polymerization has progressed to the desired degree, the latex may be used directly or may be coagulated in order to yield solid polymers. If the latex is to be applied directly as a film-forming material or as impregnation for paper, fabric, or leather, plasticizers may be incorporated even at the beginning of the reaction. Also, for coating purposes, a clear solution may be made from the latex if it is concentrated first and then treated with a solvent that is miscible with water. Coagulation of the emulsion can be accomplished in the usual way by addition of electrolytes or by a freezing procedure. Among other methods, the electrophoretic separation of the latex particles and the spraying of the emulsion into a hot gas chamber should be mentioned. The coagulated polymer is either lumped together, in which case it has to be freed of water by milling on warm rolls and drying under vacuum, or it is precipitated in more or less fine granules, thus simplifying the further drying procedures.

Emulsion polymerization as a continuous operation has been described in the patent literature and has found industrial application. One technical process mentioned uses a coiled pipe of such dimensions that at a certain temperature the monomer emulsion polymerizes completely during its passage. If necessary, a pipe system can be built that is heated to different temperatures at its various sections. Other continuous processes can be carried out in polymerization towers if the monomer has a lower density than water and the polymer has a higher one. The monomer emulsion is added at the top of the tower and agitated by stirring devices, with turbulence limited to the upper parts of the tower. As the polymerization proceeds and the polymer sinks to the bottom of the tower, new monomer is introduced at the top and latex removed at the base. Instead of one tower, a battery of interconnected reactors can be advantageously used in a similar procedure.

Pearl (Suspension) Polymerization. The method of emulsion polymerization has proved highly efficient for large-scale production of polymers of high average molecular weight. However, the presence of emulsifiers and other chemicals in the reaction mixture makes such polymers unsatisfactory in applications involving high optical clarity and outstanding electrical insulating properties. During coagulation of the latex, small amounts of all the ingredients necessary for a successful course of the reaction are occluded inside the agglomerated polymer and cannot be completely removed even by the best washing procedures. The only way to obtain a pure product from an emulsion polymer would be to dissolve and reprecipitate the coagulated polymer repeatedly, a procedure that is not economically feasible in industrial operations. Therefore, a method was sought which, while maintaining the advantages of an emulsion polymerization, would produce polymers of the purity of a bulk polymer. Such a method seems to be the pearl or suspension polymerization, the simple principle of which is to polymerize a monomer in a nonsolvent medium (usually water), in which it is kept suspended without an emulsifier.

The liquid monomer is dispersed by adequate agitation into globules of varying size, and after the polymerization is finished the polymer has the form of regularly shaped spheres. In Fig. 15-7 a number of globular polymers are shown (methyl methacrylate, vinyl acetate, methyl acrylate, and styrene as arranged from left to right), with particle sizes differing from batch to batch (½–3 mm), but almost of the same size resulting from each individual operation. Figure 15-8 represents a batch of transparent polystyrene pearl polymers. Under proper reaction conditions, polymers of high purity can be obtained. They can be separated easily from the suspension medium and, after a drying procedure, can be conveniently stored, shipped, and used for subsequent molding and extruding operations.

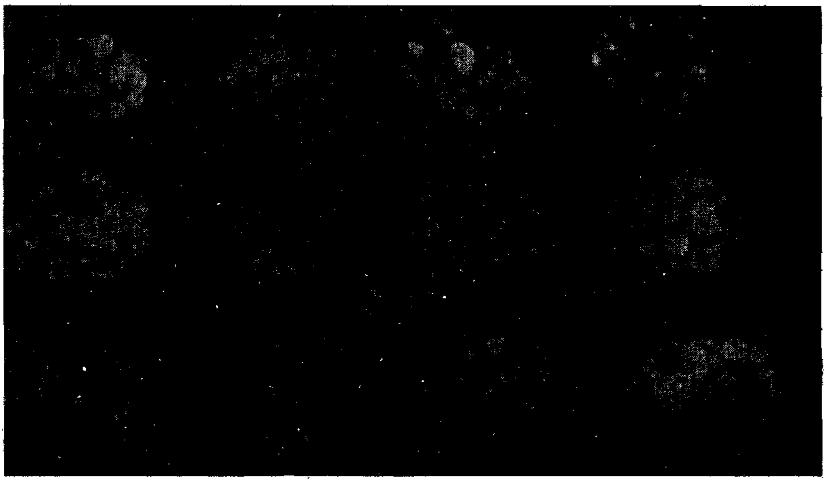

FIG. 15-7. Pearl polymers: left to right, methyl methacrylate, vinyl acetate, methyl acrylate, and styrene.

The reaction itself consists of three distinct phases. During the first one the inhibition period of the polymerization is overcome, little polymer is formed, and the viscosity of the liquid globules changes only slightly. If during this phase globules collide and coalesce, they are broken up again by the mechanical agitation. After the inhibition period is over, more polymer is quickly formed and dissolves in that part of the globule which is still monomeric. The globules thus become very viscous and sticky, and if upon collision of two spheres they coalesce, the mechanical agitation is no longer sufficient to separate them. In a brief period, all the globular particles will have agglomerated to one big lump. If, however, this sticky period is successfully overcome, the now largely converted spheres are solidified to such an extent that no agglomeration occurs on collision between them.

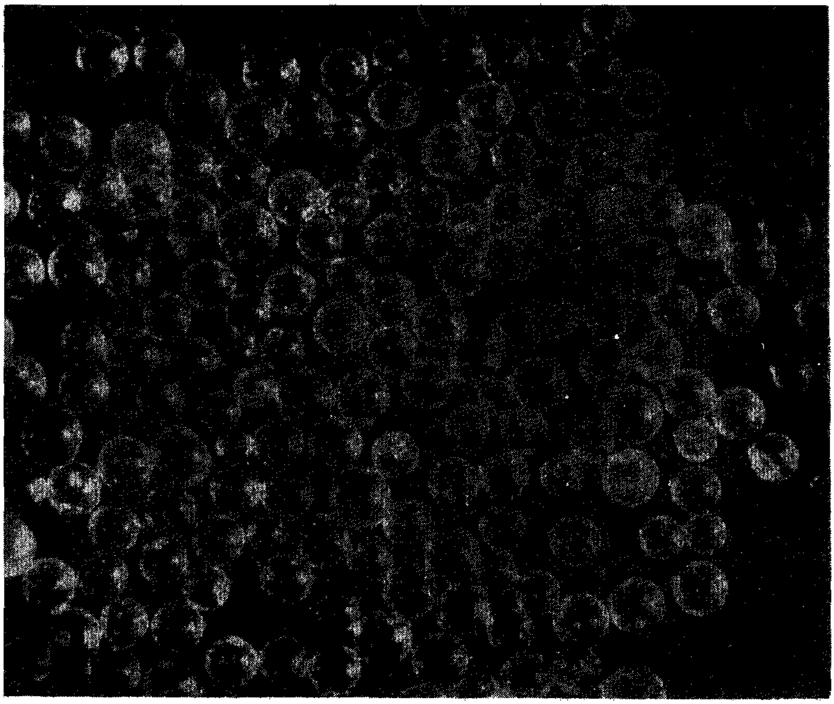

FIG. 15-8. Polystyrene pearl polymers.

In order to avoid lumping together during the sticky period, it becomes necessary to add small amounts of suspension stabilizers which adhere to the surface of the spheres and protect them from getting into direct contact with one another during the dangerous second phase of the reaction. These stabilizers can be completely removed from the surface of the spheres at the end of the polymerization by adequate washing or flotation processes.

The difference of this method from an emulsion polymerization stands out clearly by the fact that there is no necessity for coagulation since the product already has a form in which it can be handled. Occlusion of foreign matter in the polymer particles can thus be avoided.

Several patents protect the use of stabilizers, which may be of organic or inorganic origin. Among these, gelatin, starch, gum tragacanth, gum acacia, and agar-agar may be mentioned as examples of organic substances; bentonite, talc, diatomaceous earth and water-insoluble inorganic substances represent inorganic stabilizers. Some high polymeric substances such as polyvinyl alcohol and polymethacrylic acid salts may also be employed for the same purpose. It must be strongly emphasized that the efficiency of stabilizing agents varies with the different monomers and that reaction conditions have to be worked out carefully for each individual case. It is sometimes possible to use the suspension medium containing the stabilizer for a succession of runs after the polymerized pearls have been separated each time.

The catalysts found to be most effective for pearl polymerizations are of the peroxidic type and are soluble in the monomer. This fact, together with data on the energy of activation for the initiation reaction (found to be approximately 26,000 cal per mole) and the relationship of the over-all consumption of monomer and the average molecular weight of the polymer to the square root of the catalyst concentration c_k, points to a bulk

$$-\frac{dM}{dt} \sim \sqrt{c_k} \qquad \overline{DP} \sim \frac{1}{\sqrt{c_k}}$$

polymerization mechanism of the reaction.[1] It seems that pearl polymerization, in effect, constitutes an efficiently cooled bulk polymerization in which the polymerization reaction occurs inside the individual globules. The large amount of liquid surrounding each globule dissipates immediately any excessive heat built up during the reaction. The fact that one obtains a product of higher average molecular weight and a narrower distribution curve than in bulk polymerization indicates little local overheating in a suspension polymerization.

The size of the pearls can be altered at will and is determined by balanced conditions of the rate and the efficiency of the stirring; the type and amount of suspension stabilizer used; the speed of the conversion, which in turn depends on temperature and catalyst concentration; the ratio of monomer to the suspension medium; and, finally, the pH of the reaction mixture. The temperature range in which the reaction can be run is limited on the

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[1] HOHENSTEIN and MARK, *J. Polymer Sci.* **1**, 127 (1946).

lower side by the temperature at which the catalyst decomposition into radicals starts to influence the speed of the polymerization and on the upper side by the boiling point of the suspension liquid or the softening range of the polymer formed. It lies, in most cases, between 65 and 90°C.

The comparative conversion speed of a bulk, emulsion, and suspension polymerization and the average molecular weights of the polymers obtained for similar reaction conditions are presented in Table 15-6.

TABLE 15-6. COMPARISON OF BULK, EMULSION, AND SUSPENSION POLYMERIZATION OF STYRENE

Method	% conversion	Viscosity, avg mol. wt
Bulk	53.9	40,000
Emulsion	96.6	370,000
Suspension	48.6	67,000

Reaction time, 2 hr, temperature, 85°C.

Catalyst for bulk and suspension, 0.5 per cent benzoyl peroxide; for emulsion, 0.5 per cent potassium persulfate.

The data indicate that emulsion polymerization converts much faster than either bulk or suspension polymerization and that the average molecular weight of the emulsion polymer is higher than the suspension polymer, which, in turn, exceeds the bulk polymer. Although suspension polymerization proves inferior to emulsion polymerization as far as rate of the reaction and molecular weight of the polymer is concerned, it yields a product of superior purity. Compared with a bulk polymerization, the suspension polymerization produces polymers of equal purity and of slightly higher molecular weight and proceeds without the difficulties of temperature control encountered in the former method.

Pearl polymerization is industrially carried out in closed kettles, provided with a condenser and with an efficient stirring mechanism. The finished product is separated from the liquid by sieving procedures, then washed to remove the suspension stabilizer, and finally dried.

IV. POLYMERIZATION KINETICS

Kinetics of Polycondensations

The principal feature of a polycondensation upon which all kinetic considerations are based is its stepwise reaction character. A sound kinetic theory therefore depends on the following two basic principles which have been demonstrated to be correct: (1) that all the intermediate species are stable molecules and (2) that the rate of condensation is independent of the degree of polymerization, i.e., the reactivity of the functional groups is independent of the molecular weight of the molecule to which it is attached. It is thus possible to formulate a polycondensation kinetic scheme in terms of the analogous mechanisms which have been developed for low-molecular-weight materials undergoing the same reaction.

Ester formation between an acid and an alcohol is an acid-catalyzed reaction, and in the presence of a strong acid catalyst the rate is proportional to the hydroxyl and carboxyl concentrations. This may be written

$$\frac{d(Q)}{dt} = k[\mathrm{COOH}][\mathrm{OH}] \tag{1}$$

where Q is the number of ester bonds. A similar kinetic scheme is valid for polymeric esterifications, amidations, etc., involving reactants with two functional groups on each molecule. The usual method of following the extent of the reaction is by titration of the unreacted acid groups. If the initial concentration of acid is made equal to that of alcohol, it remains so throughout the reaction. Since

$$\frac{dQ}{dt} = -\frac{d[(\mathrm{COOH})]}{dt} \tag{2}$$

Eq. (1) may be written

$$-\frac{dc}{dt} = kc^2 \tag{3}$$

which integrates to

$$\frac{1}{c} = kt + \frac{1}{c_0} \tag{4}$$

where c denotes the concentration of —COOH groups at the time of titration and c_0 is their initial concentration. In the absence of added catalyst, the organic acid group acts both as catalyst and reactant

$$\frac{dQ}{dt} = k[\mathrm{COOH}]^2[\mathrm{OH}] \tag{5}$$

leading to third-order kinetics. Assuming equal initial concentrations of reactants, the rate equation becomes

$$-\frac{dc}{dt} = kc^3 \tag{6}$$

which yields upon integration

$$\frac{1}{c^2} = 2kt + \frac{1}{c_0^2} \tag{7}$$

Experimental data do not follow these equations very closely. This problem also arises in low-molecular-weight esterifications and is apparently due to the change in polarity of the medium as the ester formation proceeds. The catalytic efficiency of an acid is very sensitive to the polarizing forces in the surrounding medium; the very process of esterification, however, involves the formation of a nonpolar molecule from two relatively polar reactants. This changes the situation and is reflected in a relation of the reaction rate versus time slightly different from the one given in the above formula.

Similar kinetic equations may be formulated for esterifications involving polyfunctional monomers, i.e., molecules with more than two functional groups. However, further complications arise. One of these is that cross-linked gels or thermosetting resins are formed and diffusion of the reactants becomes increasingly a rate-controlling factor. Another difficulty is represented by the different reactivities of like functional groups attached to the same molecule. For instance, the glycerol–phthalic acid reaction possesses two esterification rates corresponding to the primary and secondary glycerol hydroxyl groups, respectively. Also with this particular system, the hydroxyls are on neighboring carbons and steric hindrance plays an important role in preventing further reaction once partial esterification has taken place. As was mentioned earlier, the titration of free —COOH groups is used to determine the extent of reaction in ester formation. Since the glycerophthalate resin becomes insoluble during the reaction, titration is possible only up to the gel point, even though polymerization proceeds beyond that point. The reaction after the gel point has been followed in some cases by measuring the amount of water liberated.

An important parameter in all polycondensations is the "extent of reaction," i.e., the fraction of the reactive groups which have reacted up to a specified time t. This quantity is usually represented by the letter p and can be expressed by the equation

$$p = \frac{N_0 - N}{N_0} \tag{8}$$

where N_0 is the concentration of polyfuntional molecules at the start and N is their concentration at time t. Since p may be directly determined by titration, it represents an easy method to calculate some data pertaining to the reaction itself as well as to the polymer molecule formed.

For instance, the number fraction m_x of X-mers, i.e., polymer molecules containing X monomer units with respect to the originally present total number of reacting units (N_0), can be derived from these titration values. In order to form an X-mer, x-1 reactions must take place because the end groups remain unreacted. The probability of forming an X-mer is, therefore, given by the equation

$$P_x = p^{x-1}(1 - p) = \frac{N_x}{N} \tag{9}$$

This probability is equal for the whole mole fraction of X-mers in the polymer mixture and can, therefore, also be expressed as N_x/N, i.e., as the ratio of X-mers (N_x) to the number of reacting units N at the specific reaction time t.

In accordance with the previously given definition of the extent of the reaction p, N can be expressed as

$$N = N_0(1 - p) \tag{10}$$

If this expression is substituted in Eq. (9), the following equations can be obtained:

$$\frac{N_x}{N_0(1 - p)} = p^{x-1}(1 - p)$$
$$\frac{N_x}{N_0} = p^{x-1}(1 - p)^2 = m_x \tag{11}$$

The ratio N_x/N_0 is the expression for m_x and can thus be calculated from the known values of N_0 and p.

In similar fashion it is possible to calculate the *weight* fraction ω_x of X-mers by using the equation

$$\omega_x = xp^{x-1}(1 - p)^2 \tag{12}$$

The average $\overline{DP}$ of the polymer molecule at time t of the reaction can also be brought in relationship to the extent of the reaction p. It is given by the ratio of the total number of reacting units N_0 to the number of molecules present at time t.

$$\overline{DP} = \frac{N_0}{N} = \frac{N_0}{N_0(1 - p)} = \frac{1}{1 - p} \tag{13}$$

In condensation polymerization systems containing a mixture of monofunctional and polyfunctional molecules, the question arises as to the exact conditions under which an infinite network molecule will be formed. The theory has been worked out from a probabilistic argument. The calculation as originally carried out by P. Flory[1] was based on the assumption of equal reactivity for all active groups and on the further supposition that intramolecular condensation may be ignored. If a group reacts with one of the chain ends of a branched molecule, the probability that the reaction leads to an extra chain end on the molecule is called α. If α is greater than one half, the number of chain ends increases with the extent of the reaction, an infinite network is formed, and the resultant product is infusible. Otherwise, the network molecule does not grow without bound and the final material may remain thermoplastic. The quantity α may be calculated from the extent of the reaction at time t and the initial proportion

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[1] FLORY, *J. Am. Chem. Soc.*, **69**, 30 (1947); *Chem. Revs.*, **39**, 137 (1946).

of the reactants and depends, of course, on the functionality f of the reacting units: $\alpha = p^2$ and $\alpha = 1/f - 1$ (see also p. 954).

In actual fact a considerable amount of intramolecular reaction occurs in many polycondensation systems. This has the effect of reducing α, in that some of the reactive chain ends are used up. Because of this complication and because of the unequal reactivity of active groups, the present theories discussed above do not fit experimental data exactly. Nevertheless, the primary argument that the general scheme of polycondensation kinetics is largely in line with the kinetic mechanisms of the same reactions leading to low-molecular-weight compounds has been adequately demonstrated from experimental results on a number of chemical systems.

Kinetics of Addition Polymerization

All kinetic considerations must be based on experimental data pertaining to reproducible measurements of some characteristic of a reaction. In the case of a polymerization reaction, the most easily accessible and most reliable data are those of the over-all rate of the reaction, a quantity which indicates the average amount of polymer formed per unit time.

For a long time this quantity was about the only experimental basis for kinetic studies of polymerization, and only in recent years was it possible to determine the individual rates of the different reaction steps with the aid of an ingenious and modern experimental technique.

An equation for the over-all rate of polymerization, which would explain the experimentally observed data and would take into account kinetic terms for all individual reaction steps, would be extremely involved and unwieldy. Fortunately, it is possible to make one simplifying assumption which leads directly to an expression relating known quantities, for instance, the concentration of monomer in a solution at the start of the reaction, to measurable characteristics, like the over-all rate. This assumption postulates the presence of a "steady state" during a certain stage of the polymerization reaction.

The steady-state approximation was first enunciated by Bodenstein.[1] It states that in a reaction in which transient species, such as atoms or radicals, are involved, a steady state sets in, characterized by an equal rate of formation and disappearance of the species. This principle, applied to the case of a polymerization reaction, means that at a certain reaction stage the amount of active centers formed is equal to the amount of growing chains terminated:

$$R_{\text{initiation}} = R_{\text{termination}}$$

Using the steady-state approximation, kinetic equations can be developed which hold for a wide class of polymerization reactions.

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[1] BODENSTEIN, *Z. physik. chem.*, **85**, 329 (1913); *Z. Electrochem.*, **42**, 443 (1936).

Free-radical Polymerization Kinetics. A general scheme for these reactions is the following:

Initiator forms free radicals: $C \xrightarrow{k_i} C^*$

Initiator radical reacts with monomer to form a new free radical: $C^* + M \xrightarrow{k_{p_1}} R^*$

Propagation: $R^* + M \xrightarrow{k_p} R^*$

Termination by recombination: $R^* + R^* \xrightarrow{k_t} P$

Termination by disproportionation: $R^* + R^* \xrightarrow{k_{t_2}} P + P$

The differential equations governing this reaction can be set up as follows:

$$-\frac{d[C]}{dt} = 2k_i[C^*] \tag{14}$$

$$-\frac{d[C^*]}{dt} = -2k_i[C^*] + k_{p_1}[C^*][M] \tag{15}$$

$$-\frac{d[M]}{dt} = k_{p_1}[C^*][M] + k_{p_2}[R^*][M] \tag{16}$$

$$-\frac{d[R^*]}{dt} = -k_{p_1}[C^*][M] + k_{t_1}[R^*]^2 + k_{t_2}[R^*]^2 \tag{17}$$

C^* and R^* are chemically unstable species, and shortly after the beginning of the reaction they attain a certain concentration, the steady-state concentration, which remains constant throughout the reaction; consequently dR^*/dt and dC^*/dt are both equal to zero. Also, in the steady state, the rate at which polymer is formed is equal to the rate at which initiator decomposes; therefore,

$$k_i[C] = (k_{t_1} + k_{t_2})[R^*]^2 \tag{18}$$

Setting $k_{t_1} + k_{t_2} = k_t$ and noting that the term $k_{p_2}[R^*][M]$ in Eq. (16) is so predominant over the term k_{p_1} $[C^*][M]$ that the latter can be neglected for all practical purposes, one obtains

$$-\frac{d(M)}{dt} = k_{p_2}\left(\frac{k_i}{k_t}\right)^{1/2} [M][C]^{1/2} \tag{19}$$

This equation states that the over-all rate of polymerization is proportional to the monomer concentration and to the square root of the initiator concentration. This has been found to be correct in a number of monomer-initiator systems, for example, in the methyl methacrylate plus azo-bis-isobutyronitrile system and in styrene plus benzoyl peroxide. Figure 15-9 shows a plot of rate of polymerization versus the square root of the initiator concentration for the case of the styrene–benzoyl peroxide combination, and the resulting straight line is in conformity with the equation.

The degree of polymerization of the polymer is obtained from the ratio of the propagation reaction to that of termination, or the ratio of the propagation reaction to that of initiation, since in the steady state the initiation and termination rates are equal. The degree of polymerization may then be expressed as

$$\overline{DP} = \frac{k_{p_1}[C^*][M] + k_{p_2}[R^*][M]}{(k_{t_1} + 2k_{t_2})[R^*]^2} \tag{20}$$

The first term in the numerator is very small. Assuming also that termination is by recombination only, k_{t_2} becomes zero and Eq. (20) can be written as

$$\overline{DP} = \frac{k_{p_2}}{k_{t_1}} \frac{[M]}{[R^*]} \tag{21}$$

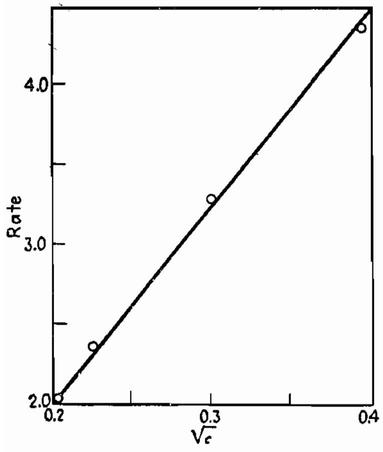

FIG. 15-9. Polymerization of styrene at 27°C. Dependence of rate on square root of the catalyst concentration. [*Calculated from the data of Schultz and Husemann, Z. physik. Chem.*, **B 39** (1938).]

It is preferable to express $[R^*]$ in terms of $[C]$ and $[M]$, the initiator and monomer concentrations at time t. This can be achieved by applying the steady-state approximation and calculating $[R^*]$ and $[C^*]$ from the differential Eqs. (15) and (17). Thus

$$[R^*] = \left(\frac{k_{p_2}}{k_{t_1}} [C^*][M]\right)^{1/2} \tag{22}$$

$$[C^*] = \frac{2k_i[C]}{[M]} \tag{23}$$

Substituting these terms in Eq. (20) one obtains the simplified expression

$$\overline{DP} = k_{p_2}{}^{3/2}\left(\frac{k_i}{k_t k_{p_1}}\right)^{1/2} \frac{[M]}{[C]^{1/2}} \tag{24}$$

If $k_{p_1} = k_{p_2}$, this becomes

$$\overline{DP} = k_{p_2}\left(\frac{k_i}{k_t}\right)^{1/2} \frac{[M]}{[C]^{1/2}} \tag{25}$$

Equation (25) shows that the average polymerization degree is inversely proportional to the square root of the initator concentration. This, as well as the linear dependency of the over-all reaction rate on the square root of the initiator concentration, holds true at least during the earlier stages of the polymerization. As the polymerization proceeds, the effects of viscosity and diffusion begin to make themselves felt and complicate these relationships.

The above kinetic analysis has been simplified for purposes of illustration by omitting the fact that chain-transfer reactions may occur. In the absence of solvent, chain transfer may occur between the radical R^* and the monomer M or the polymer P.

$$R_n^* + M \xrightarrow{k_{tr_1}} P_n + M^*$$
$$R_n^* + P_m \xrightarrow{k_{tr_2}} P_n + R_m^*$$

The first of these takes place near the beginning of the reaction as well as later on, while the second can become appreciable only after a certain quantity of polymer is formed.

In many polymerizations, solvent as well as monomer is present and the reaction

$$R_n^* + S \xrightarrow{k_{tr_3}} P_n + S^*$$

takes place.

The extent of chain transfer in a polymerizing system depends on the nature of the reactants, the solvent, and the reaction conditions. Thus, it may be almost completely absent or occur quite often. If there is an appreciable occurrence of chain transfer, then the average molecular weight of the polymer is affected. The frequency of chain transfer and therefore the molecular weight can be regulated to a certain degree by the addition of efficient chain-transfer agents, i.e., substances which are very susceptible to the reaction $R_n^* + S \rightarrow P_n + S_n^*$. The equation which relates the degree of polymerization in the presence of a chain-transfer agent $\overline{DP}$ to the degree of polymerization of the polymer formed in its absence $\overline{DP}_0$ under the same conditions is

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + \frac{k_{tr}}{k_p}\frac{[S]}{[M]} \tag{26}$$

The quantity k_{tr}/k_p is called the chain-transfer constant and varies from 10^{-6} for poor chain-transfer agents to 0.1 for very good ones.

If in a polymerization reaction all three of the above transfer steps are frequent, they must be taken into account in setting up the differential equations governing the reaction rates. In particular, the following new termination steps must be introduced:

Disproportionation:

$$S^* + R^* \rightarrow P + S$$
$$S^* + R^* \rightarrow P + T$$
$$S^* + S^* \rightarrow S + T$$

Combination:

$$S^* + R^* \rightarrow P$$
$$S^* + S^* \rightarrow 2S$$

where T is a molecule similar to S but containing an additional double bond.

The inclusion of all these steps hopelessly complicates the kinetic equations which may be written but cannot be solved in general, though with partial simplification some analysis is possible. For details the reader is referred to textbooks on polymer kinetics.

Ionic-polymerization Kinetics. The kinetics of ionic polymerization share some common principles with that of the free-radical reaction. Both are based on the basic steps of initiation, propagation, termination, and chain transfer, and in both the ultimate average molecular weight depends on the ratio of the reaction rates of propagation and termination. There are, however, important differences. In ionic polymerization the termination step appears to be unimolecular, while it is bimolecular in free-radical type polymerization. The dependence of the kinetic scheme of the reaction on the various parameters is therefore different in the two reactions. Likewise, the fact that a cocatalyst has to be brought into the ionic reaction scheme has to be taken into account.

Several kinetic mechanisms have been proposed which explain some of the experimental results obtained with cationic polymerization systems, but since the dependence of rate on monomer, initiator and cocatalyst seems to vary considerably with the type of monomer and initiator used, no one scheme fits all the data. A mechanism which takes into account the importance of the cocatalyst and gives a correct dependence on monomer concentration is the following:

$$C + AB \rightleftharpoons CA^+B^-$$

Initiation:

$$CA^+B^- + M \xrightarrow{k_i} M^+B^-$$

Propagation:

$$M^+B^- + M \xrightarrow{k_p} M_2^+B^- \rightarrow M_3^+B^-$$

Termination:

$$M_n^+B^- \xrightarrow{k_t} P_n + CA^+B^-$$

where C is, for instance, a metal halide initiator and AB is a cocatalyst, for instance, water.

The rate equations are

$$-\frac{d[M]}{dt} = k_i[CA^+][M] + k_p[M^+][M] \tag{27}$$

$$-\frac{d[M^+]}{dt} = -k_i[CA^+][M] + k_t[M^+] \tag{28}$$

$$-\frac{d[P]}{dt} = -k_t[M^+] \tag{29}$$

The reaction between catalyst and cocatalyst is assumed to be very rapid so that the concentration of the ionic species conforms to $[CA^+B^-] = K[C][AB]$, where K is an equilibrium constant. The concentration of the

polymerizing ion reaches a steady state shortly after the beginning of the reaction, and therefore $d[M^+]/dt = 0$.
Consequently

$$[M^+] = \frac{k_i[CA^+][M]}{k_t} = \frac{k_i}{k_t}[C][AB][M] \tag{30}$$

Substituting this result in the second term on the right hand side of Eq. (27) yields

$$-\frac{d[M]}{dt} = \frac{k_i k_p}{k_t} K[C][AB][M]^2 \tag{31}$$

The first term on the right of Eq. (27) has been omitted since it is negligibly small. Equation (31) shows that the rate of reaction is proportional to the square of monomer concentration and to the first power of initiator and cocatalyst concentration.

In actual fact, chain-transfer reactions may take place which can change this order. These are

$$M + M_n^+ \xrightarrow{k_{tr_1}} M^+ + P_n$$
$$S + M_n^+ \xrightarrow{k_{tr_2}} S^+ + P_n$$

Only a few experimental data are available on these transfer reactions though their occurrence has been verified by molecular-weight studies.

The degree of polymerization can be expressed likewise in terms of the ratio of the reaction rates

$$\overline{DP} = -\frac{d[M]/dt}{d[P]/dt} = \frac{k_p}{k_t}[M] \tag{32}$$

if no appreciable amount of chain transfer occurs.

If chain transfer to monomer is the principal mechanism of chain termination, the degree of polymerization is independent of monomer concentration as is shown in the following expression:

$$\overline{DP} = \frac{k_p}{k_t} \tag{33}$$

V. SOLUTION PROPERTIES OF POLYMERS

One of the methods used to study the behavior of polymer molecules is an investigation of their properties in solution. Of particular importance is the study of dilute polymer solutions, in which the molecules are separated from each other so as to eliminate possible interference. This technique has yielded much fundamental information. For instance, the molecular weight of polymer molecules and the variation (distribution function) of the molecular species in one polymeric sample can be determined by measurements of certain physical characteristics of a very dilute polymer solution. Likewise, size and shape of polymer molecules, their resistance to deformation, the association and dissociation of molecular complexes, and other properties can be obtained by such studies.

It has to be emphasized that these parameters require a study of molecules separated from each other by means of high dilution of the solution. There are, however, other characteristics of polymer molecules which must be studied in concentrated solution or in the solid state.

Colligative Properties

Freezing-point Depression, Boiling-point Elevation. The freezing-point depression, vapor-pressure drop, and boiling-point elevation of a liquid caused by the presence of a dissolved solute are a set of closely related phenomena which arise because of the requirements of thermodynamic equilibrium between two phases. The magnitude of a freezing-point depression (or vapor-pressure drop or boiling-point elevation) depends on the molality of the solution. If the weight of solute per unit volume of solvent is known and the molality is determined from the freezing-point depression, the molecular weight of the solute may be directly calculated. In the event that the solute is a mixture of molecular species, the number-average molecular weight is obtained since the molality measures the number of molecules. For high-molecular-weight materials the number of moles is very small even when the weight concentration is high. Consequently, the freezing-point depression is small. Therefore, molecular weights by freezing point depression, or, in fact, by any of the above-mentioned procedures are difficult to obtain when the molecular weight is above 2,000 and can be determined only with the most refined equipment if the molecular weight is as high as 10,000.

Osmotic Pressure

Another related method of determining molecular weights is based on the osmotic pressure of a solvent-solute system. The magnitude of the osmotic pressure for nonpolymeric systems can be very large, of the order of several feet of water. However, it is impossible to make molecular-weight determinations if the solute is a small molecule because suitable semipermeable membranes cannot be found. Membranes do exist, though, which are permeable to ordinary solvents but impermeable to polymers. The osmotic pressures generated in these polymeric solutions are large enough so that molecular weights in a range from 10,000–200,000 can be easily determined.

The basic equation relating molecular weight to osmotic pressure was derived by Van't Hoff and is

$$\pi = \frac{RT}{M}c \qquad (1)$$

where π is the osmotic pressure, c the concentration, T the temperature, and M the molecular weight. For polymer solutions, this is an oversimplification because there is another term arising from intermolecular interactions between polymer molecules. The modified equation is

$$\pi = \frac{RT}{M}c + A_2c^2 \tag{2}$$

The molecular weight is determined by a series of osmotic-pressure measurements on solutions of varying concentration. A plot of π/c versus c is roughly linear, and the intercept on the ordinate yields π/c at infinite dilution. (See Fig. 15-10.) Substituting this value in Eq. (1) the number-average molecular weight M can be calculated.

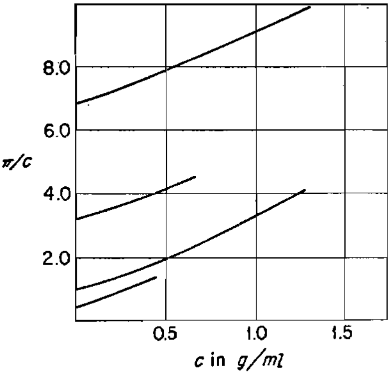

FIG. 15-10. Plots of π/c vs. c for a series of polyisobutylene fractions in cyclohexane. [*Krigbaum and Flory, J. Am. Chem. Soc.*, **75**, 1775 (1953).]

The quantity A_2 in Eq. (2) is an important measure of polymer-solvent interaction. Its thermodynamic significance is somewhat complicated, the magnitude of the effect being determined by both the heat and entropy of solution. For any given polymer, A_2 is highest in the best solvent and lowest in the worst. If A_2 becomes appreciably negative, the solvent becomes too weak to keep the polymer in solution and precipitation takes place.

Certain limitations exist which affect the procedures in osmotic-pressure measurements. The most serious of these at the present time is that all available membranes are partially permeable to the low-molecular-weight fractions of the polymer. Consequently, the results of osmotic-pressure determinations may be too low and the molecular weights calculated from them too high. This problem is most disturbing for low-molecular-weight polymers with molecular weights in the 10,000–30,000 range.

Osmotic-pressure measurements are carried out in an apparatus which essentially consists of two chambers separated by a membrane, one chamber containing pure solvent and the other the polymer solution. A capillary extends vertically from each chamber, and the difference of height of the liquid in the two capillaries at equilibrium is equal to the osmotic pressure of the solution.

As mentioned before, a most important problem in osmotic measurements is to find and prepare a good and suitable membrane. Another basic requirement of a good osmometer is to provide a large area of contact between membrane and solution so that equilibrium may be rapidly attained; also the membrane must be clamped rigidly in order to avoid erratic fluctuations in the height of the liquid in the capillaries.

Two commonly used osmometers are those of Fuoss and Mead[1] and Zimm and Meyerson,[2] respectively. A picture of another efficient apparatus designed by Krigbaum[3] is shown in Fig. 15-11.

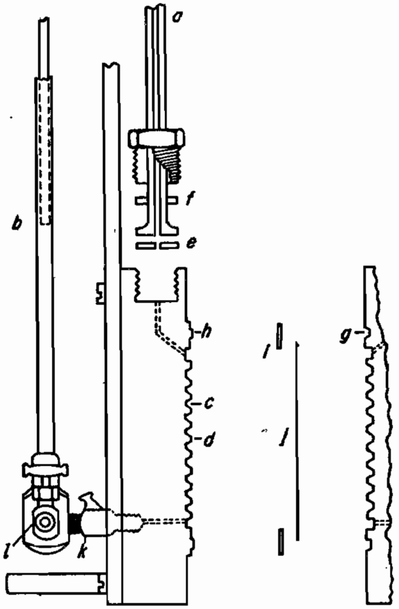

FIG. 15-11. Diagram of the block-type osmometer used by Krigbaum showing one cell in detail. Precision-bore 1-mm capillary (*a*) is flanged and ground flat at its base. The packing nut, acting through the Teflon washer (*f*) seals the capillary foot against lead gasket (*e*). The cell consists of channels (*c*) with "island" membrane supports (*d*). Ridge (*h*) fits into the wider channel (*g*) when the blocks are bolted together using lead gasket (*i*) between left block and membrane (*j*). The cells may be filled and emptied through needle valve (*k*) and connection (*l*). The standpipe (*b*) facilitates changing the level.

Viscosity

In the later 1920's Staudinger[4] and his collaborators discovered that a small amount of polymer in solution is sufficient to increase its viscosity greatly over that of the pure solvent. They recognized that this increase was a function of molecular weight, and the so-called "viscosity law" was formulated as a result of their studies. It states

$$\frac{\eta - \eta_0}{\eta_0 c} = KM \qquad (3)$$

where η is the viscosity of the solution, η_0 the viscosity of the solvent, c the concentration of the polymer in grams per liter, M the molecular weight, and K a constant which depends on the solvent-polymer system and the temperature. At a later time when more accurate molecular-weight data became available, it turned out that this relationship was not exactly correct, and Mark[5] among others suggested that a more appropriate formula was

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[1] FUOSS and MEAD, *J. Phys. Chem*,, **47**, 59 (1943).

[2] ZIMM and MYERSON, *J. Am. Chem. Soc.*, **68**, 911 (1946).

[3] KRIGBAUM and FLORY, *J. Am. Chem. Soc.*, **75**, 1775 (1953).

[4] STAUDINGER and HEUER, *Ber.*, **63**, 222 (1930).

[5] MARK, "Der feste Koerper, p. 103, S. Hirzel Verlag, Leipzig, 1938.

$$[\eta] = KM^a \tag{4}$$

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c} \tag{5}$$

where $[\eta]$ is called the intrinsic viscosity, and a is a constant usually between 0.5 and 1.0. Hydrodynamic theories of viscosity developed by Kirkwood,[1] Debye,[2] and Brinkman[3] led to similar results except that a was said to vary with the molecular weight from 1.0 at low molecular weights to 0.5 at very high molecular weights. These theories were developed for polymers where the hindered rotation about the carbon-carbon bond is not too high. A model of such a polymer molecule would look like a long coiled chain.

The above-mentioned hydrodynamic theories were modified by Flory[4] in such a way that the exponent a remained constant over a wide range of molecular weights. Flory's theory also predicted that a would take on values from 0.5–0.8, depending on the solvent-polymer interaction. It states that in cases where Van't Hoff's law is strictly valid [see Eq. (1)] a equals 0.5, and where the deviations from Van't Hoff's law are very large, a approaches 0.8. The results of the Flory theory are in good agreement with experiment and are today probably the best way to interpret the results of viscosity measurements in terms of molecular parameters.

The viscosity of polymer solutions is usually determined by measuring the flow time of a definite quantity of solution through a capillary. The driving force is the height of the fluid in the viscometer. A difficulty arises because polymer solutions are sufficiently oriented in ordinary capillary viscometers so that even at a low rate of shear the viscosity determined does not correspond to its real value at zero shear. In order to get values which are reproducible, regardless of the viscometer used, the viscosities, therefore, have to be determined at several rates of shear and extrapolated to zero shear rate as well as to zero concentration. This is particularly important for high-molecular-weight polymers where the shear dependence of viscosity is most pronounced.

The intrinsic viscosity of a polymer is often used to express its average molecular weight by means of the equation $[\eta] = KM^a$. Once the constants K and a have been determined independently and by an absolute method for a specific polymer-solvent system (for instance, polystyrene in toluene), the unknown average molecular weight of any sample of this polymer can be calculated from this equation by measuring its intrinsic viscosity in the same solvent (see also pp. 934 and 936).

[1] Kirkwood and Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

[2] Debye and Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

[3] Brinkman, *Appl. Sci. Research*, **A1**, 27 (1947).

[4] Flory, *J. Chem. Phys.*, **17**, 303 (1949).

Light Scattering

A beam of light by its very nature causes an electromagnetic disturbance in any matter through which it passes. This disturbance leads to an oscillation of the electrons in the illuminated system with the same frequency as the incident beam of light. As a result, light generated by the motion of the electrons is given off in various directions to the incident beam. This scattered light is known as Rayleigh scattering, after Lord Rayleigh who first investigated this problem.

The amount of light scattered by a polymer solution arises from solvent scattering plus polymer scattering, and as a general rule the latter is much larger. The light scattering of a polymer can be related to the osmotic pressure of its dilute solution by thermodynamic considerations based on concentration fluctuations in the solute-solvent system. This is an important observation since the molecular weight as well as the solvent-polymer interaction may thus be obtained from light-scattering measurements. There is some difference in the interpretation of osmotic and light-scattering results, and in fact, a weight-average molecular weight is obtained from light scattering as opposed to a number-average molecular weight from an osmotic-pressure determination (see pp. 933 and 934).

The equation which relates the light scattering of a polymer to its molecular weight is

$$\frac{Hc}{R_{90}} = \frac{1}{M} + 2A_2c \qquad (6)$$

where

$$H = \frac{32\pi^3Nn^2}{3\lambda^4}\left(\frac{dn}{dc}\right)^2 \qquad (7)$$

In this equation R_{90} is the intensity of light scattered at 90°, c the concentration, M the molecular weight, n the refractive index, λ the wavelength of the light in the solution, and N is Avogadro's number. A graph of Hc/R_{90} versus c for a series of varying concentrations is usually linear and may be extrapolated to zero concentration to yield the molecular weight.

The results for molecular weight obtained from Eq. (6) have to be modified when the size of the individual polymer molecule becomes greater than one-twentieth of the wavelength of light. The reason for this modification may be explained as follows: if the polymer molecule is small in comparison with the wavelength of light, it acts as a single large scattering unit; the electromagnetic disturbance in one part of the molecule is in phase with the disturbance throughout the rest of the molecule. If the molecule is of an intermediate size (a characteristic linear dimension is one-fifth the wavelength of the incident light), the scattering from different parts of the molecule is somewhat out of phase, and the intensity of the scattered beam is less than if the same molecule had been smaller. This phenomenon is sometimes called destructive interference. As may be seen from Fig. 15-12, the amount of destructive interference depends on the total path length of the light from the source to the viewer. From simple geometric considerations it can be shown that the destructive interference increases as the angle between the scattered and incident beam increases. The amount of destructive interference as a function of angle is thus a direct measure of the size of the molecule.

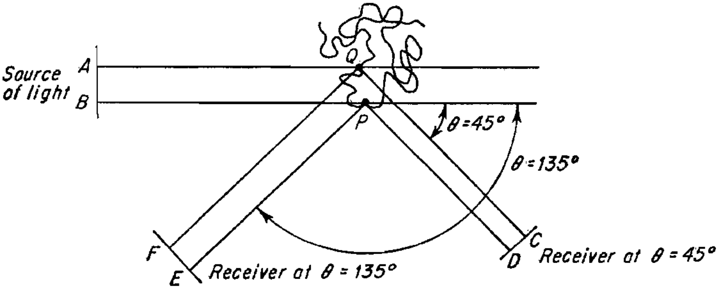

FIG. 15-12. Destructive interference in light-scattering measurements.
A light beam originating at AB is scattered by polymer segments at Q and P. The destructive interference depends on the difference in path length of the rays of light scattered from Q and P, respectively. The difference in path length is greater in the backward than in the forward direction, and consequently the intensity of scattering as a function of angle is a measure of molecular size.

The modification of Eq. (6) as a consequence of the destructive interference of the scattered light is given by

$$\frac{Hc}{R_\theta} = \frac{1}{MP(\theta)} + 2A_2c \tag{8}$$

and in particular

$$\frac{Hc}{R_{90}} = \frac{1}{MP(90)} + 2A_2c \tag{9}$$

when the scattering measurement is at 90° to the incident beam. In this equation R_θ represents the intensity of light scattered at an angle θ to the incident beam. $P(\theta)$ is a function of the shape and size of the polymer molecule and is a direct measure of the destructive interference. $P(90)$ has been tabulated for differently shaped molecules as a function of the measurable quantity $Z = R_{45}/R_{135}$, which is called the dissymmetry coefficient.

A more satisfying procedure for determining molecular weight and size of polymer molecules by light scattering was developed by Zimm.[1] The method is based on the same general principle of destructive interference

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[1] ZIMM, *J. Chem. Phys.*, **16**, 1093, 1099 (1948).

as a measure of molecular size and leads to a corrected molecular weight. The Zimm procedure uses a plot of experimental data collected at varying scattering angles and extrapolated to zero angle [at which $P(\theta) = 1$] as well as to zero concentration. This is shown in Fig. 15-13. The extrapolation to zero angle makes it possible to determine the molecular weight directly from the graph without computing a correction from dissymmetry measurements. The molecular size may be taken directly from the experimental slope of the zero concentration line (Fig. 15-13) without making any assumptions about molecular shape or configuration.

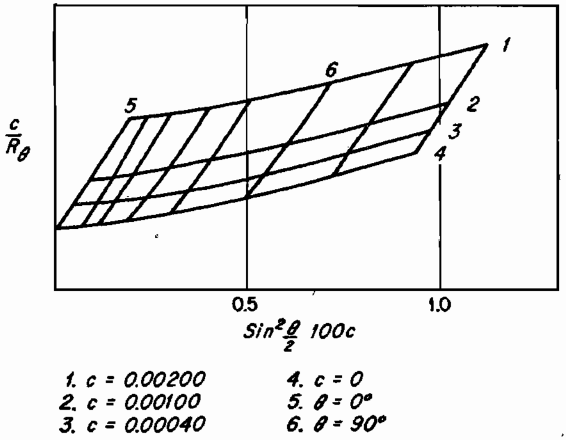


FIG. 15-13. Use of light scattering for determining molecular weight and size of polymer molecules. Zimm plot of polystyrene in dichloroethylene at 22°C. [*Outer, Carr, and Zimm, J. Chem. Phys.* **18**, 830 (1950).]

While the light-scattering molecular weight is a weight average, the molecular size is a *z* average (see p. 934). This means that in a polydisperse polymer the molecular size measurement would excessively reflect the contribution of the highest-molecular-weight fraction in the system.

Ultracentrifuge and Diffusion

If a fine suspension of sand is shaken in a fluid and allowed to stand, the sand slowly settles, the rate of settling depending on the viscosity of the fluid, the frictional resistance of the particle, and the net force acting on the particle. However, if these particles are in the molecular size range, no settling takes place since the molecules tend to diffuse from a higher concentration region to a lower one, thus effectively counteracting the gravitational force.

Polymer molecules will not settle from solution in an ordinary gravitational field since the tendency to diffuse back into the more dilute region is too great. If the gravitational field is intensified, however, sedimentation does take place. The rate of sedimentation depends, among other factors, on the molecular weight of the polymer, and thus by measuring both sedimentation and diffusion rates separately, molecular weights of polymers can be determined.

Consider a polymer molecule of mass m which is whirled in a circular path of radius x at an angular velocity ω. The net force acting on a molecule of mass m is given by

$$F = V_m(\rho_p - \rho_s)\omega^2 x \tag{10}$$

where V_m is the volume of a molecule of mass m, ρ_p the density of the polymer, and ρ_s the density of the solvent. This causes the molecule to move with a velocity dx/dt so that

$$f\frac{dx}{dt} = V_m(\rho_p - \rho_s)\omega^2 x \tag{11}$$

where f is the friction constant of the molecule which can be related to the diffusion constant by the equation

$$D = \frac{kT}{f} \tag{12}$$

If the sedimentation constant s is defined as the velocity of sedimentation when $\omega^2 x$ is unity, Eq. (11) may be rewritten

$$s = \frac{V_m(\rho_p - \rho_s)D}{kT} \tag{13}$$

Multiplying the top and bottom by Avogadro's number N and recognizing that the molecular weight is

$$M = NV_m\rho_p \tag{14}$$

the following equation is obtained:

$$M = \frac{s}{D}\frac{RT}{(1 - \rho_s/\rho_p)} \tag{15}$$

This result is based on the hypothesis that the forces to be considered are only those acting on an isolated molecule. In actual fact, the presence of other polymer molecules in the solution complicates the hydrodynamic pattern so that both s and D are functions of concentration. If s and D, or s/D, are plotted versus concentration and extrapolated to zero concentration, the intercepts s_0 and D_0, or $(s/D)_0$, when substituted in Eq. (15), yield the correct value for molecular weight.

The sedimentation rate is measured by observation of variations in the concentration of polymer solutions in a cell while the cell is whirled at high speed inside the rotor of an ultracentrifuge. The polymer molecules are driven by centrifugal forces toward the outer region of the cell, and a boundary will show between it and the inner region of the cell containing the pure solvent. As the centrifugation continues, this boundary will move outward until equilibrium has been achieved between the sedimentation and the rediffusion rate. Optical techniques are used to follow the movements of the boundary; they depend on the fact that a ray of light, passing through a medium of varying refractive index, is bent most sharply in the region where the refractive-index gradient is largest. Thus the concentration gradient inside the cell can be correlated with refractive-index measurements.

The essential parts of an ultracentrifuge used for sedimentation-rate determinations are a high-speed drive, a stroboscopic apparatus for viewing the centrifuge cell, and an optical system with a photographic device for recording concentration in the moving cell. The driving mechanism is either a direct drive geared to a high-speed motor or a gas-driven system depending on the impact of a jet of air (or hydrogen) impinging on a turbine attached to the rotating system.

Equation (15) relates the molecular weight to the *rates* of both sedimentation and diffusion. It is therefore necessary to carry out independent diffusion measurements on the same polymer-solvent system for which sedimentation rates are measured in the ultracentrifuge. There is, however, another method of molecular-weight determination by ultracentrifuge which does not require any complementary diffusion measurements. It is based on the observation of the *time* necessary to establish equilibrium between sedimentation and rediffusion of the polymer in the cell in a centrifugal field. The equilibrium ultracentrifuge is operated at an intermediate speed, and the polymer settles slowly in the centrifuge cell until the gradient of concentration is such that the rate of back diffusion exactly balances the rate of settling. When this state is attained, the distribution of the polymer in the cell no longer changes with time. Equation (11) may be applied to this case, and when rewritten in terms of properties per mole it becomes

$$\frac{dx}{dt} = \frac{M}{f_M}\left(1 - \frac{\rho_s}{\rho_p}\right)\omega^2 x = \frac{M}{f_M}(1 - \bar{V}\rho)\omega^2 x \tag{16}$$

where f_M is the molar friction constant, $\bar{V}$ the partial specific volume of the polymer, and ρ the density of the solution, which is equal to the density of the solvent ρ_s within a fraction of a per cent since the solutions in this case are quite dilute.

The quantity of solute crossing a unit area in time dt in the centrifugal field is given by

$$dm_s = c\,dx = \frac{Mc}{f_M}(1 - \bar{V}\rho)\omega^2 x\,dt \tag{17}$$

The quantity of solute which crosses a unit area in a unit time because of back diffusion is given by

$$dm_D = D\frac{\delta c}{\delta x}\,dt \tag{18}$$

At equilibrium, $dm_D + dm_s = 0$, and consequently

$$\frac{Mc(1 - \bar{V}\rho)\omega^2 x}{f_M} = -D\frac{\delta c}{\delta x} = \frac{RT}{f_M}\frac{dc}{dx} \tag{19}$$

Integrating between points x_1 and x_2 and rewriting the result to obtain an expression for M, the following equation is arrived at:

$$M = \frac{2RT\ln(c_2/c_1)}{(1 - \bar{V}\rho)\omega^2(x_2^2 - x_1^2)} \tag{20}$$

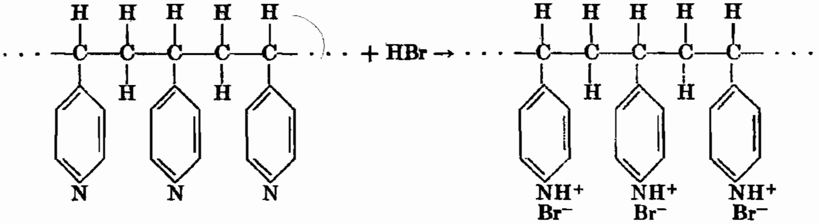
This equation is valid at infinite dilution, but at finite concentrations c_2 and c_1 must be replaced by their respective activities. Note that points x_1 and x_2 may be any two points in the cell, and consequently molecular weights may be calculated by using the values of c at different points along the cell. This is potentially very useful for a polydisperse system. The equilibrium position of a species of one molecular weight is different from the position of another molecular-weight specimen. Using the above equation it becomes possible, in principle at least, to determine the molecular weight all along the cell, and a molecular-weight distribution of the polymer may be computed.

One of the problems which arises when the equilibrium centrifuge is used for molecular-weight determinations is that the rate of approach to equilibrium is very slow. A single run may take several weeks or longer before equilibrium is reached, and this is an important impediment to the use of this method.

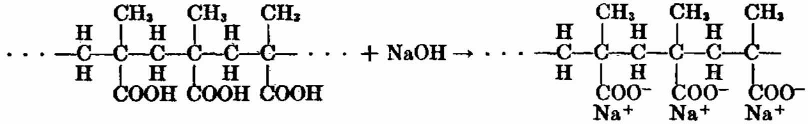
VI. POLYELECTROLYTES

The polymers that have been mentioned so far consist of electrically neutral molecules in which the atoms are joined by covalent bonds. There exists, though, among them a group of polymers which ionize in certain environments (aqueous, as a rule) and therefore are called polyelectrolytes. They may occur in nature, for example, proteins are anionic at high pH and cationic at low pH; however, they also may be prepared synthetically.

Synthetic polyelectrolytes may be either cationic or anionic; for instance, polyvinyl pyridine forms polymeric cations in aqueous acid solution as shown below



while polymethacrylic acid forms polymeric anions in alkaline solution



When polyelectrolytes are dissolved in a solvent in which they do not ionize, they exhibit the same general solution behavior that is characteristic of nonionic polymers. This is not so if a polyelectrolyte is dissolved in an ionizing solvent; then, very substantial changes may be noted.

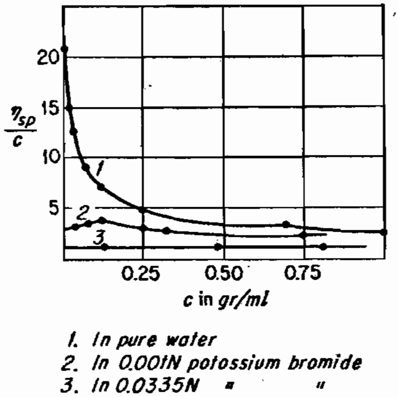


FIG. 15-14. Viscosity-concentration plot of a polyvinyl pyridinium bromide. [*Fuoss and Strauss, J. Polymer Sci.*, 3, 246 (1948).]

Suppose that solutions of the sodium salt of polymethacrylic acid in water are prepared at several dilutions. In the concentrated range (0.2 or 0.3 per cent), a number of the sodium ions are bound or are in immediate proximity to the polymeric ion. Consequently, the polymer is essentially uncharged and interacts with the neighboring molecules in a manner that is not too different from a similar uncharged polymer. In a more dilute solution, let us say 0.02 per cent, the sodium ions are on the average farther from the ionized polymer than in the more concentrated solution. Thus the negative charges on the polymer molecule itself may repel each other, causing the flexible polymer chain to uncoil, until at very high dilution it even may reach its maximum length. The change in configuration of the chain greatly influences the viscosity of the solution; the specific viscosity increases as a function of decreasing concentration, as shown in Fig. 15-14. In the presence of other electrolytes, the ionization of the polymer is suppressed and the viscosity/concentration graph appears to be more nearly like that of a solution of uncharged polymer.

Polyelectrolyte molecules in highly dilute aqueous solutions exert strong electrical repulsions on each other. These repulsive forces are long range (proportional to $1/r^2$) by comparison with normal dispersion forces (proportional to $1/r^6$), and as a consequence the intermolecular interactions persist down to the lowest measured concentrations. In osmotic-pressure measurements on polyelectrolytes, the Donnan[1] membrane equilibrium must be satisfied and experimental results indicate that the second virial coefficient in the osmotic-pressure equation (p. 915) becomes very large.

While in this brief section reference has been made only to viscosity and osmotic-pressure properties of polyelectrolytes, the difference between them and uncharged polymers persists in all dilute solution measurements. The characteristic effect is that in the absence of foreign salts in the polyelectrolyte system the behavior in dilute solutions is governed by the very long-range molecular interaction forces.

VII. POLYMERS IN THE SOLID STATE

Glass-Rubber Transition

A study of the solid state behavior of polymeric systems is important because of the engineering applications of polymeric materials. These applications stem from their physical properties in the solid phase, which in turn are a natural consequence of the unique molecular structure of polymer molecules.

The melting point of a pure crystalline solid is sharp, the solid being transformed into a liquid as the temperature changes by 0.01°C or less. Amorphous polymers act quite differently: in the solid state they have the structure of a super-cooled liquid, like glass; on heating they change not to a liquid, but to a rubbery type of material, flexible, elastic, and still a solid. As the temperature is further increased by 20–100°C, the rubbery solid will melt to a true liquid. This liquid is usually very viscous, it may exceed the viscosity of the usual type of organic liquid by an order of 10^7 times. Melting, of course, occurs only if the polymer is not cross-linked; the polymerization of polyfunctional monomers yields three-dimensional cross-linked polymers of infinite molecular weight which exhibit the glass-rubber transition but do not melt.

The glass-rubber-liquid transitions bear a direct relationship to the molecular structure of the polymer itself. In the glassy state the kinetic energy of the individual segments of the coiled and intertwined polymer chain is not sufficient to permit a specific segment to escape from the

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[1] Donnan and Guggenheim, *Z. physik. Chem.*, **A162**, 346 (1932).

cage of its immediate neighbors. The segments are essentially fixed in space with respect to each other, and the bulk material behaves as a solid.

As the temperature is raised, the kinetic energy of the segments increases. The rubbery state is achieved when local mobility of individual segments and groups of segments becomes considerable, even though the total long-chain molecule may not yet possess enough energy to move as an entire unit with respect to the neighboring molecules.

The elastic deformation characteristics of rubber are such that it is possible to stretch a sample to five or ten times the original length without rupture. This stretching is accompanied by uncoiling of the polymeric chains which become more or less aligned in the stretched state. It requires force to produce this stretching effect because the coiled-chain configuration is more probable than the stretched chain and, consequently, is thermodynamically favored. In the cases where the coiled configuration has a much lower free energy than the stretched polymer the rubber is stiff and a relatively large force must be exerted in order to produce deformation. If this free-energy difference is less marked (this would depend on the particular chemical nature of the polymers in question), then the polymer is soft and easy to stretch in the rubbery state. A striking proof of the alignment of polymer chains in the stretched state is shown in the x-ray diffraction diagrams of stretched and unstretched rubbers (Fig. 15-15). The broad halos in the picture of the unstretched rubber demonstrate that in this state the rubber is a liquidlike material as far as molecular arrangement is concerned. The sharpening of the lines in the diagram of the stretched material shows that molecular arrangement is more nearly crystallike in that the chains are regularly arranged parallel to the axis of stretching.

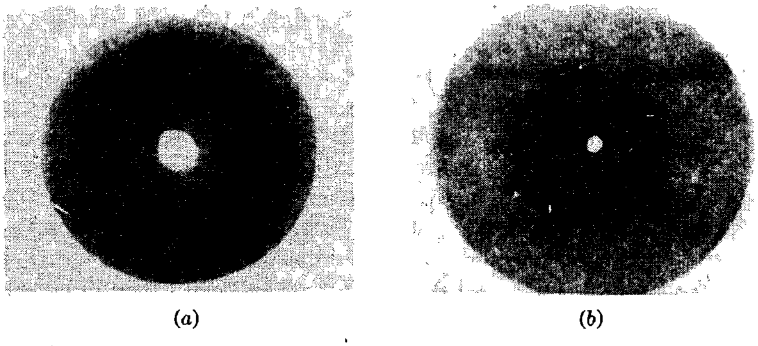
(a) (b)

FIG. 15-15. X-ray pattern of (a) unstretched and (b) stretched rubber.

There is a definite difference in elastic behavior between linear and cross-linked rubbers. A sample of a cross-linked, or vulcanized, rubber is deformed on stretching and returns to its initial shape and length when the force is released. No flow or permanent deformation takes place, since the cross-links between the individual polymer molecules are primary chemical bonds of high stability. In a linear rubber the intermolecular forces are weak—are in the nature of secondary bonds such as Van der Waals forces and hydrogen bonds. Thus when external force is applied, the molecules can and do move with respect to each other, but for very high molecular materials this motion is very slow. Experimental results show that samples of linear rubbers do not return exactly to their original form after being stretched for a while but show a permanent though often small change in dimension. If the molecular weight is very high, say greater than 500,000, then the elastic properties may predominate, and the flow becomes negligible. For many applications where plastic flow must be completely avoided, cross-linked rubbers with primary chemical bonds holding the molecules together are a necessity.

Highly cross-linked polymers differ from slightly cross-linked ones in many respects. A very highly cross-linked polymer will never become rubbery because there is no possibility for the uncoiling of chains or even sections of a chain, if cross-link junctions of molecules occur too often; on the other hand a small amount of cross-linking yields a flexible rubber. Generally, the deformation that can be tolerated in any given type of rubber may be controlled by adjusting the amount of the cross-linking introduced.

Crystallinity and Orientation

Many polymeric materials tend to crystallize on solidification. They do not form perfect crystals, one reason being that they contain molecules of varying molecular weights. This is usually not the most important factor, the real difficulty is that, at the temperature at which crystallization would normally occur if true thermodynamic equilibrium were attainable, the mobility of the polymer molecules often is so low that the molecules will not crystallize in any reasonable time. However, the degree of crystallinity may be controlled to a certain extent by the rate of cooling, the slowly cooled polymers having a higher density than the rapidly cooled (quenched) materials at any given temperature. The higher density is due to the fact that the molecules in a crystalline array pack more tightly than in the amorphous state. After the cooling has proceeded somewhat beyond the glass transition temperature, changing the rate of cooling will no longer affect the density-temperature curve. This is so because the configuration of the polymer molecules is frozen in, and the molecules no longer can rearrange to a state of higher crystallinity.

The degree of crystallinity varies with the chemical structure of the polymer, as well as with the rate of cooling. Some of the polymers which crystallize relatively easily, for example, nylon 66 (poly-hexamethylenediamine adipate) can be stretched to form fibers of very high tensile strength. If these fibers are examined by x-ray methods, it is found that the amount of crystallinity has not changed appreciably on stretching, but that the crystalline regions are strongly oriented in the direction of the fiber axis. The properties of these oriented fibers differ considerably from unoriented polymers, which are usually much weaker and more brittle.

The crystallites contain groups of segments of chain molecules all fitted into a pattern of high local regularity. A single crystallite is made up of segments from many molecules, but a single molecule may be partly in crystalline and partially in amorphous regions. The segments of the molecular chains in oriented crystallites are aligned more or less along the direction of stretch. Figure 15-16 illustrates schematically the molecular arrangements in amorphous, crystalline, and oriented regions.

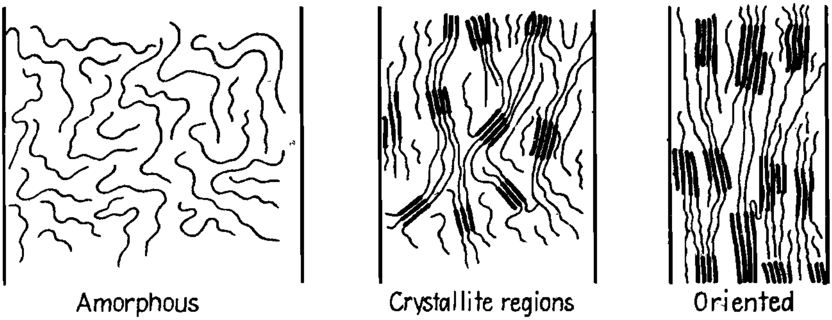

FIG. 15-16. Arrangements of polymer molecules with respect to each other.

A fiber will remain in the oriented state at room temperature indefinitely; however, if heated to an elevated temperature in the absence of an external stress, the fiber will revert to the essentially random arrangement of the unoriented crystalline polymer. The crystallites themselves are destroyed by melting.

Viscoelasticity

Samples of bulk polymers respond to applied stresses in several ways: some materials behave as elastic solids, some as viscous liquids, and still others exhibit viscous as well as elastic properties. The latter are called viscoelastic solids. If a constant force is applied to a viscoelastic sample, the extension of this solid may be divided into three parts: (1) an instantaneous elastic deformation, (2) a delayed elasticity or creep, and (3) a viscous flow. This may be seen best by referring to **Fig. 15-17** which illustrates an example of a tensile force F_0 applied at zero time, maintained until time $t = t_1$, and then removed. The graph contains a plot of extension versus time. The elastic extension of the sample is represented by the line OA in the figure, the extension along the curve AB represents a combination of viscous flow and creep, though by the time point B is reached the creep phenomenon is essentially complete. The line BC is linear in time and is a measure of the viscous displacement alone. At time t_1 the force is removed and the sample contracts elastically, whereby $OA = CD$. From D to E the sample slowly returns to its final length, which is h units greater than the initial length. The relative amounts of instantaneous elasticity, creep, and flow can be obtained from such a curve and may vary considerably from one material to another. For many materials, $h = 0$ which means that no permanent flow takes place.

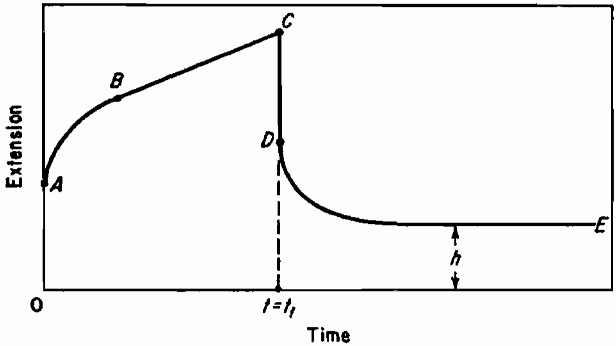

FIG. 15-17. Effect of force on viscoelastic solids: a typical creep curve; at $t = t_1$, force is removed.

While creep experiments of the type described above are often employed in the analysis of mechanical properties, they are not the only ones used for that purpose. Two other important techniques are the stress-relaxation method and the measurement of dynamic properties.

A stress-relaxation experiment is carried out by stretching the sample to some definite length at zero time and by measuring the force necessary to maintain that length as a function of time. The stress-relaxation measurements tend to yield the same sort of information that is obtained in creep experiments, but the results can be expressed in different ways. It is also possible, in principle, to calculate the stress-relaxation data from creep measurements, but this is rather complicated and not often done.

Dynamic measurements of viscoelastic behavior are based on a different conception. The nature of a stress-relaxation or a creep experiment is such that no accurate measurements can be made for times less than 1 sec; in some cases 10 sec or more pass before the first measurement is made. Very often interesting phenomena of polymer viscoelasticity occur in a small fraction of one second and, consequently, cannot be measured with the techniques employed in static tests, i.e., creep and stress relaxation. If, however, a vibrating force of the form $F_0 = \sin \omega t$ is imposed on a viscoelastic system, where ω is a number of the order of 100 per second, then the viscous and elastic contributions may be measured as a function of frequency.

A flexible polymer molecule exhibits many modes of motion, and the chain configuration of the molecules requires that this motion be cooperative in the sense that the oscillation of any particular group of segments drags along the other attached sections of the molecule. In solid polymers this cooperative behavior extends to intermolecular interaction, since segments of one molecule are bound to another either through small crystalline regions or by knotlike entanglements between the long wormlike chains. Consistent with the constraints imposed, small and large groups of segments or entire molecules and groups of molecules will tend to move in the periodic force field. Small sections of low inertia are able to remain in phase with a rapidly oscillating force field and will follow all but the highest-frequency stresses. On the other hand, relatively large and heavy molecular groupings will oscillate only at very low frequencies. By observing the frequency dependence of the viscosity and elastic coefficients, the relative importance of the mobility of small and large molecular sections in the particular material that is under investigation can be determined.

Melt Viscosity and Flow

A simple picture of liquid flow of plain fluids has been developed by Eyring,[1] using a free volume model and the theory of absolute reaction rates. Eyring's conception forms also the basis for some studies of liquid polymer flow, and a qualitative description of the ideas involved will be given in the following paragraph.

The structure of a low-molecular liquid is similar to that of a solid in that atoms and molecules are arranged in a regular array. But while the exact order of the molecules in a crystalline solid is sustained over a distance of several thousand units, this is not so in a liquid where the latticelike arrangement is disturbed more frequently and tends to persist only for 10–50 molecules in a row. These deviations in regularity in the liquid result in free space which is distributed between the molecules. In a normal nonpolar liquid, this free space is about 10 per cent of the volume occupied by the solid at atmospheric pressure at the melting point.

Consider a single molecule *A* in a liquid surrounded by neighboring molecules of the same structure. These molecules form a cage through which molecule *A* cannot easily pass. In order to gain passage, molecule *A* must

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[1] Eyring in Laidler, "Chemical Kinetics," McGraw-Hill Book Company, Inc., New York, 1950.

obtain sufficient translational energy to push the surrounding molecules apart, and there also must be some free space available in the direction in which the translation takes place. In the absence of external forces, this sort of process would lead to a diffusion of molecule A from its original position. If, however, a shearing stress is applied, a strong bias is imposed which tends to favor the motion in one direction. If the caged molecule A has enough translational energy and some free volume in which to move, than flow takes place. If there is insufficient translational energy (low temperature) or very little space between the molecules (at high pressure), little flow takes place and the viscosity coefficient is high.

The above picture is suitable for nonpolar molecules of roughly spherical shape. An attempt to apply this sort of model to a linear polymer chain requires certain obvious modifications. A simple way of doing this is to treat the polymer molecule as a string of beads, each bead representing a monomer unit. In order for a given bead to move relative to its neighbors, it must have the necessary energy and also the space required for the movement. In addition, the motion must be consistent with the configurational constraints which the other connecting beads in the chain impose. The possibility of motion of a monomer segment when it is part of a polymer chain, as compared to the motion of an unconnected, i.e., unpolymerized monomer (a single bead), is clearly very small indeed and accounts in a rough way for the relatively high viscosity of polymeric liquids. There is still another factor which may further impede the flow of polymers, namely, the temporary existence of microcrystallites and of knotted molecule configurations in the liquid. They may form network structures and thus further constrain the polymer chains from moving relative to one another.

The necessity for cooperative motion of an entire polymer chain when a single segment makes a jump from one position to another is an indication that the bulk viscosity of polymers is dependent on their molecular weight. This dependence has been investigated by Flory,[1] who found that the viscosity of linear polyesters and other condensation polymers fits the equation

$$\ln \eta = A + BM_w^{1/2}$$

quite closely, but this relation is not valid for all linear polymer systems.

It is clear that a controlling factor in the flow of a bulk polymer is the mobility of the individual segment, or in other words the effectiveness of the constraints imposed on its motion by the neighboring segments on the chain. In an investigation of this effect, one must take into account the manner in which the separation of segments on a chain affects the ease with which a given segment may move. For instance, a jump of a segment from its position in the liquid cage will not occur very easily if another one on the same chain, which is only five or six segments away, is fixed in space.

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[1] Flory, "Principles of Polymer Chemistry," p. 309, Cornell University Press, Ithaca, New York, 1953.

However, a fixed segment on the same chain which is 100 or 150 units apart from the first does not easily impede its motion since there are many configurational adjustments of the polymer chain which are consistent with the motion of segment 1 while keeping segment 150 fixed. Recently, Bueche[1] was able to calculate the viscosities of liquid polymers, using a model which takes the cooperative nature of the segments of the polymer molecule into account. He finds that this may be done by considering the motion of a single polymer molecule in a continuous medium. The difference between this calculation and that for dilute solution viscosities depends on a function constant which is a measure of the drag on the polymer in a shearing field. This constant is clearly dependent on molecular weight because it depends on the number of entanglements between the reference molecule and the surrounding material. The detailed argument leads to theoretical equations which are in general agreement with experimental findings, particularly in the high-molecular-weight range. In brief, Bueche finds that the melt viscosity of polymers at a low rate of shear should be proportional to the 2.5 power of the molecular weight for values of 100,000 and higher.

Ultimate Strength

The theoretical and experimental developments which have been successful in elucidating the physics and chemistry of polymeric systems have not, in general, led to useful results in learning about ultimate properties. For instance, the actually measured breaking strength of polymeric materials (and others as well) is far less than is calculated from bond energies. It is in the very nature of a destructive process that a discontinuity exists in the physical parameter at the breaking point. Consequently, the formulation of the problem in precise terms is difficult to achieve.

If a sample of material is torn or broken, the break occurs in the weakest region of the sample. This means that the test of strength is not a measure of cohesion of the bulk material but rather a measure of cohesion in an area where defects in structure or stress concentration are at a maximum. In principle, this aspect of the problem might be overcome if the samples were chosen smaller and smaller so that no defects are present, but unfortunately the defects are microscopic and in general occur frequently at points which, though widely separated in terms of atomic dimensions, are close together in macroscopic samples.

It is clear that the destruction of samples must be associated with weak regions in the material. Since ultimate properties are in part a measure of the weakest points of the sample, it is not surprising that there is a wide divergence in experimental data. It is characteristic that nondestructive

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[1] Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).

measurements of physical and mechanical properties of polymers such as elastic modulus or dielectric strength do yield reproducible data, while destructive measurements give rather widely varying results.

VIII. CHARACTERIZATION OF POLYMERS

To characterize a given polymer sample it is necessary first to describe properly the molecules themselves and then to devise a series of special tests by which this sample can be compared with other polymeric and nonpolymeric materials. Data on molecular characteristics, together with a knowledge of the structure of a polymer chain, make it possible to understand and, in some cases, even to predict to a certain degree its mechanical, optical, and electrical properties.

Molecular-weight Averages

A high-polymeric material must be visualized as a more or less heterogeneous mixture of long-chain molecules of the same chemical composition but of varying chain length. The molecular weight of a high polymer can, therefore, be given only as an *average* molecular weight taken over the whole range of molecular species present. This premise, then, raises two questions: (1) What does the *average* molecular weight of a high polymer signify, and how can it be determined? (2) Can an expression be found which describes mathematically or graphically the distribution of the varying molecular-weight species in the polymer sample? Can a distribution curve be drawn for individual polymers?

It must be pointed out immediately that there exist various types of molecular-weight averages. The two most important ones are the *number-average molecular weight,* which is the average taken over the number of polymer molecules present, and the *weight-average molecular weight,* which is the average taken over the weight of these molecules. The z and $z + n$ *averages* indicate more complicated relationships in which the influence of larger molecules is emphasized, and the *viscosity average* is a relative figure which depends on the determination of certain constants by absolute methods.

1. The *number-average molecular weight* $\overline{M}_n$ and *number-average degree of polymerization* $\overline{DP}_n$ are defined by the equations

$$\overline{M}_n = \frac{\Sigma n_i M_i}{\Sigma n_i} \tag{1}$$

$$\overline{DP}_n = \frac{\Sigma n_i DP_i}{\Sigma n_i} \tag{2}$$

where n_i is the number of molecules belonging to any of the species and $\overline{M}_i$ and $\overline{DP}_i$ are the corresponding molecular weights and degrees of polymerization. These number averages can be determined by osmotic measurements or by the analytical determination of end groups.

2. The *weight-average molecular weight* $\overline{M}_w$ and *weight-average degree of polymerization* $\overline{DP}_w$ are defined by the relations

$$\overline{M}_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} \tag{3}$$

$$\overline{DP}_w = \frac{\Sigma n_i DP_i^2}{\Sigma n_i DP_i} \tag{4}$$

They can be determined (*a*) by light-scattering measurements,[1] (*b*) under certain conditions by viscosity measurements,[2] and (*c*) by sedimentation and diffusion measurements. The last methods, however, lead also to more complicated averages.[3]

To illustrate the difference between the two most important molecular-weight averages, consider a hypothetical polymer containing 10 molecules of molecular weight 1,000 and 1 molecule of molecular weight 10,000. The number-average molecular weight would be

$$M_n = \frac{10 \times 1{,}000 + 1 \times 10{,}000}{10 + 1} = 1818.18$$

The weight-average molecular weight for this system is

$$M_w = \frac{10 \times 1{,}000^2 + 1 \times 10{,}000^2}{10 \times 1{,}000 + 1 \times 10{,}000} = 5{,}500$$

The more homogeneous a polymer sample is with respect to the molecular weight of its species, the closer will be the values for its weight and number averages; in a very homogeneous sample, they coincide. In natural and commercial synthetic high polymers, with the exception of certain proteins, the ratio between the weight and number average is 1.5 or larger, and the z averages are about 3.0 or more times larger than the number averages.

3. The so-called *z-average molecular weight* $\overline{M}_z$ and *Z-average degree of polymerization* $\overline{DP}_z$ which are given by

$$\overline{M}_z = \frac{\Sigma n_i M_i^3}{\Sigma n_i M_i^2} \tag{5}$$

$$\overline{DP}_z = \frac{\Sigma n_i DP_i^3}{\Sigma n_i DP_i^2} \tag{6}$$

can be determined by sedimentation equilibrium measurements.

4. The *viscosity-average molecular weight.* In many laboratories and in industry the intrinsic viscosity $[\eta]$ of a polymer is used for the determination

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[1] DOTY, ZIMM, and MARK, *J. Chem. Phys.*, **13**, 159 (1945).

[2] HUGGINS, in OTT, "Cellulose and Cellulose Derivatives," High Polymer Series, vol. V, p. 943, Interscience Publishers, Inc., New York, 1943; PFEIFFER and OSBORN, in OTT, *op. cit.*, p. 956.

[3] KRAEMER and NICHOLS, in SVEDBERG and PEDERSON, "The Ultracentrifuge," p. 418, Oxford University Press, New York, 1940.

of molecular weight because the procedure is quicker and requires simpler equipment than the absolute methods such as osmotic pressure, light scattering, and diffusion-sedimentation. The intrinsic viscosity is a measure of molecular weight because the equation $[\eta] = KM^a$ is valid for a wide class of systems. K and a are constants for a given polymer-solvent combination at a specific temperature and are determined by calibration with one of the above absolute methods.

There are certain problems which come up at this point because ordinary polymer samples are polydisperse, that is, they contain molecules which vary widely in molecular weight. Consider a situation where K and a are determined by an absolute method using polydisperse samples. The relationship $[\eta] = KM^a$ will yield a molecular weight characteristic of the calibrating method, i.e., if osmotic pressure is used for calibration, then the number average M_n is obtained; light-scattering calibration will give a weight average M_w. However, if the molecular-weight distribution of an unknown sample differs from that of the samples used in calibration, the intrinsic viscosity yields only an apparent molecular weight, as K and a are based on the distribution characteristics of the calibrating samples. Since, in general, the molecular-weight distribution of polymers differs one from another, depending on the details of the polymerization procedure, the intrinsic viscosity as a tool for valid molecular-weight determination is of limited value if used as indicated above.

However, there is a way of using the intrinsic viscosity–molecular weight relationship which is of more general applicability. This depends on the determination of K and a with carefully fractionated (monodisperse or nearly monodisperse) polymer samples. Under these conditions, the number-average molecular weight is almost equal to the weight average, and all methods of molecular-weight measurement are equally useful for this determination. The intrinsic viscosity $[\eta]$ is then a valid parameter for monodisperse samples. It may also be used for the same polymer of any degree of polydispersity, as is evidenced by the following reasoning. The viscosity of a polymer solution can be expressed as a power series in concentration

$$\eta = \eta_0[1 + [\eta]c + ac^2 + bc^3 + \cdots] \tag{7}$$

where a and b are constants which will not be discussed further here. This equation may be rewritten

$$\frac{\eta - \eta_0}{\eta_0} = \eta_{sp} = [\eta]c + ac^2 + bc^3 + \cdots \tag{8}$$

where the specific viscosity η_{sp} is defined by the above relation. Assuming this relationship as valid for a component of the polymer sample of molecular weight M_i, then Eq. (8) becomes

$$\eta_{sp_i} = [\eta]_i c + ac^2 + bc^3 + \cdots \tag{9}$$

If the solution is sufficiently dilute, the terms following the first on the right-hand side of Eq. (9) may be neglected, and

$$\eta_{sp_i} = [\eta]_i c \tag{10}$$

The specific viscosity of the polymer solution containing molecules which vary in molecular weight is obtained by summing this over all molecular weights M_i. Therefore

$$\eta_{sp} = \sum_i [\eta]_i c_i = \sum_i K M_i^a c_i \tag{11}$$

Since the total concentration c is $\Sigma\, c_i$, one obtains

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{\sum_i K M_i^a c_i}{\sum_i c_i} \tag{12}$$

If a viscosity-average molecular weight is defined by

$$M_v = \frac{\left(\sum_i c_i M_i^a\right)^{1/a}}{\Sigma c_i} \tag{13}$$

then Eq. 12 becomes

$$[\eta] = K M_v^a \tag{14}$$

This relationship then is correct for any polydisperse polymer-solvent system for which K and a constants have been determined on sharp fractions.

As a rule, the experimental values of a lie between 0.5 and 1.0. If a were equal to 1, the viscosity-average molecular weight becomes equal to the weight average. If a is less than 1, M_v is somewhat less than M_w but greater than M_n.

Distribution Curve

Distribution curves indicating graphically the variation of molecular weight throughout a polymer sample give a more complete characterization of the polymer than do average molecular-weight values. Attempts have been made to arrive at such distribution functions directly by ultracentrifugation,[1] light scattering,[2] or by a turbidimetric titration method,[3] which has been used successfully in some cases. The most successful, though time-consuming and tedious method, is to subdivide the polymer sample into a sufficiently large number of sharp fractions. The molecules in each fraction should have almost similar molecular weights. By calcu-

[1] Kraemer and Nichols in Svedberg and Pederson, "The Ultracentrifuge," p. 418, Oxford University Press, New York, 1940.

[2] Zimm and Doty, *J. Chem. Phys.*, **12**, 203 (1944).

[3] Morey and Tamblyn, *J. Appl. Phys.*, **16**, 419 (1945).

lating the proportion of the weight of each of these fractions to the total weight of the polymer and plotting the values obtained versus the actually determined average molecular weight of the respective fractions, a step curve can be prepared which then can be interpolated by a continuous curve. The accuracy of this interpolation obviously depends upon the number of experimental fractions available for the construction of the step curve. By graphical differentiation of this integral distribution curve, differential distribution curves (Fig. 15-18) are obtained which offer a highly descriptive picture of the relative frequency of the various molecular-weight species in the polymer. Such distribution curves have received considerable attention in industry because they allow a rigorous standardization of polymers and permit the discovery of aberrations and changes during the large-scale production of polymers. As an example, the degradation of cellulose may be cited as it occurs during the various pulping processes. Since the properties of the pulped cellulose are strongly dependent on the proportion of low-molecular fractions to medium- and high-molecular ones, the pulping processes must be thoroughly controlled by distribution-curve analysis.

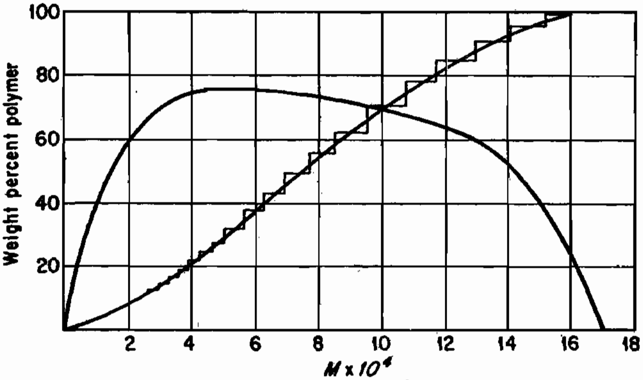


FIG. 15-18. Molecular-weight distribution for thermally polymerized polystyrene as established by fractionation. Differential and integral distribution curves. [*Mertz and Raetz, J. Polymer Sci.*, **5**, 587 (1950).]

Actual fractionation can be carried out by various methods; one involves a fractional precipitation by gradual addition of a precipitant to a solution of the polymer. Others use a decrease in temperature or the evaporation of one solvent out of a mixture to achieve a gradual precipitation of polymer. The molecular weight of the fraction can be determined by either one of the absolute methods, and if the fractions are sufficiently sharp there will be only a minor difference in the values of the weight and number averages.

Structure of the Polymer Chain

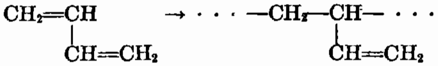
With the aid of chemical and physical methods it has been shown that in most cases monomers of the vinyl type enter a growing chain preferentially in the head-to-tail position. This had been found to be true also in copolymerizations of two or more different monomers.

$$\cdots -CH_2-CHX-CH_2-CHY- \cdots$$

Dienes influence the chemical structure of a polymer molecule, since they may enter the chain either in a 1,4 position

$$CH_2{=}CH-CH{=}CH_2 \rightarrow \cdots -CH_2-CH{=}CH-CH_2- \cdots$$

or in a 1,2 position



$$\underset{\displaystyle |\atop CH{=}CH_2}{CH_2{=}CH} \rightarrow \cdots -CH_2-\underset{\displaystyle |\atop CH{=}CH_2}{CH}- \cdots$$

The amount of 1,2 addition can be determined by ozonolysis of the residual double bond, leading to the formation of formaldehyde, which can be accounted for by oxidation to formic acid and titration of the latter.

The use of x-ray and electron diffraction has contributed considerably to our knowledge of the fine-structure of many polymers. The interpretation of diffraction diagrams of various polymers allows the drawing of certain conclusions as to the geometrical structure of the chain and the probable positions of substituting atoms in respect to the main carbon-carbon chain. Thus it has been established that polyethylene chains inside crystalline regions have a regular zigzag structure and that the C atoms all lie in one plane (Fig. 15-19). Other examples of successful interpretation of x-ray diagrams are polyvinyl alcohol and various vinyl derivatives containing halogen. The position of the OH groups and of the halogen atoms with respect to each other and to the carbon atoms of the main chain can be fixed on the basis of the x-ray analysis, and a spatial model of the polymer can be constructed.

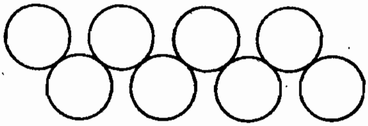


FIG. 15-19. Scheme of a polyethylene chain; zigzag configuration in one plane.

X-ray and electron-diffraction studies of proteins have shown that these polymers in their crystalline state often have a spatial configuration resembling a helix. A similar helical structure was proposed in recent investigations of highly crystalline isotactic polymers prepared with stereospecific initiator systems.

Technical Tests

Besides characterizing a high-polymeric material by a description of its molecules and its molecular arrangement, the material itself can be subjected to a variety of *mechanical, thermal, permanence, optical,* and *electrical* tests. Since the choice of a polymer for any specific application is largely based on its particular properties, the trade in conjunction with the ASTM have established standards by which polymers can be compared with one another and with other working materials. The most important among them are

Thermal and Chemical Tests. Solubility in various solvents, water absorption, softening range, cold flow.

Permanence Tests. Corrosion resistance, weather resistance, oil resistance, resistance to chemical agents, heat and light degradation, aging.

Mechanical Tests. Impact strength, tensile strength, elongation and hysteresis, creep and recovery, flexibility and foldability, mold shrinkage, heat distortion.

Optical Tests. Refractive index, light transmission, color range, scattering, light fastness.

Electrical Tests. Dielectric constant, dielectric strength, volume resistivity, power loss, power factor.

A number of specific tests have been devised for the application of polymers for special purposes, such as damping tests for frequency modulations of short or long waves, or scratch resistance on protective coatings, etc.

IX. INFLUENCE OF MOLECULAR CHARACTERISTICS ON POLYMER PROPERTIES

The chemical nature of the monomer, the average molecular weight, the distribution function, and the linear or tridimensional character of the polymer molecule determine to a certain extent the thermal, mechanical, and chemical behavior of a given polymeric material. Polymers consisting of linear-chain molecules are always soluble and thermoplastic, even if the molecular weight is very high. Materials consisting of tridimensional polymer molecules are insoluble in any conventional type of solvent and are thermosetting. Thus, thermoplastic or thermosetting behavior of a material is directly connected with the structural details of its molecules and often can be changed at will. Cross-linking agents can artificially create three-dimensional networks from straight chains and thereby convert a thermoplastic material into a thermosetting one. The

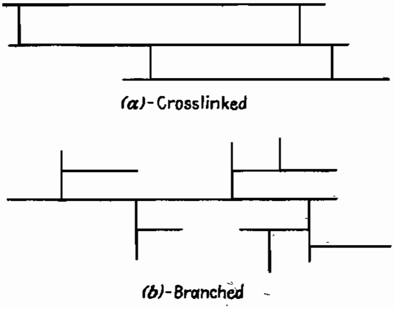


FIG. 15-20. Schematic representation of crosslinked and branched systems.

vulcanization of rubber is the most spectacular example of such a process. The change from a thermosetting to a thermoplastic polymer is performed by the opening of cross links and is, for instance, commercially carried out on a large scale in the reclaiming of rubber.

The solubility characteristics of a polymer are very sensitive to cross linking, even more so than the thermal behavior. Even slight cross linking (insufficient to cause infusibility) may render a polymer insoluble.

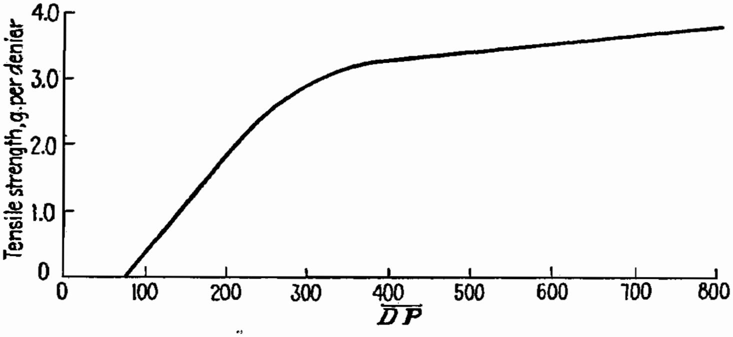


Fig. 15-21. Variation of tensile strength with increasing $\overline{DP}$ (cellulose acetate).

Less drastic is the influence of branching on the solubility of a polymer; it usually decreases the rate of solution but does not make a material completely insoluble. However, the behavior of a heavily branched polymer is similar to that of a slightly cross-linked one, and it is usually very difficult to distinguish between these two types.

The *number-average molecular weight* of a polymer affects very noticeably its mechanical properties. Impact strength, folding strength, and tensile strength are particularly adversely influenced by a low number-average molecular weight. These mechanical characteristics deteriorate almost completely at a polymerization degree of about 100 or below.

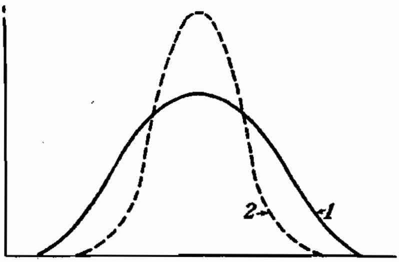


Fig. 15-22. Possible distribution curves of two polymers having similar average molecular weights.

Figure 15-21 presents a plot of tensile strength versus polymerization degree of cellulose acetate and shows that the tensile strength is practically zero until a degree of polymerization of approximately 50 has been reached. Thereafter, the tensile strength rises steadily until at about a polymerization degree of 700 the curve flattens out; still greater tensile strength can be achieved only by substantially higher molecular weights. A similar behavior has been observed for most linear polymers.

The distribution curve of a polymeric material also has a distinct influence on its mechanical properties. Curves 1 and 2 in Fig. 15-22 represent the distribution functions of two polymeric materials with the same average molecular weight. The product characterized by curve 1 contains a considerable portion of low-molecular-weight constituents which are detrimental to its mechanical properties. Its influence usually is not offset by the relatively large amount of higher-molecular-weight constituents, since, as indicated in Fig. 15-21, the contribution of these fractions to the tensile strength is relatively unimportant. Curve 2 shows the distribution curve of a more homogeneous polymer which has a higher impact, tensile, and folding strength because of the absence of appreciable amounts of low-molecular-weight fractions. In industrial practice, the lower fractions of a polymer are frequently removed by fractionation to improve the mechanical properties of the material.

X. INFLUENCE OF INTERMOLECULAR ARRANGEMENT ON POLYMER PROPERTIES

The properties and behavior of polymers is governed just as much by the arrangement of the molecules with respect to each other as by the characteristics of the individual molecules themselves. In a previous section it was stated that x-ray and electron-diffraction diagrams indicate that polymer molecules may be arranged (1) predominantly at random (amorphous state) or (2) predominantly in regions possessing a high degree of geometrical order (crystalline state) or (3) there are polymers where crystalline and amorphous regions coexist in appreciable amounts. It also has been pointed out before that highly crystalline polymers can be drawn and stretched, whereupon the crystallites may orient themselves in the direction of the applied force. Likewise, stretching of an amorphous polymer may result in the formation of crystalline regions in which the crystallites may or may not be oriented to a certain degree.

In general, typical rubbers exhibit an amorphous diagram in the relaxed state, whereas a typical fiber diagram shows a high degree of crystallinity. In between these two extremes there exists a large class of materials which has intermediate degrees of randomness and exhibits intermediate mechanical properties. Most of these so-called plastics behave mechanically as if they were a mixture of an elastic solid and a viscous liquid; they can be molded by heat and pressure and keep their new shape upon cooling.

The three forms, then, in which high polymers may appear—fibers, plastics, and rubbers—seem to be dependent upon the *internal arrangement* of the long-chain molecules, which in turn is caused by the shape and flexibility of the individual molecules and by the magnitude of the forces between them. If these forces are small, or if the molecules are bulky and fit badly into the regular pattern of a crystal lattice, then the random distribution prevails and the material shows rubbery characteristics. Strong forces between the individual chain molecules or molecular shapes that fit easily into a lattice are characteristic for a polymeric material of fibrous nature. Intermediate cases, finally, lead to typical plastics. The border lines between these three types of substances are often rather indistinct; one and the same polymer may be found in different forms, depending on pressure, temperature, and changes in its molecular arrangement due to mechanical influences. Thus, natural rubber has typical fiber properties if it is slowly cooled down in the highly stretched state. A typical plastic, such as polyvinyl chloride, can be made rubberlike by plasticization, and another one, polyvinylidene chloride, can be drawn out to a fiber. Industry uses the possibility of transition from one of the typical states into another to adjust a given polymer to special uses by establishing in it a proper balance of crystallized and amorphous domains.

CHAPTER 15

Part 2. Polymerization Practice

XI. INDUSTRIALLY IMPORTANT POLYMERIZATIONS AND POLYMERS

The following sections contain a description of industrial polymerization practices and the materials obtained from them. It should be noted that consideration is given only to those processes and products which are actually in practical use on an industrial and commercial scale. Many more products and processes are being investigated in the laboratories of scientific and industrial organizations or are being tested in pilot-plant operations. This rapid progress in polymer science and the accompanying constant change in industry have characterized the field of polimerization for the last decade.

PHENOLIC, UREA AND MELAMINE, AND ALKYD RESINS

By S. H. Rider[1]

Thermosetting resins are characterized by the fact that the chemical and physical changes that take place during "cure" are irreversible, the resin polymerizing into a three-dimensional network which is no longer soluble or fusible. In contrast to the thermpolastics, the manufacturer of thermosetting resins sells resins which are reactive intermediates to be carried to the final degree of cross-linking by the fabricator. These resins must satisfy three major use requirements:

As Sold. The resin must be in a form that is readily processed. A surface coating must be of the correct viscosity to blend and pigment. A molding powder must have the correct bulk and the proper particle size to fill the mold.

Processing. The rheological changes that take place during final processing must meet the requirements of the job. A surface coating must stay in place during baking and not sag or form an orange-peel surface. A molding powder must flow sufficiently to fill the mold, cure in an economical time, and be rigid enough at elevated temperature to be ejected from the mold.

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[1] Monsanto Chemical Co.

Final Properties. The finished article must have the desired properties. A surface coating must have the correct appearance and chemical resistance; a molded piece must have acceptable physical and electrical properties.

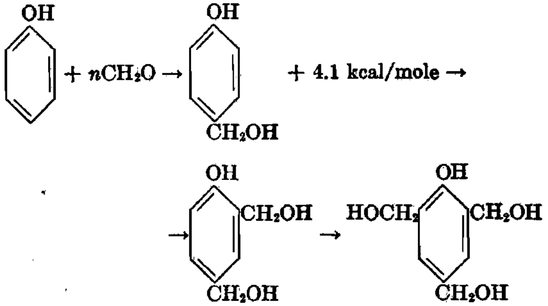
This change from a low-molecular-weight, easily processed material to a high-molecular-weight insoluble, infusible product during fabrication accounts for many of the major uses of this class of materials.

Phenolic Resins

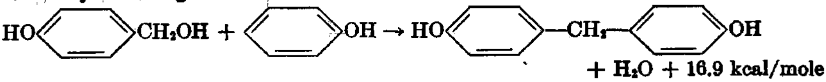
The phenolic resins represent one of the oldest and largest of the plastics family. The wide variety of physical forms and properties which may be obtained with these resins contributes to the development of a large number of end uses. Phenolics offer an excellent combination of low cost with good physical and electrical properties, fast cure, and good chemical resistance. Their main drawbacks are poor color and poor resistance to alkalies. The general manufacturing procedure is given in Fig. 15-23, showing the four main types of products and their major end uses.

The complex chemistry of phenolic resins is well described by Martin.[1] The general performance of phenolic resins, however, can be understood by a consideration of the three major reactions which phenol and formaldehyde undergo (reactions 1, 2, and 3). These reactions are varied to yield the desired end properties by controlling catalyst, mole ratio of reactants, degree of reaction, and type of phenol used. Since phenol has three highly reaction positions, these reactions can take place readily at the two ortho and the para positions. Formaldehyde is generally used as 37 per cent formalin.

1. **Hydroxymethylation:**



2. **Methylene bridge formation:**



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[1] Martin, "The Chemistry of Phenolic Resins," John Wiley & Sons, Inc., New York, 1956.

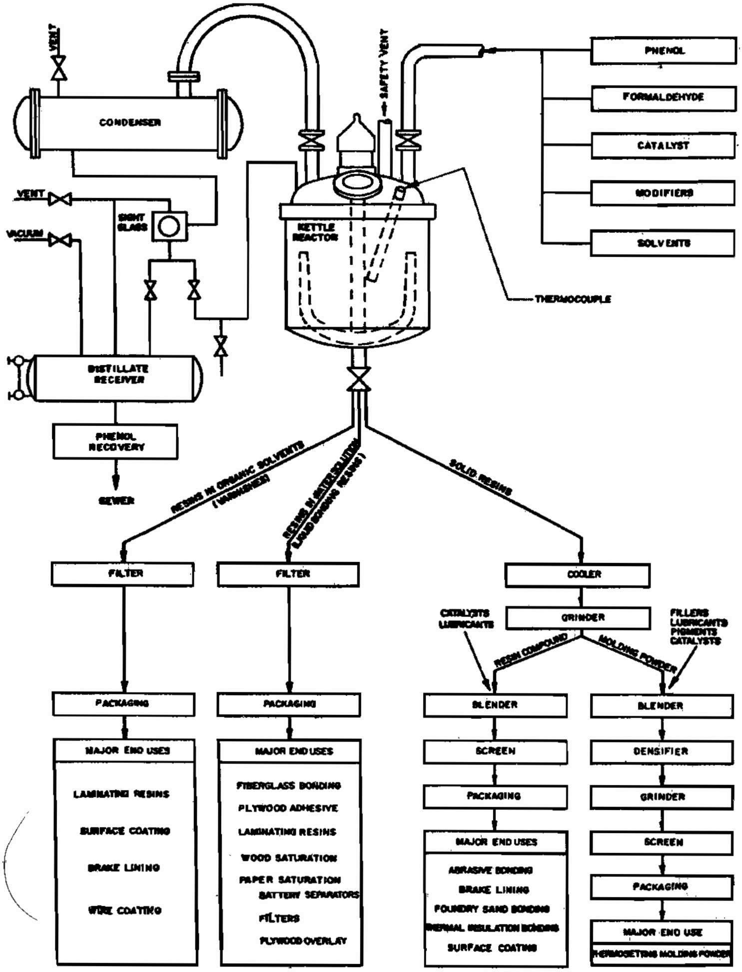
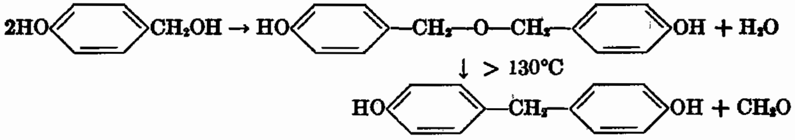


FIG. 15-23. Schematic representation of phenolic resin manufacture.

3. Ether formation:



Basic Catalyst. Under basic conditions, reaction 1 can be controlled to yield phenol alcohols (resoles). If sufficient formaldehyde is present, further heating will cause reactions 2 and 3 to progress until the resin is completely cross-linked to the insoluble, infusible state. The reaction can be halted at any point along this path if the temperature is reduced and, in some cases, if the basic catalyst is neutralized. Halting the reaction at the water-soluble point by neutralizing the catalyst produces the water-soluble bonding resins. If the reaction is carried to the water-insoluble point, the water is removed by dehydration, and by the addition of organic solvents varnishes are produced. When the water is removed and the reaction is carried to the point where the resin is brittle at room temperature, the "one-stage" solid resin results. This solid resin must be cooled rapidly to prevent further cross-linking to a gel state.

The study of the kinetics of the alkali-catalyzed reaction of phenol and formaldehyde is difficult because it represents a series of reactions as various methylolphenols are formed and react further with formaldehyde. Freeman and Lewis[1] have studied this reaction in great detail by the use of paper chromatography. However, where a more practical interest may be in the rate of addition of formaldehyde to phenol, the modified second-order rate constant developed by Debing, Murray, and Schatz[2] is of value. In this case the number of active positions was used rather than the molar concentration, phenol having three and formaldehyde, in the form of methylene glycol, having two. The rate constant was found to take the form

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - 2x)}{a(b - 2x)}$$

where x is the moles of formaldehyde consumed at time t, a the initial concentration of reactive positions for phenol, and b the initial concentration of reactive positions for formaldehyde. Using this relationship, rate constants were compared for major basic catalysts at a concentration of 0.05 mole per kg of reactants (Table 15-7).

TABLE 15-7. RATE CONSTANTS OF THE PHENOL-FORMALDEHYDE REACTION WITH BASIC CATALYSTS

Catalyst	$k \times 10^6$, *kg/mole sec*
Monoethylamine	5.0
Diethylamine	6.4
Triethylamine	17.6
Sodium hydroxide	19.4
Tetraethyl ammonium hydroxide	22.2

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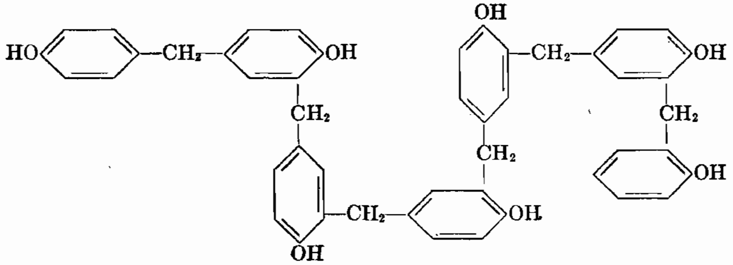
[1] FREEMAN and LEWIS, *J. Am. Chem. Soc.*, **76**, 2080–2087 (1954).

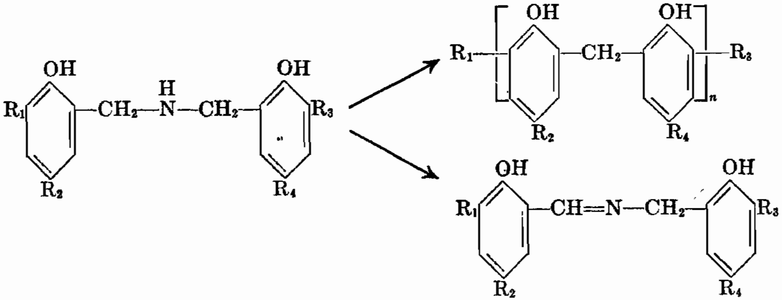
[2] DEBING, MURRAY, and SCHATZ, *Ind. Eng. Chem.*, **44**, 356–359 (1952)

Acid Catalyst. When phenol and formaldehyde are combined under the influence of a strong acid catalyst, reactions 1 and 2 proceed very rapidly with the evolution of heat to form novolacs.


Novolac Structure

The formaldehyde addition is rate controlling, with the reaction going rapidly and predominantly to the formation of methylene bridges. The formaldehyde addition rate is at a minimum at a pH of 4–5 and increases as the pH is either reduced or increased. The rate of formaldehyde consumption is dependent upon the pH and is relatively insensitive to the anion used.[1] Initially, the reaction is approximately second order. If sufficient formaldehyde is present, the resin gels; therefore under these conditions less than one mole of formaldehyde must be used per mole of phenol. The resulting product is a thermoplastic resin with a molecular weight dependent on the ratio of reactants.

This thermoplastic novolac resin requires cross-linking for cure. The most common cross-linking agent is hexamethylenetetramine. The initial reaction of "hexa" with novolacs appears to form bis and tris(hydroxybenzyl)amines. On further heating, these break down to yield methylene bridges and azomethine linkages.


Reaction of novolac with hexamethylenetetramine

Many substituted phenols may be used when special properties are needed. Mixed cresols are used extensively for electrical insulating ap-

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[1] Jones, *J. Soc. Chem. Ind.*, **65** (9), 264–275 (1946).

plications, *p*-tertiary butyl and *p*-phenyl phenol are used in surface coatings where good color and compatibility are required, and long-chain substituents are used when special compatibilities are required. The relative reactivities of various phenols to paraformaldehyde with an amine catalyst were studied by Sprung[1] (Table 15-8).

TABLE 15-8. RELATIVE REACTIVITIES OF SUBSTITUTED PHENOLS WITH FORMALDEHYDE USING AN AMINE CATALYST

Type phenol	*Relative reactivity*
3,5-Xylenol	7.75
m-Cresol	2.88
Phenol	1.00
3,4-Xylenol	0.83
2,5-Xylenol	0.71
p-Cresol	0.35
o-Cresol	0.26

Preparation of Resins. Paraformaldehyde may be used in place of formalin as a formaldehyde source. This reduces the processing time but makes control of the exothermic reaction more difficult. Furfural and acetaldehyde have also been used as the aldehydic component for special properties.

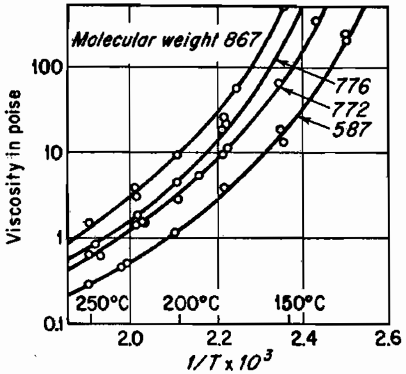

FIG. 15-24. Viscosity-temperature relationship for novolacs. [Jones, *J. Appl. Chem.*, **2**, 134–139 (1952).]

The reaction of phenol with formaldehyde is usually carried out in an autoclave. The major factors which must be considered in reactor design are heat load and agitation. Considerable heat is evolved in this condensation, and it must be dissipated either by heat transfer to the cooling water in the kettle jacket or by refluxing the water through a condenser. For water- and alcohol-soluble resins the viscosity in the autoclave seldom exceeds 20 poise; so a turbine agitator is satisfactory. For the solid resins, viscosities above 300 poise are not uncommon; thus close-fitting anchor-type agitators driven by powerful motors are necessary to get heat transfer during the dehydration step. Figure 15-24 shows the viscosity-temperature relationship for some novolacs.

The autoclave is usually constructed of stainless steel or Monel, depending on the service requirements. The vessel must be capable of operating under pressure up to 5–10 psi and down to 1 psi. The low pressures are

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[1] SPRUNG, *J. Am. Chem. Soc.*, **63**, 334 (1941).

required to facilitate the removal of water without reacting the resin excessively and to allow control of temperature by refluxing water.

Water-soluble phenolic resins are generally prepared by reacting 1.2–3.0 moles of formaldehyde per mole of phenol with an alkaline catalyst until essentially all the formaldehyde is reacted to form phenol alcohols. If the solution is to remain dilute, it may be sold in this form. If the solution is to be concentrated, the alkaline catalyst is neutralized to a pH of about 7 in order to reduce the rate of reaction at room temperature.

Varnishes are prepared by reacting 1.1–1.8 moles of formaldehyde per mole of phenol (cresols are often used for electrical and forming grade laminates) in the presence of a basic catalyst, much less catalyst being used than in the case of water-soluble resins. After reacting to a specified point, the water is removed by vacuum dehydration and a solvent is added to dissolve the resin.

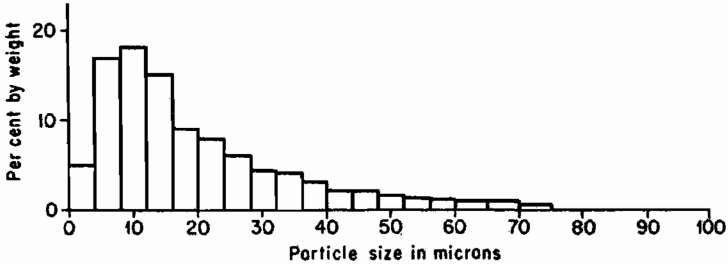


FIG. 15-25. Particle-size distribution for typical phenolic bonding resin: 99 per cent through No. 200 screen.

Novolac resins present the greatest heat-load problem so that great care is used during the heat-release period. An alternate method is to heat the phenol and catalyst, then add the formaldehyde slowly at a rate such that the heat evolved can readily be removed. When the formaldehyde is all reacted, the water is removed by vacuum dehydration and the resin dropped to the cooling surface.

The process for a "one-stage" resin is similar to the varnish except that at the end point the resin is dropped to the cooling surface.

Solid Resin Handling. When the molten resin is discharged from the autoclave at 100–150°C, it must be cooled rapidly, especially in the case of the "one-stage" resin, to prevent further reaction. Rapid cooling requires that thin layers be spread because the thermal conductivity is low; a typical novolac resin has a thermal conductivity of 0.13 Btu/(hr) (sq ft) (°F) and a specific heat of 0.33. Water- or air-cooled floors, trays in racks, and moving belts have been used to cool the resin.

For most uses the resin must be finely ground. The particle-size distribution as well as the average screen size is important. Figure 15-25 shows the particle-size distribution for a typical industrial bonding resin. Size reduction is accomplished in a number of ways, the use of ball mills, hammer mills, and roller mills being most common.

Molding Powder. A typical molding powder contains 45 parts powdered novolac resin, 5 parts hexamethylenetetramine, and 50 parts wood flour.

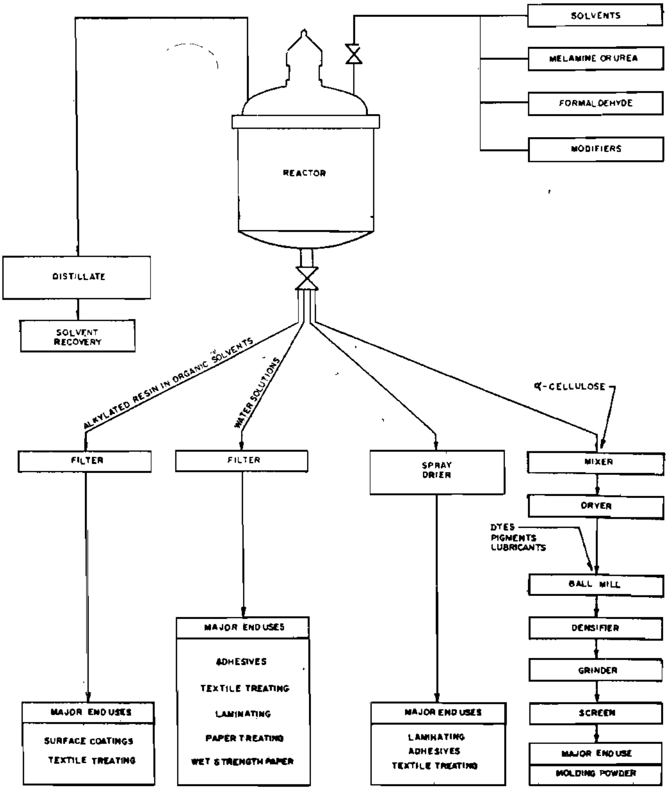


FIG. 15-26. Schematic representation of aminoplast resin manufacture.

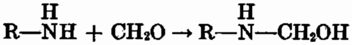
These ingredients are preblended with small quantities of pigments and lubricants, then fused together on hot differential mixing rolls. The densified material is removed from the rolls, cooled, and ground to the correct particle size and distribution.

Urea and Melamine Resins

The chemistry and end uses of urea and melamine resins are similar enough to be studied together. Urea resins are lower in cost, while melamine resins have superior water and heat resistance. Both resins have excellent color and color retention. These resins are manufactured as water solutions, solutions in organic solvents, spray-dried powders, and molding powders. Figure 15-26 shows a flow sheet of manufacture and the major end uses for which the resins are used.

The first step in the preparation of urea or melamine resins is the reaction with formaldehyde in aqueous solution to form methylol compounds.

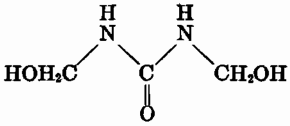
1. **Hydroxymethylation:**

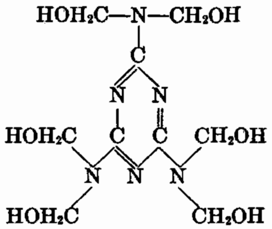


$$R{-}\overset{H}{N}H + CH_2O \rightarrow R{-}\overset{H}{N}{-}CH_2OH$$

(R is the remainder of a urea or melamine molecule in this and the following formulas.)

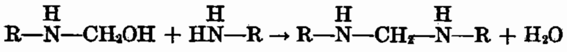
The reaction is carried out under slightly alkaline conditions and will yield crystalline derivatives of dimethylol urea or methylol melamines containing up to six methylol groups.





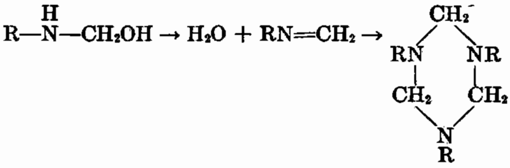
In the preparation of water-soluble resins for use or for subsequent spray drying, the solution of methylol compounds is further heated under alkaline or slightly acid conditions (pH 5.0–8.5, depending on the systems used) until the desired viscosity or solubility characteristics are obtained from increased molecular weight. The molecular weight is increased by way of reactions 2, 3, and 4. On further heating these reactions continue until a large three-dimensional network is built up which is insoluble and infusible.

2. **Methylene bridge formation:**



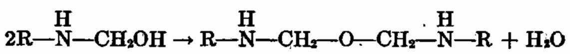
$$R{-}\overset{H}{N}{-}CH_2OH + \overset{H}{H}N{-}R \rightarrow R{-}\overset{H}{N}{-}CH_2{-}\overset{H}{N}{-}R + H_2O$$

3. **Azomethine formation:**



$$R{-}\overset{H}{N}{-}CH_2OH \rightarrow H_2O + RN{=}CH_2 \rightarrow$$

4. **Ether formation:**



$$2R{-}\overset{H}{N}{-}CH_2OH \rightarrow R{-}\overset{H}{N}{-}CH_2{-}O{-}CH_2{-}\overset{H}{N}{-}R + H_2O$$

The kinetics of the urea-formaldehyde reaction have been investigated by de Jong and de Jonge.[1] It is an equilibrium reaction with a second-order reaction forward and first order in reverse. The equilibrium is far to the right.

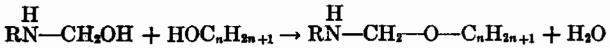
$$NH_2CONH_2 + CH_2O \rightleftharpoons NH_2CONHCH_2OH$$

The equilibrium constant was found to be only slightly affected by the pH, and the rate constants were linearly related to the hydrogen ion or hydroxyl ion concentration. The methylene bridge formation is irreversible under normal conditions, and the rate of formation was found to be about directly proportional to the concentration of hydrogen ions. This reaction is of second order.

The melamine-formaldehyde system is somewhat more complicated because of the basicity of the melamine. Okano and Ogata[2] found the hydroxymethylation to be second order, but the rate increased with increasing pH in the range of pH 3.0–10.6.

The urea resins may be cured at room temperature by the use of acid-yielding catalysts such as ammonium chloride. Melamine resins, because of their greater basicity, require large amounts of acid to reach a curing pH and so are not used in this way.

The preparation of surface-coating resins requires that the product be organosoluble and compatible with other surface-coating resins such as alkyds. This is accomplished by reacting the methylol compounds with an excess of alcohol in the presence of an acid catalyst.



$$\overset{H}{RN}\text{—}CH_2OH + HOC_nH_{2n+1} \rightarrow \overset{H}{RN}\text{—}CH_2\text{—}O\text{—}C_nH_{2n+1} + H_2O$$

This process is very complex because the acid also catalyzes reactions 2, 3, and 4. Butanol is the most common alcohol because it facilitates the removal of water from the reaction mix by azeotropic distillation. In cases where water solubility of the alkylated product is desired, as in textile treating, the alcohol used is methanol. Wohnsiedler[3] presents a more detailed treatment of the chemistry of these systems.

The wet-strength resins present a unique chemical development in that they must be positively charged to permit transfer from water on to cellulose in papermaking, and must be sufficiently high in molecular weight to bond the fibers together. This is accomplished in urea resins by co-reacting with a strong amine and carrying the reaction to a high viscosity. In melamine resins, a dilute solution of a spray-dried polymer, essentially trimethylol melamine, is treated with about 0.8 mole of hydrochloric acid per mole of melamine. The acid induces a positive charge on the polymer

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[1] DE JONG and DE JONGE, *Rec. trav. chim.*, **71**, 643–660 (1952); 71, 890–898 (1952); **72**, 139–156 (1953).

[2] OKANO and OGATA, *J. Am. Chem. Soc.*, **74**, 5728–5731 (1952).

[3] WOHNSIEDLER, *Ind. Eng. Chem.*, **44**, 2679 (1952).

and causes the molecular weight to increase so that the molecule is composed of 10–20 monomer units.[1] At this point the resin is used in the papermaking process.

The use of other reactants or modifiers such as toluene sulfonamide, substituted ureas, and substituted triazines is expected to increase.

Processing Water-soluble Resins. The condensation of water-soluble urea and melamine resins may be carried out in a relatively simple kettle equipped for agitation and heating and cooling. The exothermic heat is not great; thus a large condenser is not necessary unless dehydration is planned. The viscosities seldom exceed 10 poise and a propeller or turbine agitator is adequate. The material of construction is very important because of the strict color requirements; stainless steel should be used throughout. Copper alloys should be avoided because of color development and corrosion.

A typical urea resin would be made by charging urea and 37 per cent formalin to a kettle and adjusting the pH to 7.5 with dilute sodium hydroxide. The solution is heated to 90°C for 1 hr and then cooled to 70°C. The pH is reduced to 5.3, and reaction continued until a viscosity of 100 centipoise is obtained. The pH is then raised to 8.5 with sodium hydroxide and the batch cooled.

Surface-coating Resins. The manufacture of butylated resins is considerably more complex. The kettle must be equipped to operate under reflux with a solvent such as butanol. It must also be equipped to remove water by azeotropic distillation and remove alcohol by vacuum distillation. Viscosities at the end of the distillation cycle may approach 300 poise so that a high-powered, close fitting anchor-type agitator is recommended.

Spray Drying. The spray drying of aminoplasts requires careful control because of the low softening temperature and the hygroscopicity of the resins. Atomization, air temperature, air pattern in the drier, and the temperature and humidities of the recovery system must be carefully controlled.

Molding Powder. Aminoplast molding powders may be prepared by the dry process as are the phenolics. However, much is made by the "wet-process" in which the water solution of the resin is mixed with the filler. This mass is then dried, densified, and pulverized.

Alkyd Resins

The term *alkyd* resin has come to mean fatty acid–modified polyesters used primarily in the surface-coating field. These resins are film formers which have excellent durability, adhesion, and flexibility. The alkyds are also used in conjunction with melamine and urea resins for durable baked finishes. A wide variety of resins can be made by varying the amount and type of oil fatty acids, polyfunctional alcohols, and organic acids. The

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[1] Dixon, Christopher, and Salley, *Paper Trade J.*, Nov. 11, 1948.

fatty acids generally used are those contained in linseed, soya, dehydrated castor, castor, and coconut oils. The acids used are phthalic anhydride, maleic anhydride, and fumaric and benzoic acids. Glycerine, pentaerythritol, and ethylene glycol are the most commonly used alcohols. Resins with a high proportion of a drying oil fatty acid would be used for an architectural finish, while a low proportion of a nondrying fatty acid would give an alkyd useful for plasticizing melamine surface-coating resins.

There are three general methods of processing alkyd resins: the fatty acid process, monoglyceride process, and solvent process. In the fatty acid process, the glycerine, phthalic anhydride, and fatty acid are placed in a reactor and heated to 400–450°F (205–232°C) until the required acid number and viscosity are obtained. The monoglyceride process requires the initial reaction of a triglyceride and glycerine at about 450°F (232°C) to form monoglyceride by transesterification. The phthalic anhydride is then added and the process continued to the proper end point.

The solvent process uses about 10 per cent of a water-immiscible solvent in the reaction mixture. This solvent promotes better control by reducing the viscosity and provides a good means of water removal by azeotropic distillation.

The basic reaction of alkyds is esterification. A difunctional acid such as phthalic anhydride, a monofunctional fatty acid such as soya fatty acid, and a polyfunctional alcohol such as glycerine or pentaerythitol are reacted together under conditions of heat, catalyst, and elimination of water. Conventional esterification catalysts are effective.

The progress of the reaction may be followed by measuring the unreacted acid groups, the water given off, and the viscosity. The reaction must be stopped at a point short of gelation, but the molecular weight must be sufficiently high to form a good film.

Flory[1] has examined the kinetics of polyesterifications and found that the reactivity of the functional groups is essentially the same as the reactivity of functional groups in monofunctional esterifications. The velocity constant is independent of the molecular size up to a molecular weight of at least 10,000. Since there are molecules with a functionality greater than 2 present in alkyds, they are subject to gelation. The transformation from a viscous material to a gel is sudden. The formation of a small fraction of an infinite-network polymer is the cause of this gelation. As the reaction continues, more of the gel phase is formed and the resin becomes more tough and less extensible.

Payne[2] has calculated the gelation point for a typical alkyd resin using the formula $p = 2/f$, where p is the extent of reaction at gelation and f is

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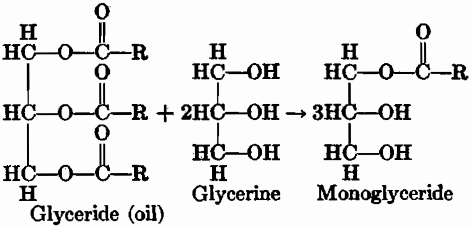
[1] FLORY in BURKE and GRUMMITT, "High Molecular Weight Organic Compounds," Interscience Publishers, Inc., New York, 1949.

[2] PAYNE, "Organic Coating Technology," vol. 1, John Wiley & Sons, Inc., New York, 1954.

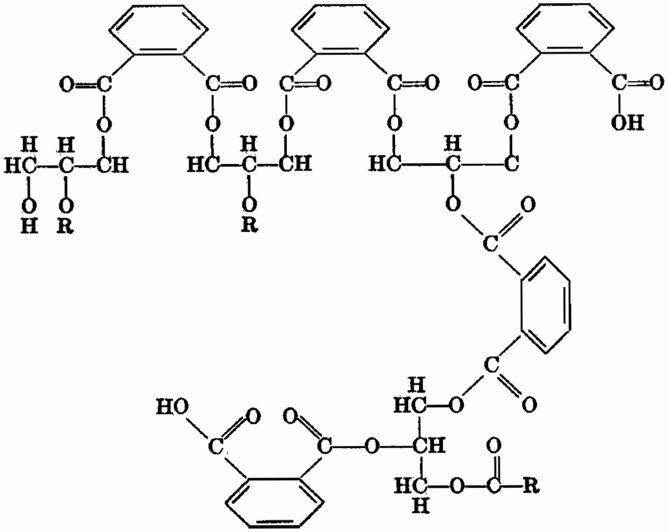
the average functionality. For a formula containing 5 moles of phthalic anhydride, 4 moles of glycerol, and 2 moles of fatty acid, the gel point occurred when 92 per cent of the functions had reacted. The average functionality of this system is $(5 \times 2 + 4 \times 3 + 2 \times 1)/(5 + 4 + 2) = 2.18$.

Since phthalic anhydride is insoluble in most oils, it is necessary to prepare monoglycerides by reacting the oil with 2 moles of glycerine.



This transesterification is carried out at 400–450°F (205–232°C) in the presence of a small amount of a catalyst such as lime or litharge. The heating is continued until the product is soluble in methanol; this takes 30–60 min.

The final cross-linking of the film (see the alkyd resin structure below) depends on further polyesterification of the alkyd to the gel point in the case of baked finishes. In air-drying coatings, the final cross-linking is due to reaction at the double bond of the drying oil–fatty acid portion of the alkyd with oxygen



Alkyd Resin
(R = fatty acid chain)

Many chemical modifications are possible through the use of materials such as sebacic acid, adipic acid, hexahydrophthalic acid, terephthalic acid, sorbitol, mannitol, and 2,3-butylene glycol. Modification of a drying oil alkyd may be made directly by polymerizing with styrene. Styrenated alkyds give good hardness and are fast drying, but they lack solvent resistance.

The kettles for making alkyd resins must provide good mixing, sufficient heat transfer to heat the contents of the kettle to 450°F (232°C) in about 2 hr, and a method of blanketing the reaction with inert gas. The inert gas reduces color formation, improves agitation and helps remove water, thereby speeding the final stages of the esterification.

Austenitic stainless steel is most satisfactory as a material of construction because it gives excellent color and can withstand the caustic soda cleaning solutions. Turbine-type agitators give good results in both the alcoholysis and alkyd processing. It is recommended[1] that the turbine diameter be not less than one-third the diameter of the kettle and that the peripheral speed of the turbine be about 600 fpm. Since glycerine is heavier than the glycerides (oils), the turbine must be placed low enough in the kettle to mix the oil and glycerine effectively for the alcoholysis step.

The inert gas should be introduced through fine openings at the bottom of the kettle. A rate of about 0.04 cfm per gal gives good results.

In solvent processing a condenser and water trap must be provided. The condenser must be designed to prevent blocking by sublimed phthalic anhydride.

LINEAR CONDENSATION POLYMERS

By E. F. Izard[2]

In order to obtain the high molecular weight required for commercial application, the reactive groups in linear condensation polymer intermediates must be very close to an exact balance. In the three commercially produced types of polymer, this balance is achieved in different ways. The three systems are polycaprolactam, polyamides (from dibasic acids and diamines), and polyesters (from glycols and dibasic acids).

Polycaprolactam. ϵ-aminocaproic acid is the best example of an amino acid where balance between reactive groups is automatic. Polymer can be produced by self-amidation of this amino acid, and in the absence of decomposition the balance is always maintained.[3] Theoretically, infinite molecular weight could be obtained by prolonged polymerization. In

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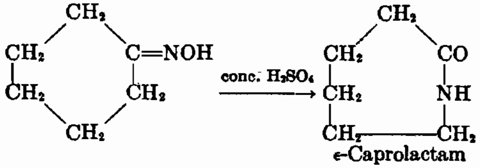
[1] Monsanto Chemical Co., "The Chemistry and Processing of Alkyd Resins," 1952.

[2] E. I. du Pont de Nemours & Company.

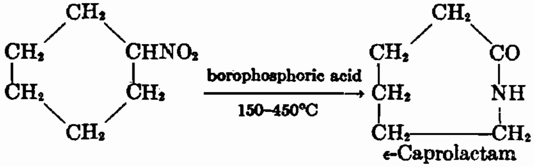
[3] Carothers, U.S. 2,071,253 (1937).

actual practice, this amino acid is not used as the starting material. Instead, a cyclic monomer (caprolactam), representing a dehydration product, is used.

Caprolactam is produced by the Beckmann rearrangement of cyclohexanone oxime.[1]



or by catalytic reduction of nitrocyclohexane[2]



The caprolactam is purified by distillation. The composition of this lactam is the same as that of the final polymer; so in the ideal case the polymerization reaction is actually some kind of addition and does not involve elimination of a by-product (see formula in Fig. 15-27; also p. 959).

There are several satisfactory commercial ways to produce polycaprolactam (6-nylon). In one method, ε-aminocaproic acid is used as a catalyst.[3] Molten caprolactam with 1–5 per cent catalyst is heated at atmospheric pressure at 240–280°C for 6–8 hr. The vessel is blanketed with steam or nitrogen to prevent oxidation. At equilibrium, the polymer contains about 10 per cent of unreacted caprolactam. Use of a small amount of the monofunctional acid assists in stabilizing the molecular weight.

A continuous version of this process is used in Germany[4] (Fig. 15-27). Molten caprolactam, catalyst, and stabilizer are metered into the top of a tower heated to 250–260°C by a heat-exchange liquid and maintained at atmospheric pressure. The product slowly passes down through perforated plates in the column as polymerization occurs and is continuously drawn off at the bottom and metered to spinning machines. This product contains 10 per cent monomer, and the final fiber must be extracted to remove the monomer.

In another method an aqueous solution of caprolactam is heated under

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[1] Johnson and MacCormack, U.S. 2,487,246 (1949).

[2] England, U.S. 2,634,269 (1953).

[3] Schlack, U.S. 2,241,321 (1941).

[4] Ludewig, *Chem. Tech* (*Berlin*), **4**, 523 (1952).

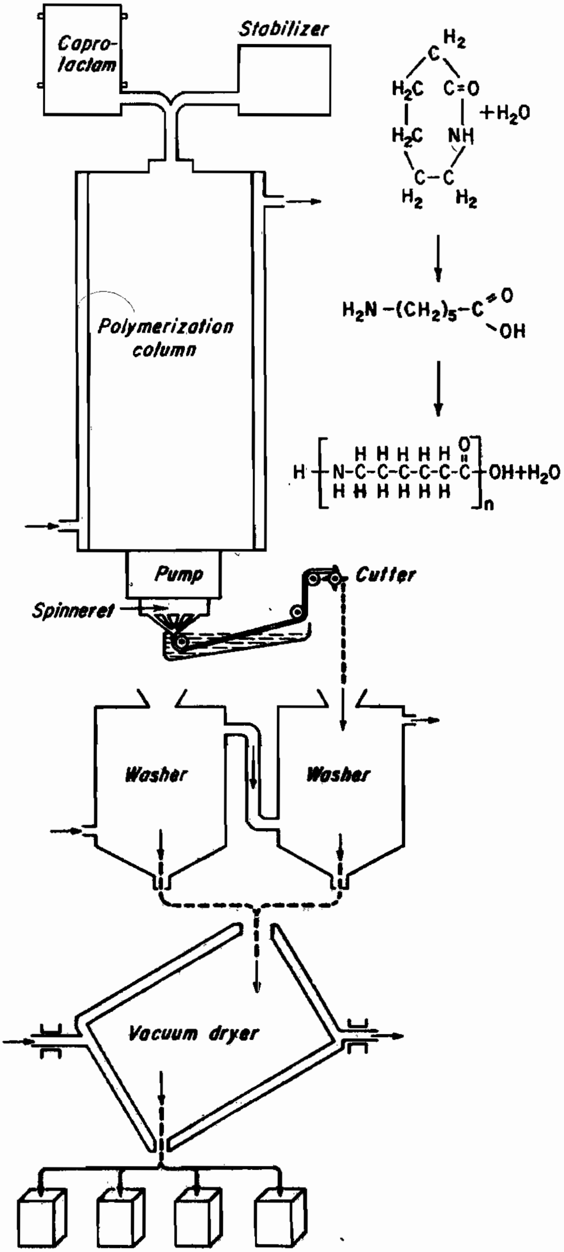


Fig. 15-27. Flow chart of production of molding compound from caprolactam.

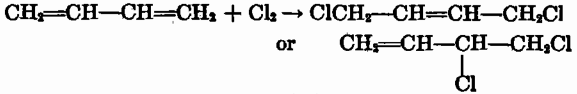
pressure in an autoclave.[1] No catalyst is used since some hydrolysis takes place to produce aminocaproic acid.

One method makes use of alkali-metal catalyst under anhydrous conditions.[2] Molten caprolactam polymerizes very rapidly in the presence of sodium or lithium catalyst. The reaction rate in this case suggests a true addition polymerization, although the mechanism is not known.

Polycaprolactam (melting point 215°C) is melt spun into filaments, can be cast into film, and is also used in making molding powder. Most nylon produced in Germany is of this type and is called Perlon. Manufacture of such fibers has been started by several large firms in the United States.

Polyamides. The first commercially produced synthetic polyamides were made from dibasic acids and diamines exemplified by polyhexamethylene adipamide (6,6-nylon).[3] Adipic acid was first commercially produced by oxidation of cyclohexanone produced from phenol, but today it is largely produced by oxidation of cyclohexane derived from either benzene or petroleum. Sebacic acid, another important nylon intermediate, is produced by caustic oxidation of ricinoleic acid from castor oil.

The commercial diamines used for nylon manufacture are usually best made by hydrogenation of the corresponding dinitriles. Hexamethylenediamine is made by hydrogenation of the adiponitrile.[4] Adiponitrile is now commercially produced by several methods. In the oldest method, ammonium adipate was catalytically dehydrated to the dinitrile.[5] In a method developed since World War II, butadiene is treated with chlorine to produce a mixture of dichlorobutenes.[6] Reaction with hydrogen cyanide in the presence of cuprous halides yields 1,4-dicyanobutene-2 exclusively.[7] Hydrogenation produces adiponitrile.



$$\begin{aligned} CH_2{=}CH{-}CH{=}CH_2 + Cl_2 &\rightarrow ClCH_2{-}CH{=}CH{-}CH_2Cl \\ &\text{or}\quad CH_2{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_2Cl \end{aligned}$$

$$ClCH_2{-}CH{=}CH{-}CH_2Cl + 2HCN \xrightarrow{CuCl} NC{-}CH_2{-}CH{=}CH{-}CH_2{-}CN$$

$$NC{-}CH_2{-}CH{=}CH{-}CH_2{-}CN + H_2 \rightarrow NC{-}CH_2CH_2CH_2CH_2{-}CN$$

In the third process, furfural, from corncobs, oathulls, or other farm wastes, is catalytically converted to furan.[8] The furan is hydrogenated to tetra-

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[1] KLARE, *Faserforscn. u. Textiltech.*, **2**, 3 (1951).

[2] Joyce et al., U.S. 2,251,519 (1941); Mighton, U.S. 2,647,105 (1953).

[3] Carothers, U.S. 2,130,948 (1938).

[4] Howk, U.S. 2,166,151 (1939).

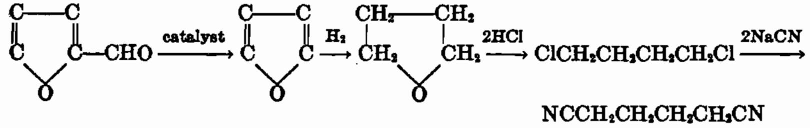
[5] Arnold and Lazier, U.S. 2,200,734 (1940).

[6] MUSKAT and NORTHRUP, *J. Am. Chem. Soc.*, **52**, 4043 (1930).

[7] Johnson and Whitman, U.S. 2,477,617 (1949); Hager, U.S. 2,468,388 (1949); Borcherdt, U.S. 2,477,573 (1949); Hager, U.S. 2,477,597 (1949); Webb and Tabet, U.S. 2,477,672 (1949); Whitman, U.S. 2,477,674 (1949).

[8] CASS, *Ind. Eng. Chem.*, **40**, 216 (1948).

hydrofuran, then treated with hydrogen chloride to give 1,4-dichlorobutane, which reacts with sodium cyanide to give adipodinitrile.



In the manufacture of a nylon polymer, the dibasic acid and diamine must be present in almost exactly balanced amounts. This can be achieved by addition of a purified aqueous solution of adipic acid to pure hexamethylenediamine in approximately equivalent amounts. Reaction takes place to form a neutral salt, hexamethylenediammonium adipate which can be recrystallized to give exactly equivalent amounts of the two reactants. This salt is used as the starting materials for polymer. Other means of obtaining exact balance include a pH determination on the aqueous salt solution and adding one or the other ingredients to bring the pH to the known value for the neutral salt. In this case, crystallization is not necessary.

In amidation, equilibrium is favorable even in the presence of water. In order to avoid loss of diamine in the early stages of polymerization with a resultant imbalance, the first step of polymerization is carried out under pressure at elevated temperature. Hexamethylenediammonium adipate with or without water is heated in a closed reactor at about 200°C and autogeneous pressure. Reaction takes place to form amide links and water and proceeds far enough to fix at least one end of all reactants. The steam pressure is then bled off and the temperature raised to 260–300°C to finish the reaction and produce high-molecular-weight polymer.

$$H_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \rightarrow -\overset{+}{H}_3N(CH_2)_6NH_3OOC(CH_2)_4CO\bar{O}-$$

$$n[\overset{+}{H}_3N(CH_2)_6NH_3OOC(CH_2)_4CO\bar{O}-] \rightarrow H[HN(CH_2)_6NHCO(CH_2)_4CO]_nOH + (2n-1)H_2O$$

Molecular weight can be controlled by addition of a small amount of monobasic acid. This polyamide melts at 265°C and is highly crystalline. The polymer can be run directly to spinning machines to produce fiber, or it can be extruded as a heavy ribbon which is chilled and chipped.[2] The polymer may be remelted to spin into fiber, or it may be used for extrusion of molded objects, or it can be made into molding powders.

Polyamides of this kind are widely used as textile fibers for wearing apparel, as cord for reinforcement of heavy-duty tires, and in a myriad of molded objects which can replace metal parts.

[1] Peterson, U.S. 2,174,527 (1939).

[2] Graves, U.S. 2,289,744 (1943).

Polyesters. The first synthetic fiber forming polymer produced by Carothers and coworkers[1] was an aliphatic polyester made from trimethylene glycol and a hexadecamethylene dicarboxylic acid. This polymer was low-melting (70°C) and hydrolytically unstable. In 1941, Whinfield and Dickson synthesized the first high-melting symmetrical linear aromatic polyester, polyethylene terephthalate, and found it to be a very useful product.[2]

In the esterification reaction, equilibrium is not favorable to formation of ester, and in order to get a high yield the by-product must be continually removed from the beginning. To achieve high molecular weight in the final product, almost exact balance must be obtained between the two reactive groups, that is, hydroxyl and carboxyl functions. Fortunately the chemical nature of esters makes this balance possible in an entirely different way. In amides, amide exchange is a very slow reaction and is not depended upon to take part in the polymerization reaction. In esters, however, ester exchange is quite easy and makes possible a new commercially feasible method of getting high-molecular-weight polymer.

Polyethylene Terephthalate. Terephthalic acid is usually produced commercially by oxidation of *p*-xylene. Terephthalic acid is a high-melting (above 300°C) insoluble product. It would be very difficult to react with an equivalent amount of a glycol to produce polymer. However, dimethyl terephthalate is fairly easily prepared by several commercial methods.[3] This ester (melting point, 141°C) is easily purified and is used to prepare the polymer.

The basic process involves transesterification or ester alcoholysis between glycol (in excess) and the dimethyl terephthalate. In the first stage, glycol (2 moles) is reacted with dimethyl terephthalate (1 mole) in the presence of a catalyst at atmospheric pressure. The catalyst may be litharge; salts of zinc, magnesium, calcium, cobalt, etc.; lithium, sodium, or their alkoxides; cerium oxide; germanium oxide; or antimony oxide.[4] Reaction begins at 150–160°C, and the methanol produced is continuously removed in a fractionating column. As the reaction proceeds, the temperature rises and drives the reaction toward completion. At the end, the reaction temperature is about 230°C and the product an equilibrium mixture of glycol, bis-hydroxyethyl terephthalate, and low polymer. In this product all carboxyls are now esterified with glycol, but the glycol is in great excess.

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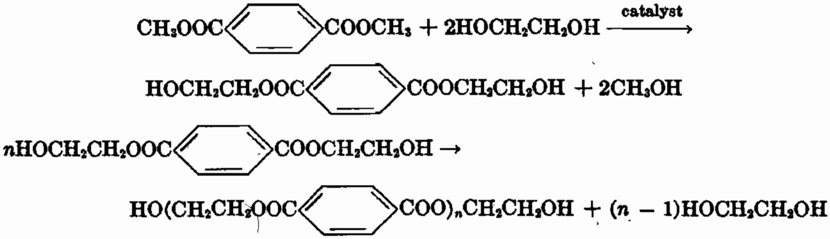
[1] CAROTHERS and HILL, *J. Am. Chem. Soc.*, **54**, 1579 (1932); Carothers, U.S. 2,071,250 (1937).

[2] Whinfield and Dickson, U.S. 2,465,389 (1949); Br. 578,029 (1946); U.S. 2,465,150 (1949); Br. 579,462 (1946).

[3] See Chap. 12.

[4] Izard, U.S. 2,534,028 (1950) and 2,597,643 (1952); Casassa, U.S. 2,518,283 (1950); Hofrichter, U.S. 2,641,592 (1953); Auspos and Dempster, U.S. 2,578,660 (1951) and 2,643,989 (1953); Billica, U.S. 2,662,093 (1953).

However, transesterification is still possible between the free hydroxyls and the combined esters.



In the second stage, the temperature is raised and vacuum is applied to remove the free glycol. Reaction continues to produce polymer and glycol, which is removed, and the two reactants approach exact balance and high molecular weight is achieved.[1]

Polyethylene terephthalate thus produced is a high-melting (250–265°C) crystalline product insoluble in most commercial solvents. The molecular weight of the product is not well known, but reproducibility is controlled by measuring either the melt viscosity or the solution viscosity of the product. The product can be extruded directly into filament or into film. The fiber can be drawn to give a highly oriented product of high strength. Some varieties are very resilient. The fibers have found application in clothing fabric for outer wear, shirts, etc., as well as fillers for pillows, sleeping bags, etc. The film can be oriented in two directions to yield a very tough product. It is useful for electrical insulation, sound-recording tapes, heavy-duty packaging, and in many other fields. A special variety of film is used as a photographic-film base.

Other polyesters can be made by starting with the appropriate methyl esters. Copolymers can be made by using a mixture of methyl esters as starting materials.[2] Several alternative processes exist for producing polyesters;[3] these include direct esterification, use of other esters than methyl esters, use of chlorohydrins and sodium salts of acids, use of acid chlorides and glycols, and many others.

In England and Canada and several European countries, polyethylene terephthalate fibers are sold under the name Terylene. In England the film is called Melinex, in Germany, Hostaphan. In the United States the products are trade-marked and marketed as Dacron polyester fiber, Mylar polyester film, or Cronar photographic film base.

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[1] Billica, U.S. 2,647,885 (1953); Hofrichter, U.S. 2,650,213 (1953).

[2] Snyder, U.S. 2,647,032 (1953).

[3] SCHILDKNECHT (ed.), "Polymer Processes," chap. VII, pp. 259–262, Interscience Publishers, Inc., New York (1956).

UNSATURATED POLYESTER RESINS

By E. W. Moffett[1]

The products to be considered in this section are commonly called "polyester resins." However, they need better definition to distinguish them from several other commercial polyesters which are also called resins. Perhaps the shortest definition is that an unsaturated polyester resin is composed of two major components, one of which is a linear polyester prepared from a glycol and an *unsaturated* dibasic acid, and the second is a *vinyl monomer in which the first is soluble and with which it will copolymerize.* The sirup so formed is commonly but incorrectly called a polyester resin. No really effective definition has been devised. The above definition is satisfactory for the sirup. The common name is used for both the copolymerizable solution and the polymerized final product. In the latter state, the unsaturation has ceased to exist.

Commercial development of this field was aided by a fortuitous set of circumstances. Maleic anhydride became available commercially shortly prior to World War II and cheap styrene for synthetic rubber during this conflict. Glass fibers in woven cloth form appeared at about the same time. A demand for radomes for aircraft caused a search for a strong plastic material which literally would be a window for radar waves. Glass cloth–reinforced unsaturated polyester resins provided the strength necessary as well as the desired electrical properties. From this commercial start in 1944, the unsaturated polyester resin production has grown to an estimated 70 million lb in 1956. The major part of the resin is used with reinforcing fibers of some type.

Chemistry of Unsaturated Polyester Resins. *Polyester Component.* This part of the composition is prepared first and is sometimes called the alkyd portion. The starting materials are glycols and unsaturated dibasic acids or anhydrides. By way of example, the first member of the series may be ethylene maleate, and its preparation can be represented by the equation

$$n\mathrm{HOCH_2CH_2OH} + n\mathrm{HO_2CCH{=}CHCO_2H} \rightarrow \mathrm{HO[CH_2CH_2O_2CCH{=}CHCO_2]_nH} + (2n - 1)\mathrm{H_2O}$$

A simplified structure is often written for such polyesters as —G—M—G—M—G—M—, where G and M are glycol and unsaturated dibasic acid residues, respectively. Ethylene maleate is seldom used because of limited compatibility in the commonly used monomers. Propylene glycol is used most often in commercial rigid resins, while diethylene and dipropylene glycols are used to impart flexibility.

The unsaturated acids used are almost exclusively maleic or fumaric,

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[1] Pittsburgh Plate Glass Co.

the former being the cheapest and available as its anhydride. However, many of the commercial polyesters also contain *saturated* dibasic acids. The polyester structure may be depicted as —G—M—G—A—G—M—G—A—G—M—. Here A represents such acids as *o*-phthalic, adipic, and succinic. The former is a common component because of the price and the properties imparted. Isophthalic acid is becoming available, and initial evaluation indicates that it will be useful. Tetrachlorophthalic and hexachloro-2,6-endomethylene-Δ^4-phthalic acids are used to impart fire retardance.

Monomer Component. The polymerizable monomer chosen might be any one of hundreds. The early work[1] was done with methyl methacrylate and vinyl acetate, but the large production of styrene made available a cheap monomer with nearly ideal properties. Other vinyl compounds might be used. However, the useful group is limited by another factor. *The monomer must copolymerize much faster with the polyester double bonds than with itself.* Otherwise, a mixture of copolymer and polymer is obtained which usually is incompatible. Allylic type monomers copolymerize with polyesters but usually at a slow rate. Styrene probably constitutes 85 per cent of the total amount of monomer used commercially in this field. Besides being available at a low cost, it has other advantages. It copolymerizes rapidly. Its boiling point is sufficiently high so that it can be added to the hot polyester without volatilization. This same property prevents excessive evaporation at room temperature during commercial use. Its solvency is high so that a large amount of polyester can be dissolved in it. The products of commerce contain 20–45 per cent by weight of styrene.

Other monomers are used to a limited extent. Diallyl phthalate has been used for some time. It provides the ultimate in nonvolatility but is four times as expensive as styrene. Resins containing vinyl toluene have found use recently.

Minor Components. Besides the two major components, commercial considerations necessitate a third type of compound. If an unsaturated polyester and pure styrene are mixed together, copolymerization may take place quickly. This is particularly true if the polyester is warm or hot at the time of addition. However, commercial styrene contains 10ppm of *t*-butyl catechol as a storage stabilizer, and some storage stability is thus imparted to the polyester resin. This low amount is usually inadequate. One of the first major problems in the industry was to find an inhibitor which would provide sufficient time for ordinary shipping and consumption. Fortunately, several types of compounds have been found which provide adequate stability for 6 months to a year. Hydroquinone and some of its alkyl-substituted derivatives are effective stabilizers. Catechol[2] and some

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[1] Kropa and Bradley, *Ind. Eng. Chem.*, **31**, 1512 (1939), Rust, *ibid.*, **32**, 64 (1940).

[2] Parker, U.S. 2,698,312 (1955).

of its derivatives[1] behave similarly. As an example, *t*-butyl catechol has been used. Resorcinol[2] and its derivatives are much less effective. Quaternary ammonium salts[3] and tertiary amine salts are quite effective in preventing copolymerization. Aryl and alkyl phosphites have limited stabilizing activity. Many other compounds have strong stabilizing effects, such as phenols, nitrophenols, copper compounds, sulfur and some of its compounds, carbon black and certain other pigments. However, these compounds are not used because they usually prolong or practically stop the cure of the resins.

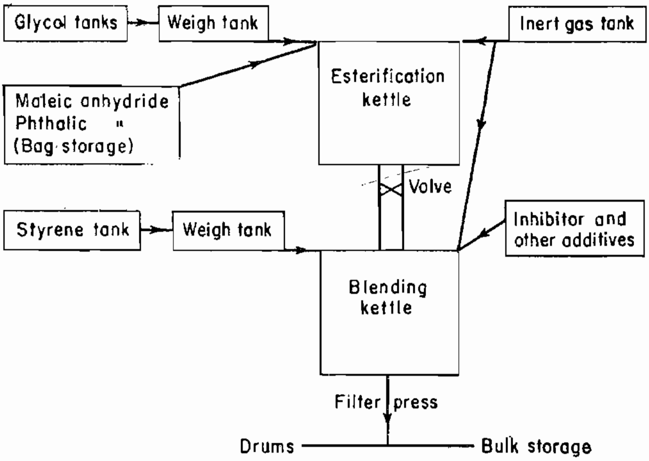

FIG. 15-28. Flow sheet, production of unsaturated polyester resin.

Other minor constituents include "light stabilizers" which are added to some resins to prevent yellowing during outdoor exposure. Salicylates and dihydroxybenzophenone derivatives are thus used. Use of the latter type is covered by patents, and their effectiveness is based on the absorption of ultraviolet light.

Production of Commercial Resins. The production of this type of resin is carried out in stainless-steel equipment, and the flow sheet in Fig. 15-28 illustrates the process.

The kettles shown are equipped with efficient agitators. The esterification kettle is charged with the proper amount of glycol, and the solid anhydride or anhydrides are charged through a manhole. The kettle is closed and swept with inert gas such as nitrogen, carbon dioxide, or flue gas to remove oxygen. Heat may be supplied electrically, by direct gas

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[1] Anderson, U.S. 2,610,168 (1952); 2,632,751 (1953).

[2] Kropa, U.S. 2,409,633 (1946).

[3] Parker, U.S. 2,593,787 (1952).

fire, or by Dowtherm heat-transfer. Heat is applied and the charge is heated to 175–200°C, depending on the product being made. The vapors formed are carried out by a slow stream of inert gas through a partial condenser which returns glycol but passes the water to a total condenser. The esterification is continued until a predetermined acid number is reached, usually in the 10–50 range. The glycol is employed in slight excess in the charge. The inert gas flow is then increased, and the batch is blown at full heat until the alkyd reaches a predetermined viscosity. When this is reached, the heat is turned off and the inert gas flow reduced.

The blending kettle is provided with coils through which hot or cold water may be circulated. This kettle is purged with inert gas and the batch dropped into it. The alkyd is cooled to 100–130°C, and the inhibitors may be added during this time. Styrene is pumped into the kettle in proper amount. Agitation and cooling must be efficient at this time to prevent a start of copolymerization. The cooling is continued to room temperature, other additives are added if used, and final adjustment to specification viscosity is done by styrene addition. The batch is then pumped, through a filter press, to storage tanks or drums.

Polyesters of this class vary from heavy, sticky gums to brittle but tacky solids. For this reason they are seldom handled in this form but are immediately diluted with the monomer of choice. The resins are available in a wide range of viscosities. Most of the marketed resins yield rigid materials when cured. Flexible resins are available but are used for blending with rigid ones to impart flexibility. The properties of a typical general-purpose resin for matched die-molding work are listed in Table 15-9.

TABLE 15-9. TYPICAL PROPERTIES OF GENERAL-PURPOSE POLYESTER RESIN

Property	*Range*
Color, APHA scale	30–60
Specific gravity, 25°C/25°C	1.12–1.14
Viscosity at 25°C,	2,000–3,000 centipoise
Stability (in the dark):	
At 25°C	6–12 months
At 65°C	3–20 days
Monomer content	25–30%
Catalyzed properties (1% benzoyl peroxide):	
Tank life at 77°F (25°C)	24–72 hr
Gel time at 180°F (82°C)	3–5 min
Cure time at 230°F (110°C)	2–4 min

Curing of Unsaturated Polyester Resins. The stages covered so far have been concerned only with that portion of the field which concerns the resin supplier. His objective is to provide a clear, colorless, stable sirup to his consumers. The converters start with the sirup, add a curing agent, and mold or cast a finished article which is usually reinforced with fibrous material. In this step, the liquid is converted to a solid. The curing agents used are organic peroxides which furnish the free radicals that initiate the copolymerization and destroy the inhibitor present. The latter factor is the reason for careful selection of the inhibitory system. The compounds used must provide storage stability but must permit rapid polymerization once a peroxide is added. Heat is usually used to speed up polymerization, but special polyester resins are available which cure to solids at room temperature in as little as 15 min. Pressures used may be from practically zero (contact) to 250 psi, depending on the article being made.

Many peroxides affect polymerization, but those used are available in quantity and the choice is based both on economics and performance. It has been shown that the activity of the organic peroxides in any polymerization is related to their decomposition rates at various temperatures. If elevated cure temperatures, 200–250°F (93–121°C), are used, benzoyl peroxide is preferred. The amount required is about 1.0 per cent. It is preferred because a long catalyzed "tank" life results at room temperature. If lower temperatures in the 120–180°F (49–82°C) range are employed, hydroperoxides are more effective. Methyl ethyl ketone peroxide and cumene and tertiary butyl hydroperoxide all find application. Lauroyl peroxide, cyclohexanone peroxide, and *t*-butyl perbenzoate are used in limited amounts. Mixtures of two peroxides are often used, one to initiate the reaction and a second to promote the polymerization once it is started.

As would be expected from polymerization studies, cure brings about two physical effects. Heat is evolved during the copolymerization and, because of the speed of the reaction, consideration of this factor must not be neglected. Fast cures in moderate thicknesses, 0.25–0.50 in, may lead to exotherms of 400–500°F (204–260°C) in a minute or less. Boiling of unreacted styrene may result, with consequent production of a useless part. The conversion from a liquid to a solid produces a denser material, and shrinkage results. The amount is naturally related to the monomer content, but most polyester resins shrink 7–10 per cent by volume during cure. Due allowance must be made for this factor in constructing molds. Inert inorganic fillers are often added to reduce shrinkage.

Very little is known about the structure of the cured polyester resin. The products definitely belong in the thermoset class. There is some correlation between maximum physical properties and a molar ratio of 1:1 between double bonds in the alkyd and monomer. However, this is not critical and simple cross-linking does not tell the full story. The styrene monomer can be present in twice the molar amount needed, and yet complete copolymerization takes place without apparent formation of styrene polymer.

Commercial Uses. Examination of a chart of the physical properties of cured "unsaturated" polyester resins in cast unreinforced form would certainly not explain the rapid progress and the growing importance which these materials have shown during the last few years. Certain moderate advantages exist in a few properties, but other, older thermosetting resins show similar characteristics. However, it is important to remember one salient feature: this class of plastics provided for the first time *a liquid 100 per cent reactive resin* which could be converted in a short time to a *solid thermoset material*, by the use of a peroxide, heat, and *low pressure*. These features permitted reinforcement with various fibrous materials. It is easy to distribute a liquid around and through the reinforcing material in a mold, while solid molding resins would tear the reinforcement. The liquid feature also permitted the making of much larger parts because less pressure is needed to force the resin into all parts of the mold. The molds are constructed accordingly and are both less expensive and much lighter per square foot of surface area molded.

For the first time, advantage could thus be taken of the excellent strength properties of fine glass fibers. These are available in the form of yarn, woven cloth, mats, and chopped strands. The laminates so formed have high flexural, tensile, and compressive strengths and excellent impact resistance.

These advantages have led to wide usage in the transportation field where weight is a factor, particularly in the aircraft industry where aircraft radomes, wing tips, wing liners, fuel tanks, and many smaller items are made from reinforced polyesters. Truck bodies and panels, roofs, bus kick plates, heater housings, and, recently, interior parts of light railroad coaches are examples of applications in surface transportation. The water and rot resistance of reinforced polyester resins has led to their use both as covering for wooden boats and as a new material for construction of boats without seams. In the building field, corrugated panels are used for windows, walls, patio roofs, and partitions and provide probably the biggest single application for these resins. In the electrical field they are used for potting, encapsulation of circuits, and in panel form. The list could be continued to include hundreds of other items; those mentioned here are merely illustrative. The industry is still in its infancy, and many opportunities for basic research and development exist.

EPOXY RESINS

By Marco Wismer[1]

Among the most interesting polymers developed during the last ten years are the epoxy resins obtained from a polycondensation of epichlorohydrin with polyphenols or polyalcohols. The epoxy resins which account for

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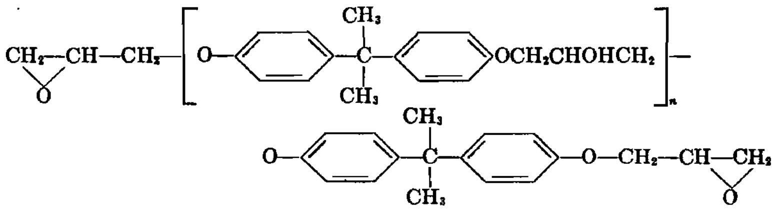
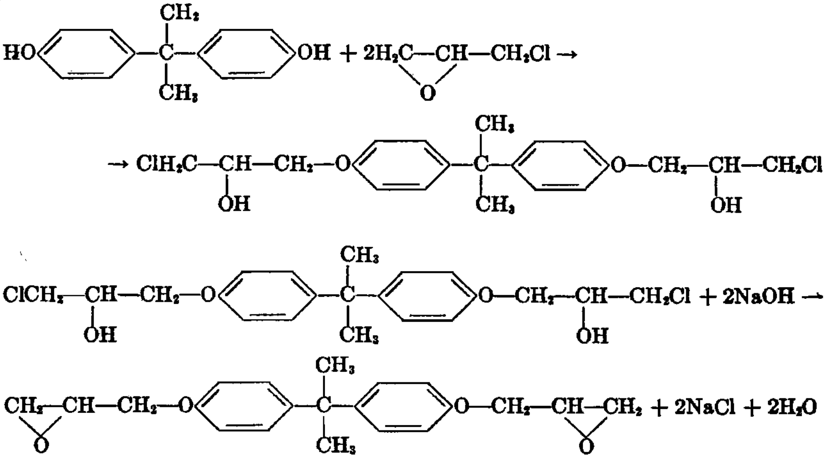
[1] Pittsburgh Plate Glass Co.

the major part of the commercial production are produced by the reaction of 2,2-bis(4-hydroxyphenyl) propane (a condensation product of phenol and acetone, commerically known as bisphenol A) with epichlorohydrin. These liquid or low-melting solid polymers represent polyethers having as reactive groups exclusively terminal epoxy and secondary hydroxyl groups.

The structure of these resins can be represented by this idealized formula:



Some chain branching may occur during the reaction; however, the resins are essentially diepoxides. The reaction leading to the formation of these resins takes place at above 50°C in the presence of an alkaline catalyst and an excess of epichlorohydrin. The primary reaction involves the opening of the epoxide groups by the phenolic hydroxyl groups. This reaction is followed by dehydrochlorination to regenerate terminal epoxy groups, as shown in the formulas below:[1]



The condensation may proceed further by the reaction of phenolic hydroxyl groups with the epoxy groups of the resin:

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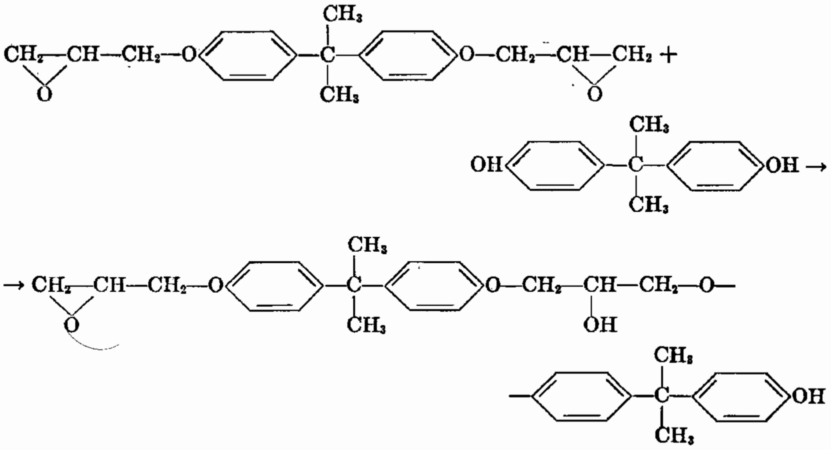
[1] Bradley et al., *J. Chem. Soc.*, **1951**, 1589; Fisch and Hofmann, *J. Polymer Sci.*, **12**, 497 (1954).



Further reaction with epichlorohydrin results in the formation of terminal epoxy groups as illustrated in the idealized structure. The molecular weight of these resins depends largely on the molar ratio of the reactants. Epichlorohydrin used in large excess acts as a chain stopper. The liquid resins are prepared (see Fig. 15-29) by using an excess of 6–8 moles of epichlorohydrin per mole of bisphenol A.[1] Two moles of caustic soda are generally used, and the reaction is preferably carried out in the absence of water. The reaction temperature may vary between 50–100°C.

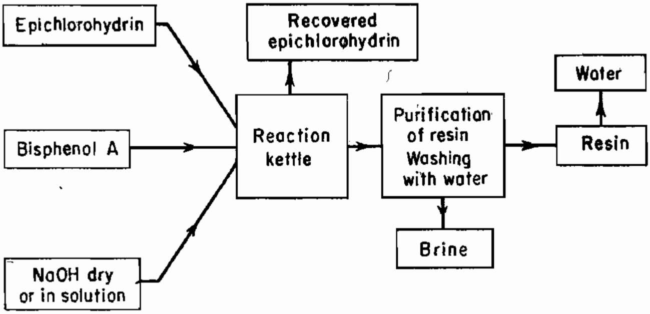


FIG. 15-29. Flow diagram for the production of epoxy resins.

The solid, higher-molecular-weight resins are obtained by decreasing the amount of epichlorohydrin used. Here, the caustic soda is preferably added in aqueous solution.[2] Some of the epoxy resins with high molecular weight in the range of 3,000–8,000 are prepared by reacting a lower-molecular-weight epoxy resin with bisphenol A.[3] This procedure helps to overcome

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[1] Werner, U.S. 2,467,171 (1949).

[2] Greenlee, U.S. 2,582,985 (1952; Greenlee, U.S. 2,615,007 (1952).

[3] Greenlee, U.S. 2,615,008 (1952).

the difficulties in purification encountered while removing sodium chloride from a high-molecular-weight resin.

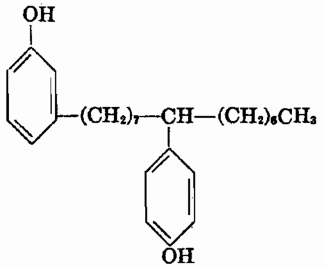
The data in Table 15-10 show the effect of changes of the ratio of epichlorohydrin to bisphenol on the physical characteristics of epoxy resins.

TABLE 15-10. CHARACTERISTICS OF EPOXY RESINS AS A FUNCTION OF EPICHLOROHYDRIN: BISPHENOL RATIO

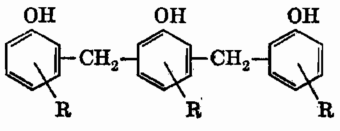
Epichlorohydrin, moles	Bisphenol A, moles	Melting point, °C (Durran-Mercury)	Epoxy equiv./kg	Hydroxy equiv./kg	Viscosity at 23°C, centipoise
6	1	Liquid	5.3	....	12000
1	1.6	59	2.3	0.28	Solid
1	1.45	70	2.0	0.31	Solid
1	1.35	85	1.5	0.33	Solid

The epoxy resins with molecular weights up to 2,000 are soluble in ketones, chlorinated hydrocarbons, alcohol ethers, esters, and aromatic hydrocarbons. They are compatible with many of the synthetic resins such as alkyds, phenolics, and amine-formaldehyde resins.

Other epoxy resins are also being manufactured, but their commercial utilization is not so far advanced as those based on bisphenol A and epichlorohydrin. For instance, resorcinol and a mixture of diphenol-poly-(hydroxyphenyl)-pentadecanes, obtained by the addition reaction of phenol with an unsaturated phenol derived from cashew-nut oil (see structure below) can be reacted with epichlorohydrin to produce epoxy resins.[1]



Epoxy resins are also produced in limited volume by the epoxidation of novolac compounds such as



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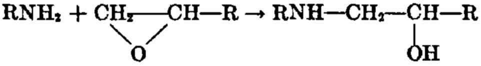
[1] Wasserman, U.S. 2,665,266 (1954).

Aliphatic polyglycidyl ethers of polyalcohols represent epoxy resins with low viscosities. Epoxy compounds based on aliphatic alcohols are preferably prepared by a two-stage process. The alcohol is first reacted with epichlorohydrin in the presence of a cationic catalyst such as BF_3, $ZnCl_2$, or $SbCl_5$. The resulting chlorohydrin ether is then dehydrochlorinated in the presence of caustic soda or of sodium aluminate. The polyols used presently are glycerol, ethylene glycol, and diethylene glycol.[1] Monoglycidyl ethers are useful as diluents for the higher viscous epoxy resins. The monoglycidyl ethers of phenol, butyl alcohol, allyl alcohol, and pentadecadienyl phenol are most commonly used.[2] The epoxy resins have outstanding stability even at elevated temperatures. They can be held in a molten stage at 120°C for several hours without undergoing appreciable changes in molecular weight.

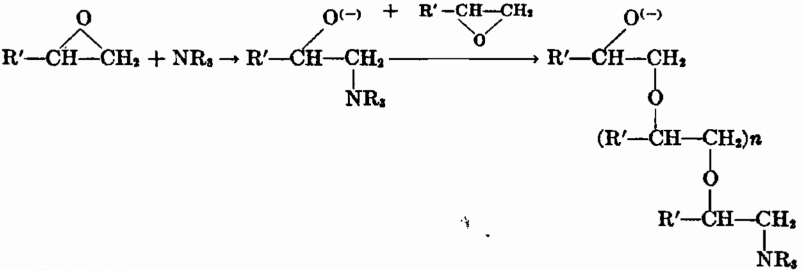
The industrial importance of these thermosetting polymers is due to the fact that they can be cross-linked to form finished products with outstanding chemical inertness, toughness, adhesion, and dimensional stability. The cross-linkage occurs by reaction of the curing agent with the epoxide group and, in some cases, also with the hydroxy group. No volatile components are formed during cure; hence there is low shrinkage. The most commonly used cross-linking agents are aliphatic amines, aromatic amines, anhydrides, polyamines, polysulfide polymers, phenolic resins, urea and melamine-formaldehyde resins, isocyanates, polybasic acids, amine borates, and boron fluoride complexes with amines.

Three different types of curing mechanism can be distinguished: Primary and secondary amines react with epoxy resins by an addition mechanism.



$$\mathrm{RNH_2 + \underset{\diagdown\, O\, \diagup}{CH_2{-}CH}{-}R \rightarrow RNH{-}CH_2{-}\underset{OH}{\underset{|}{CH}}{-}R}$$

Tertiary amines probably react by opening the epoxy groups with the pair of unshared electrons, thus promoting a polymerization of the epoxy group.[3] R denotes a C_2H_5 group.



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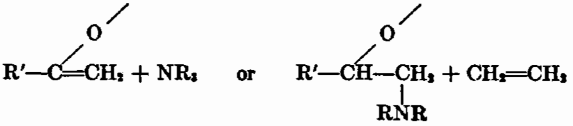
[1] Zech, U.S. 2,538,072 (1951).

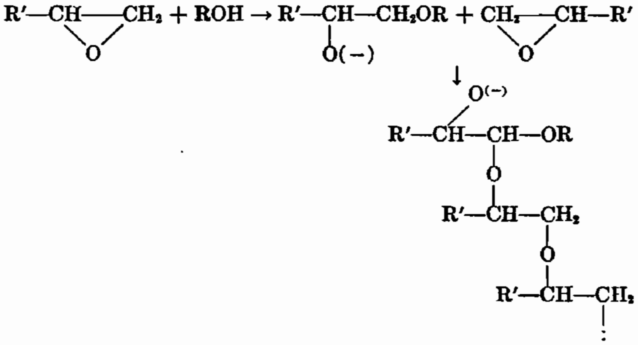
[2] Wiles and Newey, U.S. 2,528,932 (1950).

[3] Narracott, *Brit. Plastics*, April, 1953; Shechter and Wynstra, *Ind. Eng. Chem.*, **48**, 86 (1956).

The termination may occur as follows:



Acid anhydrides react first with the hydroxyl groups to form a monoester. The second carboxyl group of the anhydride is converted to the carboxylic acid, which preferably will react with a terminal epoxy group. The presence of hydroxyl groups in acidic conditions may lead to a polyether formation by the self-polymerization of the epoxy group.[1]



It is believed that curing an epoxy resin with urea and phenol-formaldehyde resins involves the reaction of the methylol groups of these resins with the secondary hydroxyl groups of the epoxy resin.

Because of their outstanding properties such as adhesion to various materials, chemical inertness, low shrinkage during cure, stability at elevated temperatures, flexibility, and toughness, epoxy resins are now used in many applications. They are a major constituent of adhesives. The paint industry is using the reaction product of fatty acids with epoxy resins for air-drying and baking finishes, whereas combinations of phenolic resins or amine-formaldehyde resins with epoxy resins are widely used as primers and top coats in baking finishes and can coatings.

Casting, potting, and impregnation of electrical units for insulation are applications in the electrical industry. Epoxy resins are also used as wire coatings. Epoxy-glass laminates are entering the printed circuit field and are also used for many structural applications where high strength at elevated temperature and chemical resistance are required. The manufacture of plastic machine tools is a major field for epoxy resins, which are especially suited for this purpose because of their low shrinkage and excellent dimensional stability.

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[1] Fisch and Hofmann, *J. Polymer Sci.*, **12**, 497 (1954).

Recent developments indicate that new processes and raw materials will soon provide new types of epoxy resins. The most significant development is the epoxidation method using peracids as means of epoxidation. Peracids are produced commercially either by the interaction of acids with hydrogen peroxide or by the oxidation of aldehydes. Peracids will epoxidize double bonds under controlled conditions, preferably in absence of water and free acids. It is anticipated that polyepoxides based on these processes will soon be available.

The first materials produced by this method which have obtained commercial importance are monoepoxides such as octylene oxide, dodecene oxide, and a mixture of 1,2-epoxy hexadecane and 1,2-epoxy octadecane. These epoxides are used as stabilizers for vinyl polymers and as diluents for epoxy resins.

SILICON POLYMERS

By R. R. McGregor[1]

Silicones are among the more recent polymeric materials to be offered to industry. The academic study of these materials may be traced back for over 100 years, but the diversity of products obtainable and their commercial applicability were not recognized until the late 1930's. By 1941, some commercial products had limited manufacture and use, and since then the industry has experienced rapid growth as to number of products and volume.

Silicones differ from conventional synthetic materials in that the basic structure is a succession of silicon and oxygen atoms rather than carbon atoms. Each silicon generally has attached to it one or more organic radicals. The number and type of organic radicals present are important factors in determining the properties of the finished polymer. The products may take the form of fluids, greases, resins, or rubbers. The properties originally noted were heat and oxidation stability and water repellency. Investigation showed that many of the products had excellent electrical characteristics, mold release ability, antifoaming action, retention of properties at low temperature, and many other features that were unique and of use to industry.

Preparation of Monomers. The first step in the preparation of these materials is the synthesis of appropriate monomers. To be effective in polymerization, a monomer must contain one or more hydrolyzable groups attached to silicon; and to develop required form and properties of the final product, there must also be one or more organic groups attached to silicon.

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[1] Dow Corning Corporation.

The hydrolyzable group on silicon is usually chlorine, the cheapest and most readily available of the halogens. The organic groups attached to silicon are restricted to a small number of which methyl ($—CH_3$), ethyl ($—C_2H_5$), phenyl ($—C_6H_5$), and vinyl ($—CH{=}CH_2$) are the most common.

1. To obtain the methyl-containing silicon chlorides, finely divided silicon is mixed with about 10 per cent copper powder. This is placed in a tumbler, heated to about 300°C, and methyl chloride is passed through the charge. A number of products are formed, the one generally being considered the most desirable being dimethylsilicon dichloride:

$$Si + 2CH_3Cl \xrightarrow{Cu} (CH_3)_2SiCl_2$$

The gases are condensed and are separated by fractional distillation. The following products are obtained:

Compound	*Boiling point, °C*
$(CH_3)SiCl_3$	65.7
$(CH_3)_2SiCl_2$	70.0
$(CH_3)_3SiCl$	57.0
$(CH_3)HSiCl_2$	41.0
$HSiCl_3$	32.0
$SiCl_4$	57.6

It will be noted that the chlorines and the organic groups are attached to the silicon in one operation.

The composition of the gases may be altered by control of temperature, rate of gas flow, amount of catalyst, and other factors. The catalyst seems to be more or less specific for this reaction and is not economically applicable to other organic groups.

2. For the synthesis of phenylchlorosilanes, a reagent such as $HSiCl_3$ (silicochloroform), obtained by the previous reaction, and benzene can be used. When this mixture is heated in the presence of a catalyst, the following reaction takes place:

$$HSiCl_3 + C_6H_6 \rightarrow C_6H_5SiCl_3 + H_2$$

3. Ethyl groups may be incorporated by a similar reaction, with or without a peroxide catalyst:

$$HSiCl_3 + H_2C{=}CH_2 \rightarrow CH_3{—}CH_2SiCl_3$$

Many olefinic compounds may be used in place of ethylene, the product containing a saturated adduct.

4. Unsaturated groups, such as vinyl, may be added, the most direct method being by the use of acetylene:

$$HSiCl_3 + CH{\equiv}CH \rightarrow CH_2{=}CHSiCl_3$$

5. The Grignard method is worthy of note because of its wide applicability. It involves two steps: the first step is the preparation of the Grignard reagent, RMgCl. The ethereal solution of it is then added to a solution of a silicon halide in ether:

$$SiCl_4 + RMgCl \rightarrow RSiCl_3 + MgCl_2$$

This method was, at first, used rather widely but is now called upon only for specialized reactions.

Polymerization of Monomers. Having obtained the monomers, the next step is their polymerization into useful products. The ability of these materials to polymerize depends almost entirely upon the ability of the chlorines to react with water:

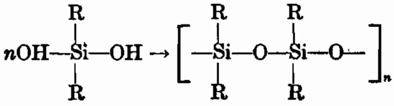
$$\equiv SiCl + H_2O \rightarrow \equiv SiOH + HCl$$

A second step then takes place almost immediately or with slight urging by heat:

$$\equiv SiOH + HOSi\equiv \rightarrow \equiv Si-O-Si\equiv + H_2O$$

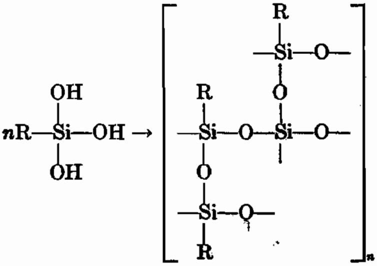
These two steps are the basic reactions in silicone polymerization. It will be recognized that the presence of two —OH groups on silicon allows the formation of linear polymers; three or more —OH groups allows the formation of cross-linked polymers. There is no evidence that hydroxyls on the same silicon ever condense to give $=Si=O$; for this reason the polymer is free to grow. Acid or base catalysis is generally used to speed up the reaction.

Polycondensations between silandiols yield straight-chain polymers



$$n\,OH-\overset{R}{\underset{R}{Si}}-OH \rightarrow \left[-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\right]_n$$

whereas similar reactions between silantriols result in the formation of highly cross-linked polymer molecules:



For the formation of fluids it is necessary to use monomers having two (and only two) hydrolyzable groups. With these as starting materials, linear polymers are formed having no cross-links. The formation of cyclics resulting from *intra*molecular condensation can be kept at a minimum by using adequate catalyst concentration and avoiding dilute solution. The viscosity (or molecular weight) can be regulated by the addition of monofunctional monomers which act as chain stoppers.

For the formation of resins, both difunctional and trifunctional monomers are required. Complete condensation of all the hydroxyls would give a hard, insoluble product which would be impossible to apply. Therefore, the mixture of monomers along with sufficient water for hydrolysis is heated, with stirring, until the mixture starts to climb the stirrer or until it is just short of gelation. At this point it is cut back with solvent and is ready for application. Subsequent removal of solvent, followed by heating (often in the presence of a metallic catalyst), brings about the formation of the fully cured resin.

The polymerization to form a silicone rubber follows a somewhat different course. A high-molecular-weight polymer is prepared from a monomer carrying two methyl groups and two chlorines. This polymer is then lightly cross-linked by the use of a peroxide such as benzoyl peroxide. The reaction apparently involves the generation of free radicals, followed by abstraction of hydrogens from methyl groups. These groups, in turn, become free radicals and react with one another, bringing about a cross-linking.

All these methods of polymerization lead to development of products having a great diversity of properties. They may be fluids, resins, or rubbers. The fluids, in turn, may be formulated into compounds (nonflowing petrolatum-like products), antifoam agents, or lubricating greases.

Silicone Fluids. The fluid having the widest use in commerce is the one containing two methyl groups attached to silicon. By the use of appropriate amounts of end-blocking agent, $(CH_3)_3SiO—$, viscosities may be prepared ranging from 0.65 centistokes to 1 million or more. These are sparkling clear fluids with an oily feel. They are soluble in aromatic and chlorinated solvents, but are poorly soluble in alcohols and in paraffins and vegetable oils. They are quite insoluble in water, but will pick up small quantities of water vapor.

Their resistance to heat and to oxidation is quite good; they are stable for long periods at 150°C in the open and at 200°C if protected from the atmosphere. They have low vapor pressure. Viscosities above 100 centistokes show a flash point of 600°F (315°C). The surface tension varies from 16 to 21, depending on the viscosity.

Electrical properties are of interest. The dielectric constant varies from 2.2–2.8, depending on viscosity. Power factor is in the order of 0.0005 up to frequencies of 10^8. They maintain an unusually constant viscosity with change of temperature. Whereas the viscosity-temperature coefficient [expressed as 1 − V 210°F (99°C)/V 100°F (37.8°C)] for a good petroleum oil is about 0.75, that for the silicone oils under consideration ranges from 0.31–0.62, depending on the viscosity.

It will be readily recognized that fluids with the properties cited would have a multitude of uses. The high degree of water repellency suggests their application for outdoor coatings and polishes. They have a marked "nonstick" property that makes them useful as release materials in plastic and rubber molding. The small change of viscosity with temperature has prompted the use of these fluids for damping and as hydraulic oils. In spite of their oily feel, they are poor lubricants for steel on steel, although with other combinations of bearing metals such as bronze on steel they are satisfactory.

Other types of fluids are prepared in which some of the methyl groups on silicon are replaced by phenyl groups. While this change of composition adversely affects the temperature-viscosity slope, it is more than compensated by depressing the freezing point from about −40 to about −90°F (−40 to −67.8°C) and at the same time provides better heat stability. They may be held at 250°C for 1,000 hr without gelation. The low-temperature characteristic allows the use of the fluid for damping at low temperature and as a low-temperature liquid that can be circulated. The high-temperature characteristic has been made use of in high-temperature baths and as a sterilizing medium.

The phenyl-containing fluids, particularly those in which the organic part is halogenated, have fair to good lubricating properties and can be used in locations where the temperature is either too high or too low to allow petroleum lubricants to function.

Silicone compounds are so named to distinguish them from the lubricating greases. They are prepared by milling into a silicone fluid a small amount of a finely divided silica. The result is a greaselike product with purely incidental lubricating properties. It possesses most of the properties of the silicone fluid except that of flow.

Various lubricating greases are formed from the fluids by the incorporation of soaps. Greases for both low (−75°C) and high (200°C) temperature are available. Typical low-temperature uses are in small exposed motors and on the free ball bearings in transits which have to operate under arctic conditions. At temperatures above 150°C the silicone greases have been found to have about ten times the life of a petroleum grease in a motor.

One of the most spectacular of the silicone products is the antifoaming material. This is prepared from a silicone fluid by the incorporation of a small amount of a special silica. The product is effective in extremely small amounts in dissipating the foam in a great variety of products. Owing to its low vapor pressure it stays with the charge when used with vacuum distillations, and because of the small amounts needed (10 ppm or less) it gives a minimum of contamination to a product.

Silicone Resins. The properties noted in the fluids are present to a large extent in the silicone resins. Both are heat and oxidation resistant, water repellent, and both have good dielectric properties.

Many types of silicone resins are prepared for many different end uses. Of these, their application in the electrical field, where they impart high temperature resistance to electrical and electronic parts and equipment, is of particular importance. Silicone-glass laminates retain their strength after long exposure to temperatures of 500°F (260°C). Certain resins are capable of being foamed in place at either room temperature or elevated temperature. They have excellent heat-insulating properties, with a heat-distortion temperature of above 700°F (371.1°C).

Silicone Rubbers. As pointed out earlier, the silicone rubbers are formed by reaction of a peroxide with a dimethyl silicone fluid. In practice, the fluid, peroxide, and appropriate inorganic fillers (titanium dioxide, zinc oxide, iron oxide, silica, etc.) are milled together. Molding at about 150°C develops the rubbery product. By alteration of the polymer and by appropriate selection of kind and amount of filler, rubbers of different types may be prepared.

The silicone rubbers differ from organic rubbers in that they retain rubbery properties over a much wider temperature span, some having a brittle point of below −130°F (−90°C) and a useful life above 400°F (210°C). They contain no plasticizers. They show marked resistance to corona discharge. Because of the presence of inorganic filler the heat transfer is good. Different stocks are made for different purposes.

There are three different types of stocks:

1. Molding stocks.
2. Pastes.
3. Room-temperature vulcanizable stocks.

In the raw form, molding stocks are heavy, relatively nonflowing materials which can be handled much like organic rubber crepes. They can be press-molded or extruded and, in fact, handled like organic rubber. The properties of the finished product vary somewhat, depending on the type of polymer and type and amount of filler used. Variations may be made in hardness, tensile strength, elongation, low-temperature flexibility, shrink upon molding, etc.

The fact that these materials have good resistance to mineral oils and to heat makes them of use as O rings, push-rod seals, valve seals and gaskets, in ovens and pressure cookers. The low-temperature flexibility has made them of use in the sealing of searchlights and bomb-bay doors. The lower-viscosity oils and solvents have a decided swelling action on most silicone rubber, but one type is now on the market which has good resistance to these reagents.

Silicone rubbers are also available as thin pastes which are suitable for application by doctor blade to cloths for the preparation of reinforced gaskets, for hose manufacture, or for application as instrument mountings. They adhere well to ceramic ware, glass, and metal and so can provide an electrically insulating coating. They can be used as calking agents in hot locations.

While the types described above all need heat for curing, a two-package product is available which cures at room temperature. Equal parts of the two components are mixed, whereupon the product sets up to a rubbery consistency. The time of set may vary from a few minutes to several hours.

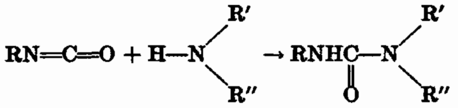
Future Possibilities. The silicone industry is a very young one, and its full potentialities are far from realized. The conventional type of polymer is constantly being improved and is finding new applications. As volume production continues to increase, the cost continues to decline, thus opening up markets that had no economic justification previously.

New types of polymers are on the horizon in which both organic and silico-organic materials will be used. Thus, there is seen the penetration of the silico-organic into the purely organic field.

ISOCYANATE POLYMERS

BY NELSON V. SEEGER[1]

Isocyantes and their simple reaction products have been known since 1849 when Wurtz[2] synthesized the first isocyanate. The great reactivity of the isocyanate was recognized when the corresponding ureas were formed by reaction with amines.



$$\mathrm{RN{=}C{=}O + H{-}N}\begin{matrix}\mathrm{R'}\\ \mathrm{R''}\end{matrix} \rightarrow \mathrm{RNH}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}N}\begin{matrix}\mathrm{R'}\\ \mathrm{R''}\end{matrix}$$

An excellent review of the synthesis and general reactions of isocyantes has been published.[3] However, it is only in recent years that their industrial potential was recognized.[4] Since 1937, a host of new polymers has been discovered based on diisocyantes and difunctional compounds such as glycols.

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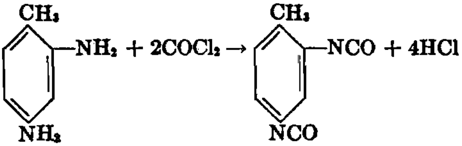
[1] Diamond Alkali Co.

[2] WURTZ, *Ann. Chem., Justus Liebig*, **71**, 326 (1849).

[3] SAUNDERS and SLOCOMBE, *Chem. Revs.*, **43**, 203–218 (1948).

[4] BAYER, *Ann. Chem., Justus Liebig*, **549**, 286 (1941); Hanford and Holmes, U.S. 2,284,896 (1942).

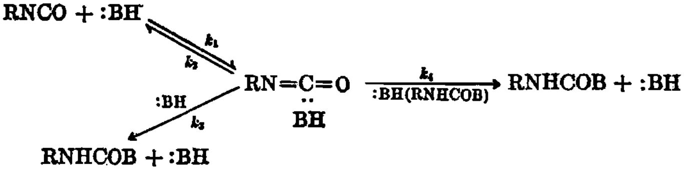
Chemistry of Isocyanates. The most important industrial process for making isocyanates is by reacting a solvent slurry of the appropriate amine or its hydrochloride with phosgene. Solvents such as toluene and *o*-dichlorobenzene have been used successfully. The following reaction occurs in the preparation of 2,4-tolylene diisocyanate, at present the one produced industrially in largest quantity:



Gas-phase processes of reacting amines and phosgene are under development. A continuous or semicontinuous liquid-phase diisocyanate reactor has also been disclosed.[1]

In general, the isocyanates will react with compounds containing an active hydrogen atom. These include water, amines, ureas, phenols, organic acids, urethanes, amides, bisulfite, and others. Reactivities of various diisocyanates differ from each other, depending on their structure. Generally, aliphatic and hydroaromatic isocyanates react more slowly than aromatic isocyanates. The introduction of alkenyl or alkyl groups into aromatic isocyanates reduces their speed of reaction, while negative groups such as chlorine and nitro strongly increase it.

It is possible to generalize the reaction of aryl isocyanates with alcohols, amines, and water.[2]



Four specific rate constants must be accounted for to explain these superficially simple reactions.

Reaction with Polyols. The diisocyanate-polyol reaction is an example of the condensation class of polymers, as described originally by Carothers.[3] The reaction proceeds without the evolution of a by-product, unless the polyol is water. For example, a simple glycol and a diisocyanate react intermolecularly as follows:

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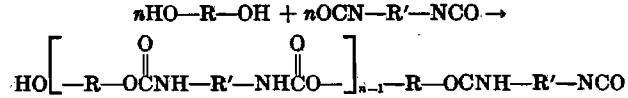
[1] Irwin, U.S. 2,683,160 (1954).

[2] Baker and Gaunt, *J. Chem. Soc.*, **1949**, **9**, **19**, **27**.

[3] Carothers, *J. Am. Chem. Soc.*, **51**, **2548** (1929).



$$n\mathrm{HO{-}R{-}OH} + n\mathrm{OCN{-}R'{-}NCO} \rightarrow$$

$$\mathrm{HO}\left[-\mathrm{R}-\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NH}-\mathrm{R'}-\mathrm{NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}-\right]_{n-1}-\mathrm{R}-\mathrm{OCNH}-\mathrm{R'}-\mathrm{NCO}$$

The process proceeds through the reaction of pairs of functional groups which combine to yield the urethane interunit linkage. Usually this functional interlink is susceptible to cleavage by reagents such as water or alcohol.

The choice of a wide variety of diglycols and diisocyanates (i.e., any type material which has two functional OH groups in its molecule as the glycolic component, and any homologue of a diisocyanate) offers the possibility to synthesize a large number of isocyanate polymers. In actual practice, the choice is limited by reason of economy and availability. The most commonly used glycolic components are of the polyester and the polyether type. The polyester glycol is made similarly to an alkyd, for example, from ethylene glycol and adipic acid. Excess glycol is used to ensure terminal —OH groups. The polyether glycols are made usually from the oxides, such as propylene oxide 1,2.

Some of the factors that influence physical properties of urethane polymers are:

1. Chemical constitution of the initial components (polyester, polyethers, and isocyanate).
2. Quantity of isocyanate used (degree of cross-linking).
3. Number of active hydrogen atoms and isocyanate groups in the starting components.
4. Reactivity of the active hydrogen atoms.
5. Reactivity of the isocyanates.
6. Bonding energy between the isocyanate group and the reactive hydrogen.
7. Type and quantity of the catalysts used.
8. Sequence in the reaction between isocyanate and polyol.

Industrially Important Polymers. Polyisocyanates are used today to make fibers, foams, elastomers, adhesives, and coatings. In the fiber field, only the linear polyurethanes,[1] Perlon U, derived from diols such as 1,4-butanediol and 1,6-hexanediisocyanate are well known.

At present, the elastic foams hold the greatest interest. They are made by reacting hydroxyl-terminated resins like castor oil, polyether glycols, or polyesters with a diisocyanate and water in the presence of a catalyst. Two simultaneous reactions occur. The first is the reaction of the diisocyanate with the hydroxyl groups in the resin, and the second is the reaction of the diisocyanate with water, liberating carbon dioxide. As the elasto-

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[1] Ger., 728,981 (1942).

meric mass forms in the first step, it becomes increasingly viscous, trapping the liberated gas and forming the foam. By changing the structure of the resin, the properties of the foams can be varied over a wide range from elastic, semirigid, to rigid.

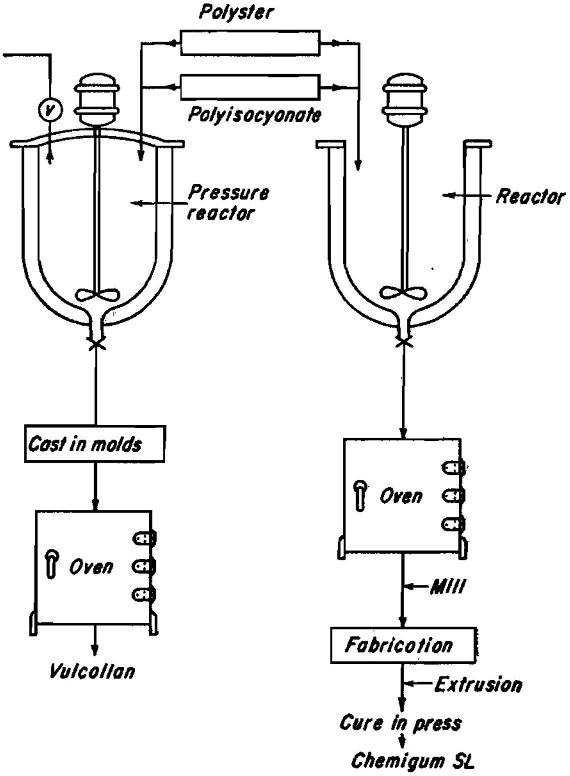

FIG. 15-30. Flow sheet for isocyanate polymer production.

Solid elastomeric urethanes are of two kinds, liquid cast[1] and millable raw-gum types.[2] The former is prepared by reacting excess diisocyanate with polyol:

$$\text{HO—R—OH} + 2\text{OCN—R'—NCO} \rightarrow \text{OCN—R'—NHCOOROCONHR'—NCO}$$

This prepolymer can then be chain extended and cross-linked with a diol, for example, 1,4-butane diol:

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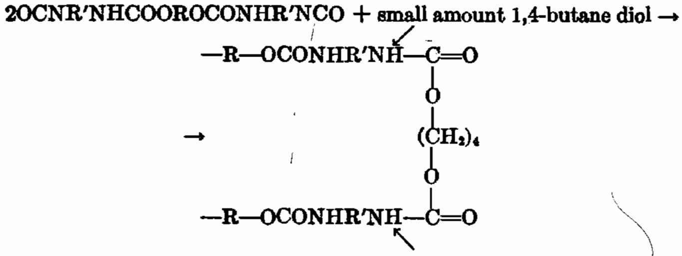
[1] BAYER, *Modern Plastics*, **24**, 149, 250 (1947).

[2] Seeger, U.S. 2,625,531, 2,625,532 (1953); Mastin and Seeger, U.S. 2,625,535 (1953).



$$2\mathrm{OCNR'NHCOOROCONHR'NCO} + \text{small amount 1,4-butane diol} \rightarrow$$

$$\rightarrow \begin{array}{l} \text{—R—OCONHR'NH—C=O} \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad \mathrm{O} \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\ (\mathrm{CH_2})_4 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad \mathrm{O} \\ \qquad\qquad\qquad\qquad\quad | \\ \text{—R—OCONHR'NH—C=O} \end{array}$$

Slanted arrows point to active hydrogen, site of possible further reactions with diisocyanate to effect cross-links.

The millable raw-gum type is made by reacting approximately equal molar quantities of polyol and diisocyanate, attaining a high molecular weight. Additional polyisocyanate is added to the rubber on a mill, and cross-linking is accomplished by heating in a mold under pressure.

Table 15-11 gives the physical properties of a urethane elastomer compared with cured natural and synthetic rubbers. One outstanding property of urethane elastomers is resistance to abrasion.

TABLE 15-11. PHYSICAL PROPERTIES OF CURED RUBBERS*

Physical properties	Chemigum SL gum stock	Natural rubber	Cold rubber black tread
Tensile, psi	5,450	3,550	2,930
Hot tensile at 200°F, psi	2,860	2,700	1,330
Elongation, %	750	790	565
Hot elongation at 200°F, %	845	950	410
Hardness (Shore A)	65	34	61
Hot cut flex, min. at 200°F	300	400+	46
Permanent set, %	4–12	3.5–4	9.5
Road wear abrasion	200	Variable	100
Hot rebound, %	84	89	70
Cold rebound, %	80	87	55.5
Schopper tear (notched), psi	2,000	1,570	846
Freezing point, °F	−38	−65	−65
Ozone resistance	Excellent	Poor	Poor
Ultraviolet resistance	Excellent	Poor	Poor

* DINSMORE, The Goodyear Rubber, Chemigum SL, *Goodyear Tire and Rubber Co. Bull.*, Apr. 2, 1954.

Another important use for polyisocyanates is in adhesives, usually as additives to rubber cements. For example, in rubber-to-metal adhesion, a chemical bond probably forms between the rubber and metal by reaction of the isocyanate groups with active hydrogens in the rubber and with the hydrated oxide layer on the metal surface.

Coatings of urethane polymers are becoming important as wire enamels, for use as metal protection against corrosion under severe conditions, and on both interior and exterior wood surfaces.

At present, the future of the isocyanate polymers appears to be one of the most promising in the chemical field.

POLYSULFIDES

By E. M. Fettes[1]

The reaction of ethylene dichloride with sodium tetrasulfide to yield rubbery polymers was discovered independently by Patrick in the United States and Baer in Switzerland. This polymer was commercially introduced in this country in 1930 under the trade-mark of Thiokol. The I.G. Farbenindustrie in Germany manufactured the product as Perduren.

The reaction of ethylene dichloride with sodium tetrasulfide proceeds with the elimination of sodium chloride. Both reactants are bifunctional and hence proceed to produce a condensation polymer of high molecular weight.

$$_nClCH_2CH_2Cl + {}_nNa_2S_4 \rightarrow (—CH_2CH_2SSSS—)_n + {}_{2n}NaCl$$

It was found that the reaction was a general one between aliphatic halogen compounds and water-soluble alkaline or alkaline-earth polysulfides. Many different organic dihalides have been found to react with sodium polysulfide to produce polymers. Commercially available dihalides include ethylene dichloride, propylene dichloride, dichloroethyl ether, triglycol dichloride, and dichlorodiethyl formal. Dichlorodiethyl formal is the chief dihalide used in the polymers produced in the United States. It is made by the reaction of ethylene chlorohydrin with formaldehyde in the presence of an acidic catalyst:

$$2ClCH_2CH_2OH + HCHO \xrightarrow{H^+} ClCH_2CH_2OCH_2OCH_2CH_2Cl + 2H_2O$$

Sodium polysulfide is usually used in the preparation of polysulfide polymers because the sodium polysulfides are inexpensive, soluble, and stable, from the monosulfide to a rank of about 4.5. Rank is defined as the value of x in the empirical formula Na_2S_x. Calcium polysulfide can be used in making polymers of tetrasulfide and higher rank. The calcium polysulfides of ranks less than 4 are not sufficiently soluble in water. Sodium polysulfides of ranks less than 2 are best prepared by the fast reaction of warm sodium monosulfide solution with sulfur:

$$Na_2S_{1.00} + 0.5S \rightarrow Na_2S_{1.50}$$

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[1] Thiokol Chemical Corporation.

Sodium polysulfides of rank 2 and higher are most readily and inexpensively prepared by the reaction of sulfur with hot (90°C) sodium hydroxide solutions:

$$6NaOH + 6S \rightarrow 2Na_2S_2 + Na_2S_2O_3 + 3H_2O$$
$$6NaOH + 10S \rightarrow 2Na_2S_4 + Na_2S_2O_3 + 3H_2O$$

The sodium thiosulfate formed as a by-product does not interfere with the polymerization and does not have to be separated and removed from the solution of sodium polysulfide.

Polymerization. The reaction of sodium polysulfide with an organic dihalide is carried out in a jacketed steel reactor with an agitator (see Fig. 15-31). The reactor should be equipped for heating with steam and cooling with water. A closed reactor is not necessary but does eliminate losses of organic dihalide by volatilization. The sodium polysulfide solution (2.0 molar) is added to the reactor, and the solution is heated to 70°C. During the heating period, solutions of magnesium chloride and sodium hydroxide are added to produce a fine dispersion of magnesium hydroxide. The magnesium hydroxide causes the polymer to form as small discrete particles instead of large chunks. A wetting agent is added also to facilitate the reaction of the insoluble organic halide with the aqueous sodium polysulfide solution. When the reaction temperature is reached, the organic halide is added slowly over a period of about two hours. The dispersion of polymer is formed slowly during this period. Cooling is necessary as the reaction is exothermic. An additional reaction time of 1 hr is used after completion of halide addition in order to ensure complete condensation.

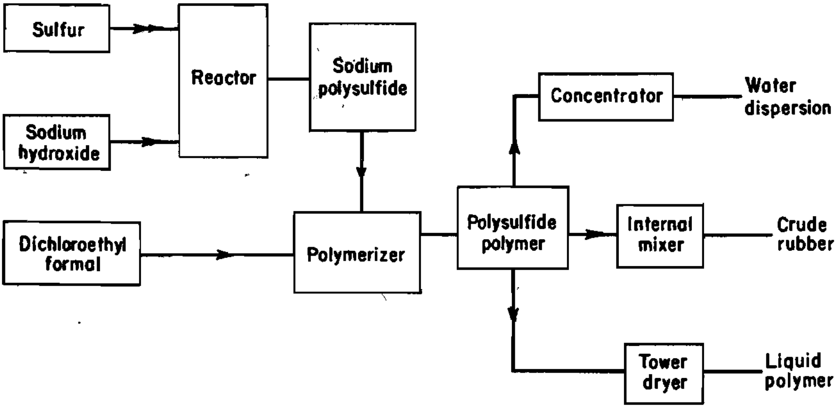


FIG. 15-31. Flow diagram for production of polysulfide polymers.

The agitation is stopped, and the polymer particles are allowed to settle to the bottom of the reactor. After 2 hr the supernatant liquid is drawn off and the polymer redispersed in clean water. This washing process is repeated until the supernatant liquid is free of inorganic salts.

The relative quantities used in the plant preparation of a branched or partially cross-linked polymer from dichlorodiethyl formal may be as follows:

	Pound moles
Sodium polysulfide ($Na_2S_{2.25}$)	1.20
Dichlorodiethyl formal	0.98
Trichloropropane	0.02
Magnesium hydroxide	0.04
Nekal BX (Na alkylnaphthalene sulfonate)	0.25

The preparation of polysulfide polymers differs from a classical condensation polymerization in that exact stochiometry of the reactants is not critical in obtaining products of high molecular weight. An excess of sodium polysulfide is used to produce a high-molecular-weight product. An excess of dihalide would yield a low-molecular-weight product with terminal chlorine groups. It has also been found that a secondary treatment of the washed latex with fresh sodium polysulfide further increases the molecular weight of the resulting polymer. The sodium polysulfide may be regarded as a coupling agent for the organic dihalide rather than a true reactant. The termination reaction is most likely the formation of hydroxyl groups by slight hydrolysis of chlorine groups by the alkaline sodium polysulfide.

The sulfur content of the polymer can be lowered as desired down to the disulfide by treatment of the washed latex with sodium hydroxide, sodium sulfide, or sodium sulfite. This technique is very useful when calcium tetrasulfide is used as the inorganic polysulfide and disulfide polymers are desired.

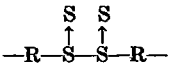
The utilization of polysulfide polymers was greatly expanded by the discovery that disulfide groups in the insoluble particles of polymer could be reduced to thiol groups by a chemical treatment. Treatment of the water dispersion with a solution of sodium sulfite and sodium hydrosulfide results in a conversion of some disulfide links to terminal thiol groups.

$$\text{—RSSR— + NaSH + Na}_2\text{SO}_3 \rightarrow \text{—RSNa + HSR— + Na}_2\text{S}_2\text{O}_3$$

The reaction is carried out in 1 hr at about 80°C. The amount of cleavage of disulfides is regulated by the amount of sodium hydrosulfide and sulfite added. Liquid polymers of a molecular weight as low as 500 can readily be made by this method.

The water dispersions of polysulfide polymer are coagulated by addition of acid. For elastomeric products, drying of the coagulum is carried out in an internal mixer or on a rubber mill with heated rolls. For liquid polymers, the fluid coagulum is passed through a supercentrifuge to reduce the water content to 5–10 per cent. The remaining water is removed in a heated drier of the falling-film type.

Structure. The polysulfide polymers are basically composed of repeating segments of the aliphatic monomer unit connected by mono-, di-, tri-, or tetrasulfide groups. Their chemical reactivity is similar to that of simple aliphatic polysulfide groups. As described, the disulfide groups can be converted to thiol groups which are capable of oxidation back to disulfide. Vigorous oxidation as with nitric acid produces sulfonic acids. The ready removal of two sulfur atoms from a polymeric tetrasulfide with aqueous solutions of sodium hydroxide fostered the belief that the sulfur atoms were arranged as in I rather than the linear arrangement II.



$$-R-\overset{\overset{S}{\uparrow}}{S}-\overset{\overset{S}{\uparrow}}{S}-R-$$

I

$$-R-S-S-S-S-R-$$

II

More recent work on the structure of organic tetrasulfides, however, strongly favors the linear structure.

No branching or cross-linking occurs during the condensation with difunctional halides. The addition of a polyfunctional halide such as 1,2,3-trichloropropane is used to produce a network structure, when desired, in the polysulfide polymers. Copolymers are readily prepared by using a mixture of halides in the initial reaction. It has been recently found that redistribution between disulfide groups occurs readily in the presence of sodium polysulfide. This mechanism is similar in results to ester interchange. A copolymer will, therefore, be a random copolymer rather than a block copolymer.

The properties of the commercial polysulfide polymers manufactured in the United States are summarized in Tables 15-12, 15-13, and 15-14. Table 15-12 shows the characteristics of the crude rubbers and Table 15-13 those of the water dispersions.

TABLE 15-12. POLYSULFIDE CRUDE RUBBERS

Thiokol	Halides	Mol. %	Rank	Terminals
Type A....................	Ethylene dichloride	100	4.0	Hydroxyl
Type FA..................	Ethylene dichloride	50	1.8	Hydroxyl
	Dichloroethyl formal	50		
Type ST..................	Dichloroethyl formal	98	2.25	Thiol
	Trichloropropane	2		

TABLE 15-13. POLYSULFIDE WATER DISPERSIONS

Polymer	Halide Component	Mol. %	Rank	(Microns) Particle Size	Terminals
Type MX	Ethylene dichloride	75	2.0	2–6	Hydroxyl
	Propylene dichloride	25			
WD-6	Ethylene dichloride	67	2.0	2–6	Hydroxyl
	Propylene dichloride	33			
Type MF	Ethylene dichloride	67	3.0	4–8	Hydroxyl
	Dichloroethyl formal	33			
WD-2	Dichloroethyl formal	99.5	2.25	8–15	Hydroxyl
	Trichloropropane	0.5			

TABLE 15-14. COMMERCIAL LIQUID POLYSULFIDE POLYMERS*

Property	LP-2	LP-3	LP-8	LP-32	LP-33
Molecular weight (avg)	4,000	1,000	500	4,000	1,000
Viscosity, poises at 25°C	400	10	3	400	15
Pour point, °F	+45	−10	−20	+50	−10
Mole %, trichloropropane	2	2	2	0.5	0.5

* These polymers are all based on dichlorodiethyl formal with either 0.5 or 2.0 mole per cent trichloropropane.

Curing and Compounding. There are two distinct classes of polysulfide polymers with respect to methods of vulcanization. The high-molecular types with terminals introduced during the polymerization reaction are one class. This includes Thiokol Types A and FA as well as the water dispersions. The other class comprises polymers which are treated to reduce disulfide linkages to thiol groups. This class includes Thiokol Type ST and all the liquid polymers.

The crude rubbers of high molecular weight with terminal hydroxyl groups are too tough to be processed on a rubber mill. It is necessary to add materials such as benzothiazyl disulfide or tetramethylthiuram disulfide to soften the polysulfide polymers chemically by a scission of long polymeric chains. These complex disulfides are widely used as accelerators of vulcanization of hevea and synthetic rubbers made from dienes, but they do not perform this function with polysulfide rubbers. An organic amine will promote the rate of softening of these disulfides, and diphenyl guanidine is commonly used. Zinc oxide is the actual vulcanizing agent for this type of polymer. It reverses the chemical plasticization and has an additional hardening effect on the polymers. The mechanism is not known with any certainty, but it appears to involve reaction of the terminal hydroxyl groups.

The rubbers and liquid polymers with thiol terminals are adjusted during manufacture so as to be of proper molecular weight for processing: the rubbers on a rubber mill and the liquid polymers on a three-roll paint mill. Curing is accomplished by incorporation of oxidizing agents which can couple two thiol groups together to form a disulfide link. The selection of suitable oxidizing agent is determined by the rate and temperature of cure desired for the particular application. Both inorganic and organic oxidizing agents have been used such as lead peroxide, zinc peroxide, cumene hydroperoxide, and benzoquinone dioxime.

The water dispersions are chiefly used in coatings and sealants and do not require vulcanization. In most cases it is necessary to soften the high-molecular-weight polymer to obtain a coating which will form a continuous film. Either ammonium hydrosulfide or tetramethylthiuram disulfide can be used in small quantities to accomplish this. The film after drying returns gradually to the original tough rubber.

As is true for most rubbers, the physical properties of cured polysulfide polymers are poor unless reinforcing fillers are used. The semireinforcing blacks are best, and are the main fillers usually employed. Zinc sulfide, titanium dioxide, calcium carbonate, and lithopone all are useful for reinforcing white or light stocks. In general, the same fillers are used in polysulfide rubbers as in the other synthetic rubbers.

Properties and Applications. The polysulfide polymers have excellent resistance to swelling by liquid fuels and solvents. In general, the solvent resistance is greatest in the polymers containing the greatest amount of sulfur. The polymers are resistant to oxygen and ozone and are relatively impermeable to gases and vapors. The uses and applications for the crude rubbers are based on utilizing these properties. The tensile strength, abrasion resistance, and heat resistance are lower than in the diene elastomers. The earlier rubbers had a strong odor, although this has been overcome in some of the newer polymers. The poor resistance to compression at extended time and temperatures has been overcome to a large extent by incorporation of polyfunctional halides in the polymerization to produce a network structure in the polymer.

The chief uses of the polysulfide crude rubbers are in (1) rollers for applying ink, paint, and lacquer; (2) hose to carry gasoline, solvents, and paint; (3) putties for metal, glass, plastics, and wood; (4) paper coatings for gaskets; (5) plasticizer for sulfur cements; (6) molded compounds in contact with fuels; and (7) fabric coatings for diaphragms.

The water dispersions are used mainly in putties and in coatings. Water-based putties have been used in sealing the joints in aircraft fuel tanks. The coatings are useful for resistance to corrosion and to wind and sand erosion. An important use is to seal concrete storage tanks to prevent leakage and deterioration of the gasoline by contact with the concrete. Recent developments have shown the best system to be a combination of polysulfide polymer with a copolymer of vinyl chloride and vinylidene chloride.

The liquid polymers have the additional advantage of ease of application. They can be converted with little shrinkage from a solvent-free liquid to a firm rubber even at room temperature. They can be utilized in many applications where conventional rubbers could not be applied. These uses include (1) impregnation of leather for many mechanical uses, (2) cast rollers for printing, (3) sealing compounds for fuel tanks, (4) calking compounds for concrete, metal, and wood, (5) flexible molds, (6) potting compounds, and (7) adhesives.

The reactive nature of the terminal thiol group of the liquid polymer makes these materials useful in modifying resins. The liquid polymers can be added to phenolic and epoxy resins to produce flexibility and resistance to impact. The final products are coreacted rather than being a mechanical mixture of two polymers. The liquid polymers have been used in phenolic adhesives and coatings. They are used with epoxy resins for making casting and potting compounds, adhesives, coatings, and laminates.

POLYETHYLENE

BY H. E. TIEFENTHAL AND J. J. KILLORAN[1]

Ethylene is basic to the American petrochemical industry and is one of the most important of all chemical raw materials. Approximately 2.2 billion lb of ethylene was produced in 1953, 2.4 billion lb in 1954, and 2.9 billion lb in 1955. It was conservatively estimated that this figure would reach 3.2 billion lb by 1956 and 4.0 billion lb by 1960. About 10 per cent of the ethylene produced in 1953 was recovered from the off-gases from refineries that crack petroleum stocks. Most of the remaining 90 per cent was derived, in roughly equal amounts, from the pyrolysis of propane and of ethane recovered from natural and refinery gases. A minor proportion was produced by the dehydration of ethanol.

Fundamentally, the manufacture of ethylene involves two principal operations: (1) the formation of ethylene and (2) separation from other materials present. There are at least eight well-recognized methods for the formation of ethylene, and at least five processes have been employed for its separation and purification. Present processes for the formation of ethylene depend upon either the pyrolytic or the catalytic conversion of paraffinic hydrocarbons. Those most generally used in this country employ

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[1] Koppers Company, Inc.

the high-temperature pyrolysis of petroleum fractions. The process most commonly used in this country for the separation of ethylene involves fractionation of the cracked gases under high pressures and at low temperatures. Ethylene for the manufacture of polyethylene must be essentially free of impurities which are known to affect the course of the reaction and the properties of the resultant polymers.

Ethylene Polymerization. Polyethylene was originally prepared by decomposition of diazohydrocarbons. Later some other interesting methods were developed, such as the action of sodium on decamethylene bromide, the Fisher-Tropsch and related syntheses, and the reduction of polyvinylchloride. However today's major processes for the industrial production of polyethylene are based solely upon the polymerization of ethylene itself. The products of these processes include liquids, greases, hard and soft waxes, and thermoplastic solids. In this section, polyethylene will refer to high-molecular-weight thermoplastic solids only. This type of polymer may be prepared by high-pressure processes or by low-pressure processes. The former are reported to be adaptable to the preparation of flexible, semirigid, and rigid polyethylenes, while the latter yield semirigid and rigid polyethylenes. It is likely that flexible polyethylenes can also be prepared by the low-pressure processes.

High-pressure Processes. Early attempts to polymerize ethylene directly resulted mainly in its conversion into various gases, liquids, and mixtures of these by exceedingly complex reactions. A very extensive series of investigations on the high-pressure, high-temperature polymerization of ethylene led to a process for the preparation of a solid reaction product.

Industrially, this polymerization process is carried out in high-pressure autoclaves at pressures of 15,000–30,000 psi and temperatures of 150–300°C. In a recently published flow diagram (Fig. 15-32) this polyethylene manufacturing process is shown to require high-purity ethylene, and the first step is to purify the plant product. This high-purity ethylene is mixed with small percentages of oxygen (0.02–0.08 per cent) which serve as the catalyst. The mixture is then heated to 150–300°C and fed to a stainless-steel tubular reactor which is controlled to maintain the reaction at 150–300°C. The effluent from the reactor passes to a separator in which unconverted ethylene is removed and recycled to an intermediate stage of the process. The liquid from the separator is polyethylene. It is chilled quickly, and the solidified product is chopped and passed on to such processing steps as milling, rolling, compounding, and pelletizing.

Even though oxygen in small percentages catalyzes the reaction effectively, many other initiators have been disclosed, including peroxy compounds, ozonides, azo compounds, azines, amine oxides, oximes, hydrazines, and hypohalites. The polymerization reaction is highly exothermic and requires strict control and elaborate safety measures in order to prevent explosive decomposition of the ethylene. In general, the molecular weight of the polymer can be controlled by the reaction conditions. The purer the ethylene and the higher the pressure, the higher the molecular weight and melting point of the resultant products. The higher the oxygen content and the higher the temperature, the more vigorous the polymerization reaction and the lower the degree of polymerization. These flexible polyethylene resins have densities up to 0.925, whereas newly announced modifications of the high-pressure process give semirigid polyethylenes having densities in the 0.925–0.940 range.

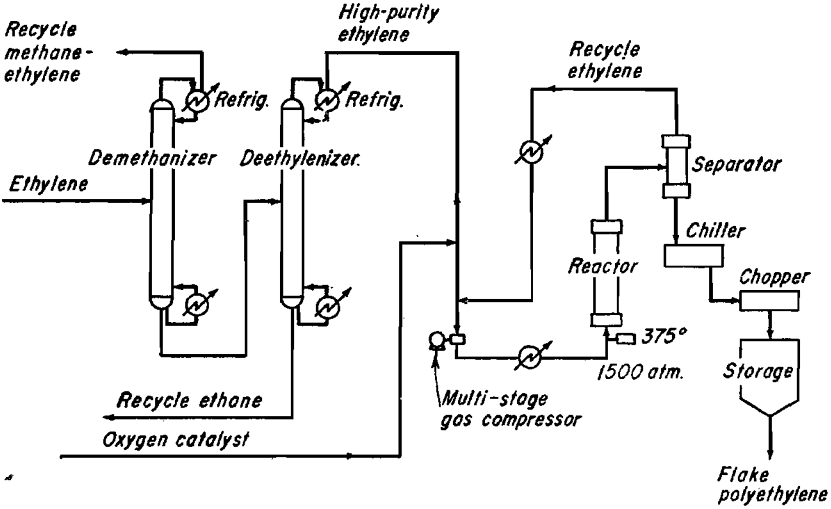

FIG. 15-32. High-pressure polyethylene process. (*Courtesy Koppers Co.*)

Low-pressure Processes. Three processes for the polymerization of ethylene have recently been developed. The commercial process of the Phillips Petroleum Company for the polymerization of ethylene is carried out at relatively low pressures (100–500 psi) in either fixed-bed or slurry-type operations. The catalyst consists of 2–3 weight per cent chromium as oxide on silica alumina, and the reaction temperature varies from 90—180°C. In fixed-bed operation, purified ethylene and hydrocarbon solvent streams are passed downflow, liquid phase over the catalyst bed. Solvent and polymer are collected, and the solvent is flashed overhead. Unreacted gases are removed from the solvent, taken overhead, and metered; the solvent is recycled to the reactor. The solvent and polymer in the first receiver are cooled to room temperature to precipitate the polymer, which is then filtered and dried in a vacuum oven. In the slurry-type operation (indicated in Fig. 15-33 by a proposed flow diagram), solvent and a small amount of fine catalyst (0.2–0.6 weight per cent of solvent) are charged into the reactor, the reactor is closed, and ethylene feed is started. Ethylene pressure is permitted to build up to 400–500 psi in less than an hour. At the end of the reaction period, the polymer is removed, dissolved in additional solvent, and filtered to remove catalyst. Polymer is recovered from the filtrate by cooling to cause precipitation and then filtered and dried. Variations of this process produce polyethylene resins with densities from 0.91–0.965.

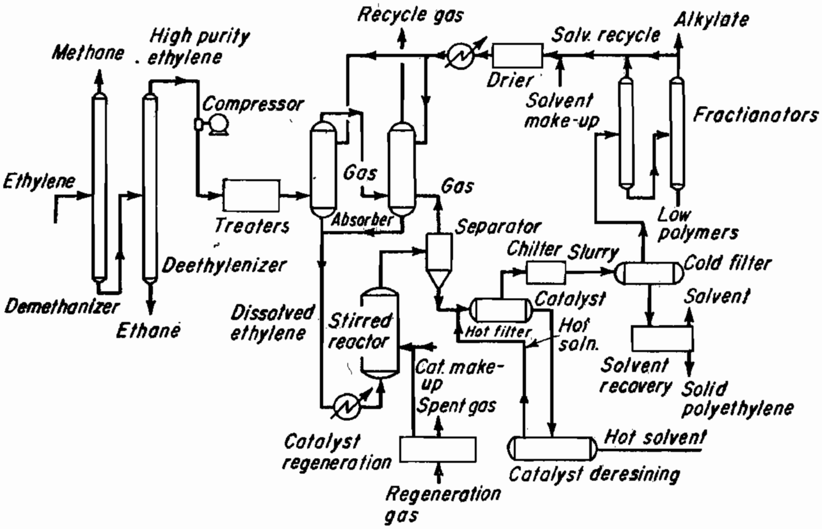

FIG. 15-33. Low-pressure polyethylene process (Phillips). [*Petroleum Refiner* **34**, 179 (1955).]

Recent patent disclosures by the Standard Oil Co. of Indiana indicate that their process for the polymerization of ethylene is also a relatively low-pressure process, and the following process information is based on these disclosures. The polymerization process is a fixed-bed process employing a prereduced catalyst, ethylene pressures of 800–1,000 psi, and temperatures somewhat greater than 200°C. The metal oxides (such as nickel, cobalt, and molybdenum) can be supported on either charcoal or alumina, and materials such as lithium aluminum hydride, boron, alkali metals, and alkaline-earth hydrides may be used as promotors. Variations of this process are reported to produce polyethylene resins with densities from 0.94–0.97.

In the third industrial process, a Ziegler type of ethylene polymerization, the catalyst can be prepared by adding diethylaluminum chloride (activator) and titanium tetrachloride (cocatalyst) to a dry hydrocarbon solvent under an inert atmosphere. The catalyst is subsequently transferred to a dry, well-purged 5-liter flask and diluted with more solvent. Ethylene is added to the rapidly stirred catalyst mixture at atmospheric pressure. The temperature rises from 20°C to 60–70°C in about ten minutes, and can be maintained at about 70°C by cooling the reactor with an air blast. After 30–40 min, alcohol is added to deactivate the catalyst, and the polyethylene powder is separated from the solvent by filtration and drying.

The patent structure surrounding the Ziegler process indicates that the activator can consist of hydrides, alkyls, or aryls of beryllium, aluminum, gallium, indium, lithium, magnesium, and zinc, and that the cocatalyst can be a compound of one of the transition elements of groups 4, 5, and 6 (e.g., titanium tetrachloride).

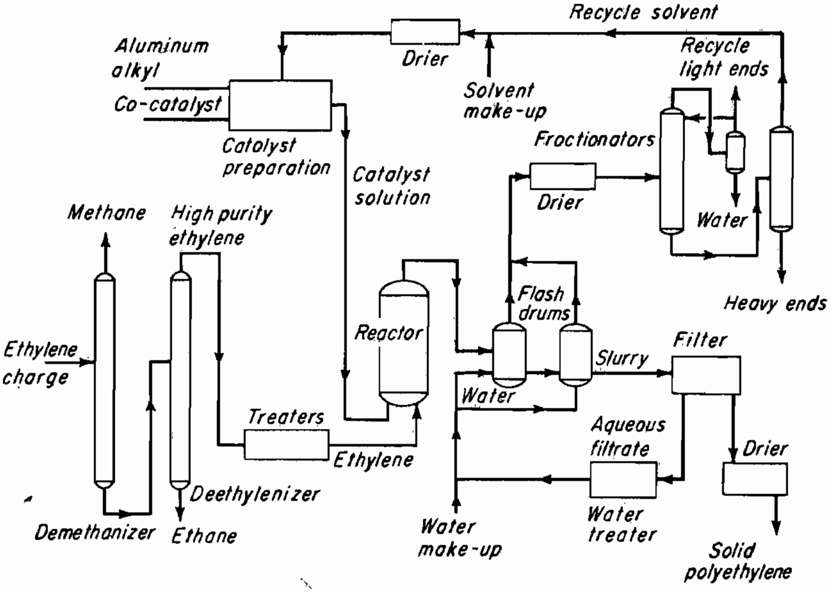

FIG. 15-34. Low-pressure polyethylene process (Ziegler). [*Petroleum Refiner* **34,** 179 (1955).]

The general principles of a unit designed to produce Ziegler polyethylene are shown in the proposed flow diagram, Fig. 15-34. A small amount of the dual catalyst, prepared in a carefully dried paraffinic solvent, is charged to the reactor. High-purity ethylene is then charged to the reactor to maintain a reactor pressure in the range of 15–100 psi. The temperature is maintained at 60–75°C. The reactor product is sent to a series of flash drums to remove the solvent and precipitate the polymer. Water is added to the flash drums to destroy the residual catalyst and remove the polyethylene as a slurry. The polymer is removed from this slurry by filtration and drying. These semirigid to rigid polyethylene resins have densities in the range from 0.93–0.96.

Polyethylene Structure. All polyethylenes have the empirical formula $(CH_2)_n$, and molecular-weight determinations classify them as true polymers. Since polyethylenes prepared by the different processes have markedly different properties, it may be inferred that structural differences are of practical importance. Furthermore, all polyethylenes possess a more or less developed crystalline structure. Commercial polyethylenes range in crystallinity from 40 to 95 per cent. Decomposition of diazomethane gives a straight-chain polymer, polymethylene $[n(CH_2N_2) \rightarrow (CH_2)_n + {}_n(N_2)]$, which is almost completely crystalline; on the other hand, the decomposition of diazomethane in the presence of small quantities of its homologues (such as diazoheptane or diazooctadecane) yields products resembling the flexible polyethylenes. Other homologues, such as diazoethane and diazopropane, decompose into highly branched polymers which are entirely amorphous. Also, polyethylene molecules with the fewer number of branches have the greater tendency to pack more closely together and thus have more favorable opportunities to form crystallites. Lesser chain branching, therefore, means a higher degree of crystallinity and a higher density. In addition, if the chains are sufficiently long and the crystallites sufficiently numerous, one molecule may pass through several amorphous and crystalline regions. Since the latter are points of reinforcement, the polymer will behave as though it were made up of much longer chains than it really is. Polymethylene has the highest density, approaching 1.0, and the flexible polyethylenes have the lowest, ranging from 0.91–0.925. The semirigid polyethylenes range in density from 0.925–0.94, and the rigid polyethylenes range in density from 0.94–0.97. For a given sample, crystallinity of a flexible polyethylene decreases from an original 55 per cent between 0 and 70°C to 10 per cent between 70–115°C, the latter being the melting point of the sample.

The structure of the crystalline regions of polyethylene has been established in detail by x-ray crystallography as being very similar to that of a solid low-molecular-weight paraffin; the unit cell is orthorhombic with $a = 7.40$ A, $b = 4.93$ A, and $c = 2.53$ A; the molecules are lying fully extended in parallel planes. The molecular skeleton forms a zigzag of carbon atoms, with a zigzag angle of 112° and an aliphatic C-C distance of 1.53 A. Examination of suitably prepared thin films of polyethylene between a crossed Nicol prism in a polarizing microscope shows the existence of birefringent regions typical of spherulitic aggregations of crystals. A spherulite consists of a large number of crystals radiating in all directions from a point, a particular direction of each crystal being consistently along a radius of a sphere. Spherulites can be seen only in polyethylenes having an average length of over 300 carbon atoms, and polyethylenes with the least-branched molecular structure show the largest spherulites. Other factors affecting spherulite size are thermal history and mechanical working. The microstructure of polyethylene can be altered physically by cold drawing, resulting in orientation of the crystalline regions with an attendant increase in tensile strength.

Infrared-absorption techniques show that the main difference between the spectrum of polyethylene and that of a linear high-molecular-weight polymethylene is the presence of bands with intensities varying from sample to sample, indicating the presence of methyl groups and of olefinic groups of the terminal-vinyl type ($RCH{=}CH_2$), internal-trans type ($RCH{=}CHR'$) and the branched-vinyl type ($RR'C{=}CH_2$). One must assume that the presence of branching is responsible for the observed methyl-group concentrations in substantial excess of that attributable to reasonable molecular weights. Flexible polyethylenes have olefinic structures that are predominantly of the branched-vinyl type. On the other hand, the rigid polyethylenes have the terminal-vinyl type and/or the internal-trans type. Total unsaturation in the polyethylenes is very low, ranging from 0.5–1.5 double bonds per thousand carbon atoms. It is probable that polyethylenes containing trans-olefinic groups are polymers of lower crystallinity and density because such groups break the regularity of the chain and obstruct spatial ordering of the molecules.

Irradiation of polyethylenes with beta and gamma radiation causes both chain cleavage and cross-linking. Depending on the radiation dosage, the polymer may become infusible and also insoluble in organic solvents. Partial to complete destruction of the crystalline region of the polymer occurs. The increase in tensile strength, hardness, and density of irradiated polyethylene is attributed to the formation of cross-linkages, which cause tighter packing of the polymer molecules.

A number of the physical and mechanical properties of polyethylene are directly affected by the crystallinity and hence by the degree of branching. Examples are hardness, softening point, and yield point in tension. On the other hand, some properties, such as tensile strength and flexibility at low temperatures, are principally a function of the average molecular weight and molecular-weight distribution of a particular polyethylene sample. The wide range of types of polyethylenes is a reflection of the wide variation in molecular weight, molecular-weight distribution, and degree of chain branching and, hence, in crystallinity, which can be produced by the various polymerization processes.

Polyethylene Properties. Polyethylenes are colorless materials, practically tasteless and odorless, and physiologically unobjectionable. They are among the most inert and stable of polymers. Polyethylenes are practically insoluble in all solvents at ordinary temperatures, are resistant to acids and alkalies, but are attacked by concentrated oxidizing acids. Most of the solvents which dissolve the flexible polyethylenes at 80°C only swell the rigid polyethylenes at the same temperature. Some polyethylenes develop a defect that is called stress or environmental cracking in strained sections, such as in pipes or cable insulations. This tendency is enhanced by the presence of mobile polar liquids. Stress cracking diminishes with increasing molecular weight but is more pronounced in the rigid polyethylenes than in the flexible polyethylenes.

As to other properties of polyethylene, reference is made to Table 15-15. The basic properties of the polyethylenes such as crystallinity, rigidity, softening temperature, and tensile strength increase as the density increases. Elongation and impact strength show an inverse variation with density; however, it must be considered that these properties are also dependent upon chain length. Molten polyethylene of high molecular weight shows non-Newtonian flow; the viscosity appears to decrease as the pressure increases, thus the flow rate increases. The melt viscosity decreases as the temperature is increased. The rigid polyethylenes, density 0.96, soften at 125–130°C compared to 100–115°C for the flexible polyethylenes, density 0.92. At these temperatures where fusion may begin, the polymer is still quite viscous and a higher temperature is required for extrusion and molding. The flexible polyethylenes respond to temperature increases with greater increases in flow rate than do the rigid polyethylenes.

Polyethylene Processing. Polyethylene has found widespread application in a variety of fields. Polyethylene films for food packaging have the advantage of very low moisture transmission combined with a relatively higher gas permeability. Next to polyethylene film, injection molded articles have exhibited the fastest growth, especially in the field of plastic housewares. Monofilaments from extruded polyethylene are particularly interesting since their tensile strengths can be controllably increased by cold drawing. The excellent electrical properties of polyethylene make it outstandingly well suited for insulation of wires and cables. Tubes and pipes offer a vast potential field, particularly for the rigid polyethylenes which exhibit enhanced heat resistances and high bursting strengths. Polyethylene has also been found to be useful for many applications in the field of surgery.

Halogenated Polyethylenes. Some halogenated ethylenes were successfully polymerized. Polymers of tetrafluoroethylene and trichlorofluoroethylene, as well as other halogenated ethylenes, have been introduced on the American market and have found most interesting technical applications. The outstanding characteristic of these polymers is their remarkable resistance to heat and to practically every generally used chemical agent. Softening ranges of 350°C and higher permit the employment of these

TABLE 15-15. PROPERTIES OF COMMERCIAL POLYETHYLENES*

Property Units	ASTM test method	Flexible high-pressure polyethylenes	Semirigid high-pressure polyethylenes	Rigid polyethylenes		
				Phillips Marlex 50	Ziegler types	Standard Oil
Mechanical Properties:						
Elastic modulus in tension, psi	D638–52T	14,000–35,000	......	......	50,000–100,000	
Yield point, psi	D638–52T	1,200–1,800	......	......	2,800–3,500	
Tensile strength, psi	D638–52T	1,200–2,800	1,600	4,000–4,500	2,800–5,500	
Total elongation, %	D638–52T	400–650	100–410	20–30	100–800	
Stiffness in flexure, psi	D747–50	11,000–27,000	50,000	140,000	50,000–125,000	75,000
Impact strength, Izod, ft-lb/in.	D256–54T	No break	......	3.0	1–5	
Impact strength, unnotched, ft-lb/in.	†	No break	......	......	>30	>16
Physical characteristics:						
Specific gravity 23°C/23°C, relative to water	D792–50	0.91–0.925	0.925–0.94	0.96	0.93–0.95	0.96
Crystallinity, %	‡	40–60	65–75	93	65–85	83
Water-vapor permeability, sq cm/sec-atm $\times 10^{-8}$		40–60	......	......	15–30	
Gas permeability CO_2, sq cm/sec-atm $\times 10^{-9}$		8–11	......	1.6	1.8	
Thermal properties:						
Melt index, g/10 min	D1238–52T	0.2–30	0.7–12	0.6	0.1–4.0	0.24
Melting point of crystallite, °C	§	108–116		126–135	126–135	135
Brittleness temperature, °C	D746–55T	−80 to −55	< −70	< −118	< −140 to −100	−105
Flammability, in./min	D635–44	1.0–1.5	......	1.04	0.9–1.1	
Heat capacity, cal/°C-gm		0.5–0.55	......	......	0.55	
Thermal conductivity, cal/cm-sec °C $\times 10^{-4}$	C-177–45	6–8	......	......	ca. 10	
Electrical properties:						
Dielectric strength (short time), volts/mil	D149–55T	430–570	430–570	510	500–700	
Dielectric constant (10^6 cycles)	D150–54T	2.3–2.4	2.3–2.4	2.35	2.2–2.3	
Specific resistance, ohm-cm	D257–54T	$>10^{15}$	$>10^{16}$	$>10^{16}$	$>10^{15}$	

* Data from manufacturers' bulletins.

† Method similar to ASTM D256–54T but specimen not notched.

‡ X-ray diffraction technique.

§ Polarizing microscope technique.

plastics for many purposes where other polymers so far had been found unsuitable because of their considerably lower softening points.

The use of halogenated polyethylenes for injection or compression molding is somewhat restricted because of the high temperature at which the injection and compression machines have to operate. However, thin sheets and films can be obtained without major difficulties by calendering processes. Depending on their thickness, the films and sheets are more or less translucent and pliable and resemble those of polyethylene in their appearance and elastic behavior. They are extensively utilized for protective packaging, for gasket material and, generally, in applications where their chemical and heat-resisting characteristics make the high material cost justifiable.

Future Development. The producing capacity for all polyethylenes in 1960 has been estimated at 830 million lb, of which 585 million will be high-pressure and 245 million will be low-pressure polymer. Experts foresee an advantage to the customer in having a wide array of properties and expect that the various types of polyethylene will augment each other in meeting consumer requirements without becoming particularly competitive.

"VINYL" POLYMERS

Though in a strict sense vinyl polymers are all those made from vinyl-type monomers, $CH_2{=}CHX$ where X can be any substituent, the term is used in industry and commerce as meaning mainly polymers made from vinyl chlorides and from vinyl acetate. Included are also the copolymers of these two monomers and those polymers which are derived from polyvinyl acetate, namely, polyvinyl alcohol and polyvinyl acetals. Polymers from vinylidene chloride, vinyl ethers, vinylpyrrolidone, and vinylcarbazol are also grouped loosely into this class.

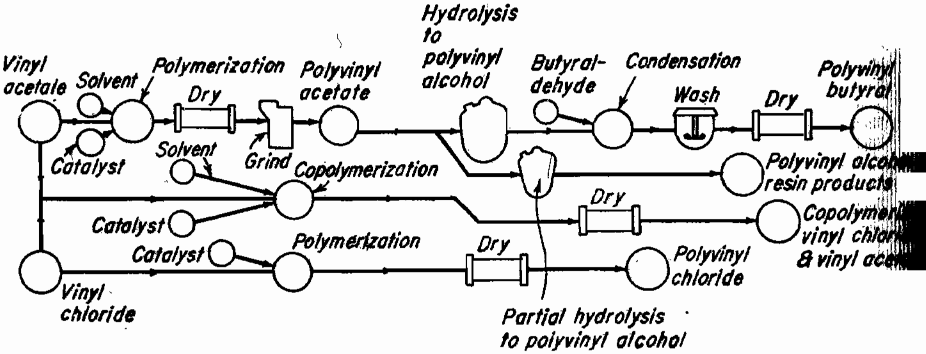

FIG. 15-35. Flow sheet for the production of polyvinyl acetate, polyvinyl acetal, polyvinyl chloride, and copolymer of vinyl chloride vinyl acetate.

Polyvinyl Chloride. Vinyl chloride monomer is produced industrially by three processes:

1. By direct addition of HCl to acetylene:

$$CH{\equiv}CH + HCl \xrightarrow{HgCl} CH_2{=}CHCl$$

2. By controlled chlorination of ethylene and subsequent removal of HCl:

$$CH_2{=}CH_2 + Cl_2 \rightarrow CH_2Cl{-}CH_2Cl \xrightarrow{-HCl} CH_2{=}CHCl$$

3. By reaction of ethylene chloride with NaOH:

$$CH_2Cl{-}CH_2Cl + NaOH \rightarrow CH_2{=}CHCl + NaCl + H_2O$$

Of these, the two first methods are at present most widely employed.

The polymerization of the gaseous monomer (bp, 13.9°C) can be performed in solution, in emulsion, and in suspension; the polymer is obtained in the form of a fine powder. It is only difficulty soluble, and elevated temperatures and special solvents such as chloronaphthalene, dibutyl phthalate, tricresyl phosphate, and benzyl benzoate must be employed. In order to achieve better solubility in a larger number of solvents, the polymers are often subjected to further treatment, which consists in an afterchlorination,[1] a treatment with acids,[2] or milling. Increased solubility of the polymer is also attained by solution polymerization at high pressures and temperatures.[3] Polyvinyl chloride is insoluble in its own monomer.

Polyvinyl chloride can be used for molding and extruding purposes. The temperature employed in these operations varies in accordance with the softening range of the polymer, which, in turn, is dependent upon its chlorine content. Normal polyvinyl chloride contains 53–55 per cent chlorine and softens at approximately 80°C, whereas strongly afterchlorinated material with a content of 68.5 per cent chlorine softens only at about 140°C.[4] All extruding and molding operations have to be carried out below the temperature at which the polymer begins to decompose (approximately 140–160°C). In order to improve the flow properties of the polymer at these lower temperatures, it is necessary to add plasticizers, which can be incorporated on hot rolls up to 70 per cent of the total weight. Highly plasticized polyvinyl chlorides are of rubbery consistency and have found widespread use in applications where elastic properties are needed in addition to good resistance to chemicals, mold, and weather. For other industrial uses, moderately plasticized polyvinyl chloride is rolled out on calenders in the form of foils and sheets or extruded into pipes and small tubes. Polyvinyl chloride is not inflammable and can therefore be worked with an open flame, thus allowing easy joining and welding operations. Fibers and yarns of afterchlorinated polyvinyl chloride have also been developed and have served for the preparation of filter cloth, fishing nets, and similar purposes.

Recently, so-called "plastisol" fabricating techniques have been developed which allow the cheap and efficient manufacture of many articles from polyvinyl chloride. Plastisols are dispersions of polyvinyl chloride in appropriate solvent mixtures or in plasticizers. Molds are either coated by

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[1] U.S. 2,080,589 (1937); Brit. 401,200; Fr. 755,048.

[2] Ger. 647,116.

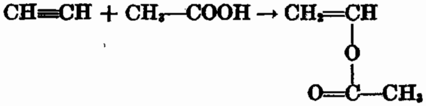
[3] Brit. 377,653; Fr. 709,562.

[4] Fr. 828.077.

plastisols or they are filled with the liquids and then drained so that only a lining of plastisol remains. In any case the conversion of the liquid plastisol to an elastic solid is achieved by raising the temperature to 350–400°F whereby fusion of the polyvinyl chloride takes place.

The presence of plasticizers in molded or extruded polyvinyl chloride items is often undesirable, particularly so if high corrosion resistance, strength, hardness, and chemical resistance are of importance. Rigid polyvinyl chlorides, with no plasticizer present, have therefore been developed which are employed most satisfactorily in a variety of applications.

Polyvinyl Acetate. Vinyl acetate is formed by the addition of acetylene to acetic acid in the presence of mercuric salts.



$$CH{\equiv}CH + CH_3{-}COOH \rightarrow CH_2{=}CH{-}O{-}C({=}O){-}CH_3$$

The monomer can be polymerized in solution, in emulsion, or in suspension. According to the method of polymerization chosen and to the particular conditions of the reaction, polymers of varying average molecular weight are obtained that differ appreciably in their properties.

Before polymerizing vinyl acetate, the monomer must be freed of metal and sulfur compounds which inhibit or retard the polymerization and are among the main reasons for a low-molecular-weight product. Acetaldehyde is usually present from the preparation of the monomer and, when found in amounts of 0.5 per cent or more, appreciably decreases the average molecular weight of the polymer. In solution polymerization, the choice of the solvent greatly influences the average molecular weight of the polymer obtained. On the other hand, the polymerization degree of a product prepared by emulsion and suspension polymerizations is controlled preponderantly by the temperature and the amount of catalyst added.

Polymers having a number-average molecular weight between 50,000 and 100,000 are soluble in a wide range of solvents, except water, benzene, and aliphatic hydrocarbons. The higher the molecular weight, the more difficultly soluble they become. Equally dependent on molecular weight is their behavior at increasing temperature. Low-molecular polymers begin to flow between 30 and 40°C, but products of an average molecular weight of approximately 100,000 become rubbery at temperatures of about 100°C. They decompose at 200°C, splitting off acetic acid and leaving an insoluble and infusible resin as a residue. Their behavior both in solvents and at higher temperatures indicates that either branching or cross-linking of the chain molecules may have taken place during the formation of high-molecular-weight polymers.

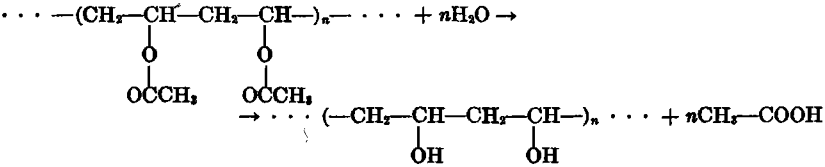
The properties of polyvinyl acetate limit its usefulness for molding and extruding operations. However, the fact that polyvinyl acetate is compatible with nitrocellulose, exhibits a strong tendency to adhere to glass and metal surfaces, and has a satisfactory light stability assures a substantial market for all grades. An important field of application is that of adhesives for use in the textile and leather industry, where the polyvinyl acetate is employed mainly in the form of aqueous emulsions (latex). Because of their light stability and good aging characteristics, vinyl acetate emulsions are the base for excellent emulsion paints for interior and also exterior application. Polyvinyl acetate is also used in the production of safety glass, in which it serves as an interlayer and adhesive between two glass plates. Most important for industry is the property of polyvinyl acetate to undergo hydrolysis partly or completely and thus serve as a starting material for a whole series of polyvinyl alcohols and polyvinyl acetals.

Copolymer of Vinyl Chloride–Vinyl Acetate. A series of copolymers of these two monomers can be prepared which differ in solubility, molding characteristics, and chemical stability according to the relative proportions of the monomers used and the average molecular weight obtained. The materials that are most important industrially contain between 85 and 95 per cent vinyl chloride and have an average molecular weight of 10,000–30,000. The polymerization procedure can be carried out either in solution or suspension, depending on the final use to which the copolymer is put. If a completely transparent product is desired, a polymerization in solution, which may be carried out as a continuous process, is preferred. According to this procedure, the monomers are placed in a mixture of solvents that acts as precipitant for the polymer while dissolving the monomers completely. In this way the polymer formed can be continuously removed from the reaction mix, and new monomer and solvent mixture may then be added to restore the original proportions. The vinyl chloride-vinyl acetate copolymers so obtained show a narrower distribution curve than those resulting from a straight solution copolymerization. The reason for this seems to be that the low-molecular-weight copolymers formed remain dissolved in the solvent mixture, and thus a partial fractionation of the precipitated copolymer is automatically achieved.

The principal technical applications for the copolymers are in the following fields: (1) molding and extrusion compounds, (2) films and coatings, (3) lacquers, (4) synthetic fibers. Products best suited for a particular use are prepared by adjusting the vinyl chloride content and the average molecular weight to the physical and mechanical properties desired. In general, it can be said that a high vinyl chloride content or a high molecular weight is responsible for less solubility and plastic flow, and imparts higher resistance to chemicals and temperature.

Large quantities of polyvinyl chloride-acetate copolymer are employed for extrusion purposes, for the preparation of self-supporting films, and for coatings on paper and fabric. The dielectric characteristics of the copolymers permit their use as insulators for low-voltage wires and similar extruded electrical equipment. The films have found wide application in industry for packaging or for the production of artifical leather and raincoats. If a copolymer solution is spun through fine spinnerets, the solvent evaporates, and filaments that can be twisted and made into yarns are formed. Although x-ray studies of such fibers do not show appreciable orientation, their strength and elasticity can be greatly enhanced by stretching them along their fiber axis. Fabrics woven from these fibers are used for decorative and industrial purposes.

Polyvinyl Alcohol. The monomer of polyvinyl alcohol, vinyl alcohol ($CH_2{=}CHOH$) is an unstable substance which, when formed by addition of water to acetylene, quickly isomerizes and forms acetaldehyde or ethylene oxide. The only way, therefore, by which polyvinyl alcohol can be obtained is by a hydrolysis of polyvinyl acetate.



$$\cdots-(\mathrm{CH_2}-\underset{\substack{|\\\mathrm{O}\\|\\\mathrm{OCCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\\mathrm{O}\\|\\\mathrm{OCCH_3}}}{\mathrm{CH}}-)_n-\cdots+n\mathrm{H_2O}\rightarrow$$

$$\rightarrow\cdots(-\mathrm{CH_2}-\underset{\substack{|\\\mathrm{OH}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\\mathrm{OH}}}{\mathrm{CH}}-)_n\cdots+n\mathrm{CH_3}-\mathrm{COOH}$$

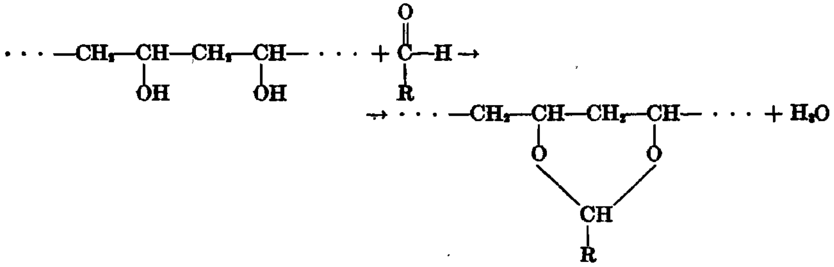
The hydrolysis can be performed in a nonaqueous medium, using acid or alkaline catalysts, and conditions can be fixed in such a manner that either a complete or partial hydrolysis is achieved. The structure and the properties of the resulting polyvinyl alcohol are determined by the molecular-weight characteristics of the polyvinyl acetate that serves as the starting material and also by the extent to which the hydrolysis is carried out. Thus, various polymers can be devised, differing from one another mostly in solubility. Polyvinyl alcohol itself is soluble in water and practically insoluble in ordinary organic solvents, whereas polyvinyl acetate is soluble in such solvents and only sparingly dissolves in water. The number of acetyl groups still present in an incompletely hydrolized polyvinyl acetate sample will therefore determine to what extent it will be attacked by organic solvents.

The main applications of polyvinyl alcohol in industry are based on its solubility behavior. For some purposes, its water solubility and the colloidal properties of its solutions are stressed; for other uses, the resistance of polyvinyl alcohol to organic solvents (and especially oils and grease) is of greatest importance. Water solutions of polyvinyl alcohol act as emulsifying vehicles for many hydrophobe liquids and are employed as such in the textile and printing-ink industries. Water-soluble films which can be easily washed off are sometimes desired for temporary protective coatings.

The sensitivity of polyvinyl alcohol films and molded or extruded articles to the dissolving action of water decreases their usefulness for some applications. In order to render the polyvinyl alcohol less soluble or even insoluble in water, it can be treated with formaldehyde or tanning agents,[1] ferric chloride, chromate and bichromates,[2] and cuprammonium hydroxide.[3] For the same purpose, it can also be reacted with dibasic acids, dialdehydes, and dimethylolurea.[4]

Polyvinyl alcohol can be plasticized with water, glycols, or glycerol. It has a rubbery consistency if enough plasticizer is incorporated and can be used for the production of oil- and greaseproof sheets and hoses.

Polyvinyl Acetals. The condensation of polyvinyl alcohol with aldehydes leads to the formation of polyvinyl acetals.



The acetals can be made directly from the polyvinyl acetate by carrying out the hydrolysis and condensation steps in one operation.

The properties of the resulting materials depend on (1) the average molecular weight of the polyvinyl acetates used, (2) the amount of acetyl groups hydrolyzed, (3) the degree of acetal formation, and (4) the nature of the aldehyde employed for the condensation.

The changes that can be made by adjusting the hydrolysis and condensation conditions and by choosing the starting polyvinyl acetate and the aldehyde offer the possibility of preparing polymers whose properties will correspond to given specifications. Generally, it has been found that the viscosity of polyvinyl acetals in solutions is greater than that of the polyvinyl acetates from which they are made. The length of the hydrocarbon chain of the aldehyde used for the reaction greatly influences the solubility and the heat-softening characteristics. The longer the chain, the more easily soluble becomes the polyvinyl acetal but the lower is its softening range. For example, of the two commercially produced acetals in which

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[1] Ger. 526,497.

[2] Fr. 807,042.

[3] U.S. 2,130,212 (1938).

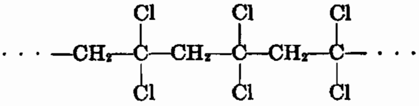
[4] U.S. 2,169,250 (1939); Fr. 852,613.

the aldehyde components are formaldehyde and butyraldehyde, respectively, the first one is quite resistant to solvents and has a softening range of 160–170°F, whereas the polyvinylbutyl acetal is soluble in many organic solvents and has a heat-distortion range of 115–140°F.

The industrial importance of these polymers is due to the fact that they combine the qualities of toughness, adhesiveness, and moisture insensibility with excellent low-temperature flexibility and shock resistance. For some uses, however, the softening ranges of the normal polyvinyl acetals are too low, and the materials are also too readily attacked by solvents. In a recent development, the addition of certain substances, introducing a number of cross links into the thermoplastic polymer, has resulted in the formation of polyvinyl acetals that show decreased solubility and better temperature resistance than the straight-chain polymers. The amount of cross-linking may reach such an extent that the product becomes practically insoluble. The processing, compounding, and final curing of such materials can be satisfactorily performed on normal rubber equipment.

Polyvinyl acetals are used as insulators for wire coatings, for the impregnation of paper and fabrics, for the production of flexible molded and extruded articles, and as interlayers in safety glass. In the last application, they are superior to any other material thus far tried.

Polyvinylidene Chloride.



$$\cdots\text{—}CH_2\text{—}\underset{Cl}{\overset{Cl}{C}}\text{—}CH_2\text{—}\underset{Cl}{\overset{Cl}{C}}\text{—}CH_2\text{—}\underset{Cl}{\overset{Cl}{C}}\text{—}\cdots$$

There are various methods by which the unsymmetrical dichloroethylene, vinylidene chloride, can be produced commercially. The first process is based on the chlorination of acetylene carried out in acetylene tetrachloride (tetrachloroethane). In the presence of ferric chloride, which acts as a catalyst, acetylene and chlorine combine at 135°C and yield vinylidene chloride. Another method of vinylidene chloride production starts from ethylene, which is chlorinated under controlled conditions to yield, 1,1,2-trichloroethane. On heating the latter substance in the presence of an alkali, hydrochloric acid is split off and a mixture of isomeric dichloroethylenes is obtained. They can be separated by fractional distillation.

Finally, the monomer can be made by chlorination of symmetrical dichloroethane in NaCl solution, whereby HCl is split off.

$$CH_2Cl\text{—}CH_2Cl + Cl_2 \xrightarrow{-HCl} CH_2Cl\text{—}CHCl_2 \xrightarrow{-HCl} CH_2\text{=}CCl_2$$

Of the three isomers of dichloroethylene,* only the asymmetrically substituted vinylidene chloride polymerizes easily. The polymerization of the monomer can be achieved either under pressure at 30–60°C or better, in

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* Asymmetric plus cis and trans symmetric.

aqueous suspension. Organic peroxides, aluminum chloride, and lead or copper compounds have been found to catalyze the reaction. Oxygen alone also seems to have a catalytic effect, since polymerization of a carefully purified and degassed vinylidene chloride proceeds considerably slower than one carried out in the presence of air. All reactions pass through a characteristically short induction period, and the polymer formed is not soluble in the remaining monomer (Fig. 15-36).

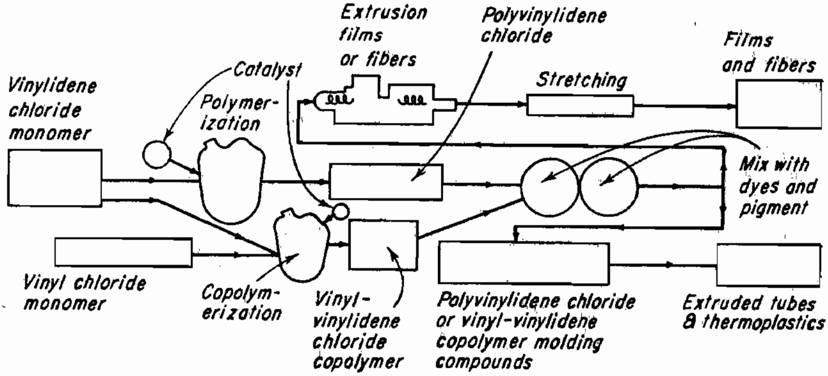


FIG. 15-36. Flow sheet for production of vinylidene chloride resins.

X-ray patterns reveal that the polymer as it leaves the reaction vessel is already crystalline to a certain extent. The crystallinity can be greatly increased by stretching the polymer below its softening range, and an orientation of the crystalline regions can ultimately be achieved. The polymer also appears in an amorphous form if it is heated above its melting point and is then rapidly quenched. In the amorphous state, however, the polymer is not stable and, depending on the temperature, reverts back to its crystalline form in time periods ranging from a few seconds to a few days.

Polyvinylidene chloride softens rather sharply at about 150–160°C but starts to decompose at 130°C, evolving hydrogen chloride. Its solubility is limited to a few solvents, mostly chlorinated hydrocarbons. The difficulties encountered in molding and extruding operations are caused preponderantly by the low decomposition point of the polymer and can be overcome by copolymerizing vinylidene chloride with other vinyl-type monomers. A copolymer with vinyl chloride softens at 120–140°C, has an increased range of solubility, and is more easily compatible with plasticizers than polyvinylidene chloride itself. It is called Saran and is commercially produced and employed as a fiber for the production of fabrics used for cloth, filters, and upholstery. In other applications, use is made of its chemical and solvent resistance in the preparation of gasket material, flexible tubing, and films.

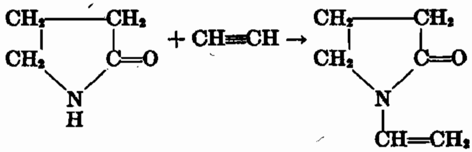
Polyvinyl Ethers. A number of polyvinyl ether homologues are available in commercial quantities. The monomers are usually prepared by decomposition of the lower polyvinyl acetates or by direct vinylation of alcohols by acetylene

$$R{-}OH + CH{\equiv}CH \rightarrow CH_2{=}CH{-}O{-}R$$

The polymerization of these ethers has to be carried out in bulk or solution at low temperatures and in the presence of ionic-type catalysts. According to the polymerization conditions used and depending on the particular monomeric ether homologue, liquid, solid, or rubbery materials are obtained.

The polymers in general exhibit good aging characteristics and adhesive qualities and are used accordingly in industry.

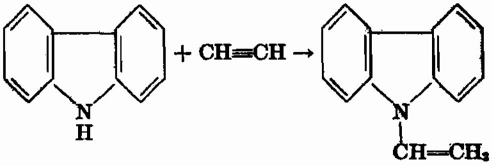
Polyvinyl Pyrrolidone. This recently developed polymer has found its major industrial applications as a consequence of its solubility in water and its low toxicity. Its monomer is prepared by the vinylation of pyrrolidone by acetylene:



The polymerization is usually carried out in an ammoniacal water solution of the monomer in the presence of a hydrogen peroxide catalyst. The polymerization medium must be alkaline, because vinyl pyrrolidone is unstable in an acidic aqueous environment.

The low toxicity characteristics of the polymer and its solution characteristics have made it valuable as a blood extender. It also is used as a dispersant and thickener for pharmaceutical and cosmetic preparations.

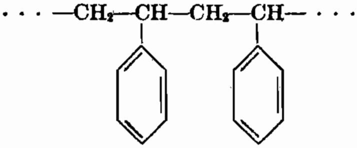
Polyvinylcarbazole. Vinylcarbazol monomer can be obtained by direct vinylation of carbazol by acetylene:



Polymerization of this solid monomer (mp, 65°C) can be carried out by any one of the usual methods of radical type polymerization, but it also can be polymerized in the presence of ionic catalysts. The latter method can yield a polymer having a softening point of 210°C.

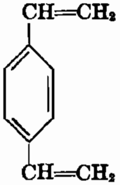
The high softening range of the polyvinylcarbazoles, usually in the range of 110–150°C, and their excellent electrical properties have been of interest for special industrial applications. A fibrous structure of the polymer can be obtained if it is extruded under certain conditions, and an X-ray diffraction diagram shows that the polymer molecules have achieved a certain amount of orientation along the direction of stress.

POLYSTYRENE

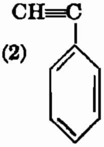


Styrene (vinylbenzene) is commercially produced in large quantities by the dehydrogenation of ethylbenzene, which is obtained by the Friedel-Crafts reaction of ethylene and benzene in the presence of hydrogen chloride and $AlCl_3$ as a catalyst. Among other by-products, divinylbenzene (1)

(1)



(2)



and phenylacetylene (2) are formed during the reaction. The monomer must be carefully freed from these substances before polymerization because small amounts of them would cause cross-linking and render the polystyrene insoluble.

The polymerization of styrene can be achieved by any one of the known methods of polymerization (Fig. 15-37). If utmost optical clarity is desired, bulk polymerization and suspension polymerization methods may be employed; for use as colored molding powders and coating materials, poly-

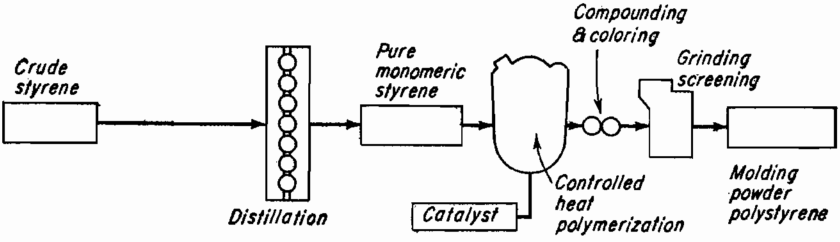


Fig. 15-37. Flow diagram for production of polystyrene resins.

merizations in emulsion and in suspension are carried out. The resulting polymers have varying molecular weights, depending on the reaction conditions employed. The average molecular weight of the polymer, in turn, influences its flow properties.

Destructive distillation of the polystyrene above 300°C yields the monomer and a number of other products that strongly indicate a head-tail structure of the polymer chain. X-ray investigations show that the polymer is amorphous. Stretching and drawing do not seem to produce crystalline or oriented areas, since no typical pattern appears on the diffraction diagram. However, films that are stretched in one or two directions or fibers drawn below the softening range show definite anisotropy in their mechanical and optical behavior. Such materials are commercially produced and are valuable where thin, flexible films of increased tensile strength are desired.

The properties of polystyrene assure this polymer a wide variety of possible applications. Its good flow properties at molding and extruding temperatures permit easy operations and swift production cycles. The dimensional stability of the molded or extruded articles, their transparency, low water absorption, resistance to chemicals, and outstanding electrical properties suggest the use of polystyrene in many industries. A number of factors, though, such as its inherent brittleness, its relatively low softening range (90–95°C), and its inflammability, detract from the value of the polymer. Substantial improvements in these properties, as well as development of new and desirable fabrication and performance features, have been achieved during the last few years and have made polystyrene one of the most versatile plastics for industrial use.

A variety of polystyrene grades have appeared on the market which give the fabricator a choice of operating conditions. For instance, an easy-flow polystyrene is tailored for fast molding cycles and deep-draw vacuum forming techniques. These flow properties are achieved by a rigorous control of the molecular weight and the molecular-weight distribution function as well as by addition of internal and external lubricants. Other types of polystyrene are those in which certain additives ensure stability against yellowing on aging and, particularly, stability against ultraviolet light from outdoor exposure or artificial sources. There are also so-called heat-resistant polystyrene grades, which have a softening range near and also slightly above the temperature of boiling water.

Polystyrene can be made into a very-low-density foam which has found use in electrical, sound, and heat-insulation applications. The inflammability is a definite setback for such applications, and experiments are under way to use halogenated polystyrene for such purposes or to incorporate inert and fire-resistant or fire-retarding ingredients. Polystyrene foam can also be produced from "expandable" beads which contain an expansion agent, for instance, some liquid which vaporizes at a desired temperature or a solid which decomposes into gaseous products. These beads, when heated in appropriate molds, foam and produce a molded, foamed article of low density. They also can be placed directly at a spot where insulation is required, for instance, a pipe joint, and foamed in place.

The polystyrene "alloys" represent an interesting and promising development. Among the most serious deficiencies of polystyrene are its low impact strength and elongation, and many industrial applications became possible only when these properties were improved by mixing polystyrene mechanically and intimately with certain elastomeric materials. As in the alloying of metals, relatively small amounts of admixed products can profoundly change the properties of polystyrene. The addition of a few per cent of rubbery material very greatly improves its impact strength and elongation properties and still does not detract significantly from its excellent molding characteristics and surface appearance.

There are two other ways, of course, to change and better the properties of polystyrene: one is the use of substituted styrenes and the second is a copolymerization with other suitable monomers. Both methods have become industrially important. An example of substituted styrenes are ring-halogenated polymers, mostly chlorinated, which have higher softening ranges than ordinary polystyrenes and show decreased inflammability and greater resistance to burning. A polymer from α-methylstyrene has also been prepared industrially and is resistant to immersion in boiling water over long periods of time. It is interesting to note that alpha-substituted styrenes, $CH_2{=}CRC_6H_5$, can be polymerized efficiently only by ionic-type initiators. Vinyl toluene monomer is also made on an industrial scale and is cheaper than monostyrene. While its polymer is of no particular importance, it is used frequently as a full or partial replacement for styrene in copolymerization reactions.

Copolymerization of styrene with other monomers has become of great industrial importance in the production of synthetic rubber. GR-S type rubbers are made from styrene and butadiene, and the necessity to produce this synthetic rubber during World War II brought about a high output of monostyrene, which in turn stimulated further industrial development and use of polystyrene. A more detailed discussion of styrene-butadiene copolymers is found later in the section on Diene Elastomers.

Copolymers of styrene with a variety of other monomers have been studied with regard to their properties and their economical, commercial, and industrial adaptability. Of these, so far only a few have been of major interest. Copolymers of styrene and of α-methylstyrene with acrylonitrile are among those which have found fairly large-scale industrial application. These copolymers show exceptionally good impact strength properties, have higher softening ranges than polystyrene, and have good resistance to chemicals. On the other hand, they are yellowish in color and lack the crystal clarity of polystyrene. Copolymers with varying amounts of fumaronitrile have been produced which show heat distortion temperatures up to 140°C and improved impact strength, but they are again yellowish in color. Maleic anhydride copolymers have also been prepared industrially but are of very much less importance than those copolymers in which the maleic acid is an integral part of a polyester chain. Such copolymers, and similar ones in which styrene is copolymerized with other unsaturated acids which form a component of a polyester chain, are the basis for new developments in the fast-growing polyester field.

Lastly, polystyrene and styrene copolymers can be cross-linked, for instance, by divinylbenzene, to give the starting material for ion-exchange resins. Cation and anion exchange resins can be prepared by fixing appropriate electron-active groups (sulfonate, quaternary ammonium, etc.) onto the cross-linked polystyrene or styrene copolymer, whereby the swelling and diffusion characteristics of the cross-linked network must be taken into account. Cross-linking can also be achieved by irradiation with beta or gamma rays, or with ultraviolet light sources. Irradiated polystyrenes have somewhat higher softening ranges and greater solvent resistance than nonirradiated materials.

The manufacture of polystyrene and styrene copolymers has grown at a rapid rate during the last decade. In 1946, the production of polystyrene in the United States amounted to 60 million lb; in 1956, polystyrene production reached 390 million lb. Further development of new polystyrene grades, of modified polystyrenes, and of new copolymers will certainly result in a continuing expansion of this field.

ACRYLATE AND METHACRYLATE POLYMERS

BY E. H. RIDDLE[1] AND P. A. HORRIGAN

There are three industrially important methods by which monomeric esters of acrylic acid, $CH_2{=}CH{-}COOR$, can be prepared, although many other processes have been suggested. The first one, which is described here, is based on the Reppe reaction of acetylene, carbon monoxide, and an alcohol in the presence of nickel carbonyl and an acid such as hydrochloric acid (Fig. 15-38):

$$HC{\equiv}CH + CO + ROH \xrightarrow[HCl]{Ni(CO)_4} CH_2{=}CHCOOR$$

The second method involves reaction of ethylene oxide with hydrogen cyanide to give ethylene cyanohydrin. This is converted directly to the

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[1] ROHM and HAAS Company, Inc.

ester of acrylic acid by treatment with concentrated sulfuric acid and an alcohol to effect simultaneous dehydration, hydrolysis, and esterification. The third method, only recently coming into commercial usage, starts with ketene and formaldehyde to give *beta*-propiolactone, which is converted to the acrylic ester by reaction with alcohol and an acid.

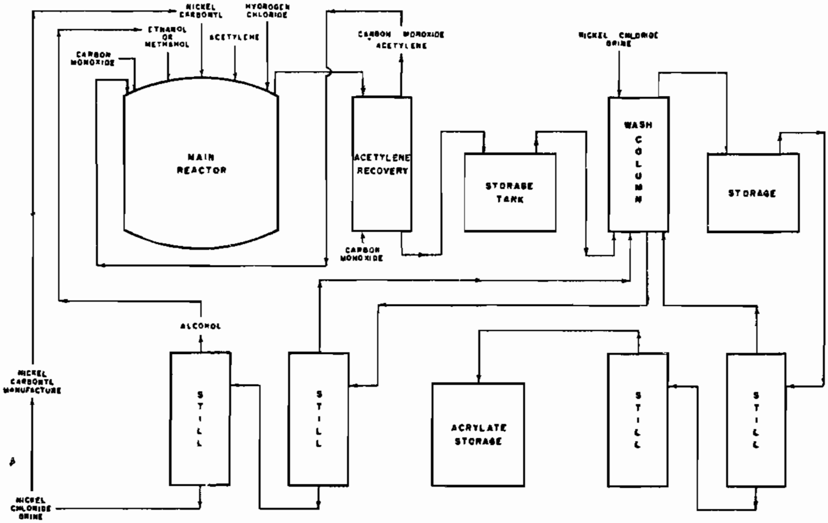

FIG. 15-38. Flow diagram: production of methyl or ethyl acrylate.

Esters of methacrylic acid are obtained directly from acetone cyanohydrin by reaction of the latter with concentrated sulfuric acid to give methacrylamide sulfate, followed by reaction with an alcohol. The process is continuous and the methacrylamide sulfate is not isolated. Acetone cyanohydrin is derived from acetone and hydrogen cyanide (Fig. 15-39).

Polymerization Procedures. Of particular importance to the acrylics is the cast or bulk method of polymerization. This method is employed to produce cast polymethyl methacrylate sheets which are widely used in industrial applications. Careful control of polymerization is required to obtain a bubble-free product with good optical clarity. A typical flow sheet for the production of cast sheet is shown in Fig. 15-40. Solution, suspension, and particularly emulsion polymerizations are also widely used with the acrylics. Such polymerization reactions involve relatively conventional batch-type processes.[1]

Properties. The exceptional properties of the acrylates and methacrylates vary over such a range that almost any combination can be tailor-

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[1] RIDDLE, "Monomeric Acrylic Esters," pp. 40–64, Reinhold Publishing Corporation, New York, 1954.

made through copolymerization of the proper monomers. Whereas polymethyl acrylate is a tough, rubbery polymer which forms a pliable film of high extensibility, polymethyl methacrylate is a hard, fairly rigid material which can be sawed, carved, or worked on a lathe with ease. In both the acrylate and methacrylate series, proceeding from the methyl to the ethyl to the butyl ester, the polymers become softer, tackier, and more extensible; this is more pronounced with the acrylate in each case than the corresponding methacrylate. These variations in softness and extensibility can be demonstrated by either a brittle-point or glass-temperature measurement. In both the acrylate and methacrylate series, the brittle points and glass temperatures decrease to a minimum as the length of the alkyl chain in the alcohol residue increases. In the acrylate series, this minimum occurs with octyl acrylate, with 2-ethylhexyl acrylate only slightly higher; in the methacrylate series, the minimum occurs at lauryl methacrylate. As a result of side-chain crystallization, the polymers of stearyl acrylate and methacrylate are waxlike solids with relatively low melting points, becoming soft and tacky above their melting points.

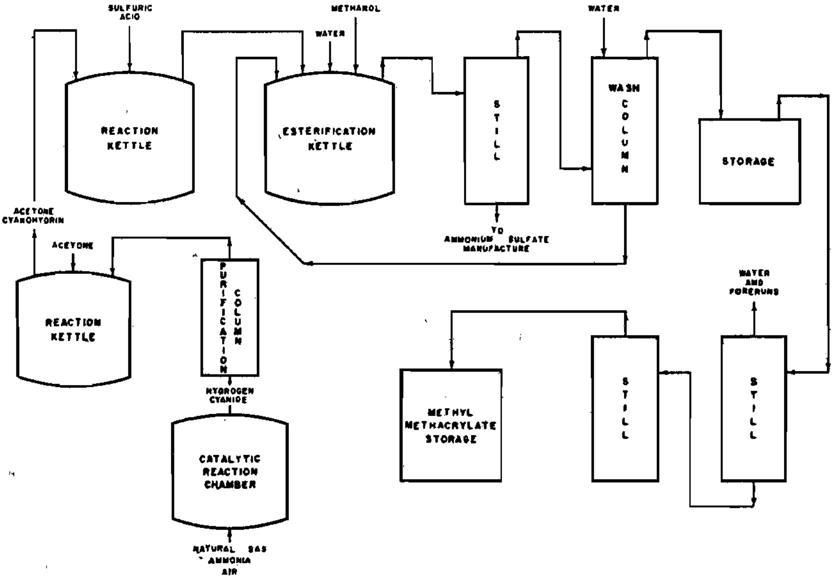


FIG. 15-39. Flow diagram: production of methyl methacrylate.

As would be expected, the solubility in organic solvents increases and the water absorption decreases as the alcohol chain in the ester group is lengthened. All the acrylates and methacrylates give polymers which exhibit the outstanding transparency and aging properties which have made these polymers of interest in a wide variety of applications. Table 15-16 gives a qualitative description of the change in various polymer properties in going from the hard methyl methacrylate polymer to the soft polybutyl acrylate. almost any degree of modification of these properties within the limits that are stated may be obtained by copolymerization of the various acrylic esters.

Because of the low softening points of the polymers of the acrylate esters, these monomers are particularly of interest for internal plasticization by copolymerization with monomers whose polymers have high softening points. This internal plasticizing method provides the ultimate in plasticizer permanence, with no migration or volatilization possible. The use of acrylates for internally plasticizing vinyl chloride, vinylidene chloride, vinyl acetate, styrene, and acrylonitrile, as well as methyl and ethyl methacrylates, is now established industrially.

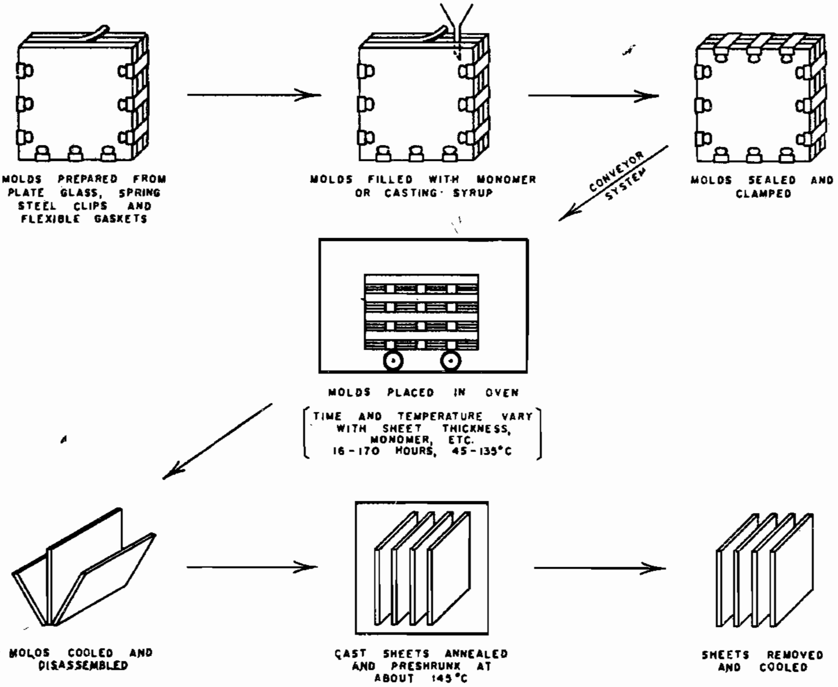


FIG. 15-40. Casting methyl methacrylate sheet.

Applications. *Products of Bulk Polymerization.* The principal example of bulk polymerization is the production of cast sheets of methyl methacrylate (see Fig. 15-40), which are well known for their outstanding optical clarity, resistance to sunlight, weather, and most chemicals, and for

TABLE 15-16. PROPERTIES OF ACRYLATE AND METHACRYLATE POLYMERS

Monomer	Tackiness	Hardness vs. softness	Tensile strength	Elongation	Water absorption	Brittle point
Methyl methacrylate	Tack-free	Fairly hard	High	Low	Slight	High
Methyl acrylate	Almost tack-free	Fairly soft	Moderately high	Moderately high	Fairly high	Moderately high
Ethyl acrylate	Tacky	Soft and plastic	Low	Very high	Slight	Low
Butyl acrylate	Very tacky	Very soft and plastic	Very low	Extremely high	Very small	Extremely low

their formability to three-dimensional shapes. The use of these cast sheets is now well established in such applications as civilian and military aircraft enclosures, instrument panels, industrial signs, lighting fixtures, window glazing where breakage is a problem, skylights, and pearlescent buttons.

Products of Suspension Polymerization. Polymerization in suspension in an aqueous system, where the polymer is obtained in the form of pearls or beads which are readily removed by filtering or screening, is particularly applicable to the production of methyl methacrylate molding powders. For softer grades, the methyl methacrylate is copolymerized with an acrylate. The beauty and durability of molded acrylic parts have led to increasing usage in automotive parts—tail lights, medallions, dials, instrument panels, and transparent roof sections—and in home appliance parts, pen and pencil barrels, brush backs, etc. Molding powder is also used for the manufacture of extruded sheet, which has found use in applications such as signs where the superior optical and surface properties of the more expensive cast sheet are not required.

Products of Solution Polymerization. Solution polymerization is used for making coating vehicles for application from solvent systems. The methacrylates have been used to a greater extent than the acrylates because of their better hardness, greater resistance to alkalies and other chemicals, and better electrical properties. However, the acrylates are also used in these systems as internal plasticizers. The methacrylate polymers and copolymers are readily prepared in a wide variety of solvents, of which aromatic hydrocarbons, esters, and ketones are most commonly used. These solutions are used for heat-resistant white enamel of good color retention, fabric coating, printing compounds used on vinyl plastics, clear metal coatings, fume-resistant enamels, vehicles for luminescent pigments, and flexographic printing inks. More recently, some publicity has been given to the use of a methacrylate lacquer for automotive finishing, with color retention, durability, and high gloss the outstanding features.

Products of Emulsion Polymerization. This is the most useful process for polymerizing the acrylate esters, producing stable dispersions with excellent film-forming properties. These acrylate dispersions are employed in the paper, rubber, textile, leather, and paint industries.

One of the first applications for acrylate dispersions was in the finishing of leather. The acrylate dispersions are used in two ways in leather finishing—as a base coat for nitrocellulose finishes and as components of water-finish systems. As base coats for nitrocellulose finishes, the acrylates produce permanently flexible and strongly adhering coatings, which, when dry, are no longer water dispersible but are soluble in the customary lacquer solvents so that excellent adhesion of subsequent lacquer coatings is obtained without difficulty. Not only does the acrylate polymer require no plasticizer, but also the sealing action of the acrylate coating goes a long way in preventing migration into the leather of plasticizers present in subsequent lacquer coats, again preserving flexibility. A large proportion of the country's shoe upper, upholstery, and garment leather has been finished for many years with acrylate dispersions.

An increasingly widespread use of acrylates in the leather field is as a component of water-based finishes. In such cases, the acrylate improves the adhesion, flexibility, and leveling of the finish, and depending upon the amount and type used, improves the washability. The softer types are often used as plasticizers for aqueous dispersions of other resins which are too brittle, without modification, for flexible coatings.

In the textile field, acrylate dispersions also provide highly desirable types of finishes. Applied to cotton and rayon, they contribute a firmer hand, improved tensile and tear strength, and better abrasion and wear resistance. They are free from color, and remain so. They are not easily removed by washing, hence are characterized as "permanent" finishes.

In the paper industry, acrylate dispersions are used for clear, greaseproof coatings, as binders for clay coatings, and as heat-sealing adhesives.

Acrylate copolymers produced by emulsion polymerization are being used as elastomers which, after vulcanization, have a combination of heat resistance and oil resistance useful in specialty applications such as gaskets for automatic transmissions in automotive engines. Two types of copolymers are being used. In one, ethyl acrylate is copolymerized with about 5 per cent of a chloro-containing monomer such as chloroethyl vinyl ether; in the other, either ethyl acrylate or butyl acrylate is copolymerized with about 5–15 per cent of acrylonitrile.

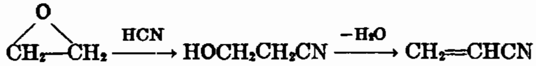
The application having the greatest possibilities for growth is emulsion paints. Paints made from acrylic dispersions have the usual desirable properties associated with acrylic polymers, particularly color retention, toughness, flexibility, and adhesion. The acrylic polymer does not oxidize and does not become yellow or brittle on aging. Flexibility and toughness are inherent properties of the acrylic polymers, and therefore no fugitive plasticizers or softeners are needed in the manufacture of acrylic paints. Resistance to attack by alkalies is excellent so that acrylic paints can be used over fresh plaster or masonry without danger of the films becoming soft or blistered. Moreover, acrylic paints have the valuable property of "breathing" so that water vapor is not trapped under the film, causing blistering and cracking, while at the same time the paint film has excellent water resistance.

ACRYLONITRILE POLYMERS

By W. M. Thomas[1]

In the late 1930's, German chemists found that acrylonitrile-butadiene copolymers have unusual resistance to hydrocarbons. This discovery led to the development of nitrile rubbers, of which Buna N was the first, and created a demand for commercial quantities of acrylonitrile. Of the many possible synthetic methods, only two have been important commercially: catalytic dehydration of ethylene cyanohydrin and addition of HCN to acetylene in catalyst solution.

The cyanohydrin route involves the following steps:



$$CH_2{-}CH_2(O) \xrightarrow{HCN} HOCH_2CH_2CN \xrightarrow{-H_2O} CH_2{=}CHCN$$

According to one process,[2] a mixture of ethylene oxide and hydrocyanic acid is added in batches or continuously at 60–70°C to an aqueous solution of a sterically hindered amine, e.g., diisopropyl amine. The product is fed to a stripping column in which the amine catalyst and water are removed from the higher-boiling cyanohydrin. A preferred procedure in the subsequent dehydration step comprises[3] adding the cyanohydrin to a catalyst (e.g., sodium formate) at about 200–240°C, distilling off the acrylonitrile and water, and then fractionating the acrylonitrile.

In the acetylene process, methane is first converted to acetylene by partial oxidation.

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \qquad \Delta H = 91 \text{ kcal per mole}$$
$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H = -9.6 \text{ kcal per mole}$$

These main reactions along with side reactions take place in a burner at 1550°C. The gas is quenched in water and is purified to about 99.5 mole

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[1] American Cyanamid Company, Inc.

[2] U.S. 2,453,062 (1948).

[3] U.S. 2,461,492 (1949).

per cent C_2H_2 by a combination of solvent absorption and fractional distillation. The required HCN is prepared in 98 per cent purity from methane, ammonia, and air:

$$CH_4 + \tfrac{3}{2}O_2 + NH_3 \xrightarrow[\text{Pt catalyst}]{1000°C} HCN + 3H_2O \qquad \Delta H = -113.3 \text{ kcal per mole}$$

Combination of C_2H_2 with HCN takes place at about 90°C in an aqueous solution containing 35–60 per cent CuCl. A flow sheet for the process is given in Fig. 15-41.[1] Ammonium chloride is added to increase the solubility of CuCl. Exact composition and operating conditions of the catalyst are regulated carefully to minimize production of undesirable acetylene derivatives such as monovinylacetylene, divinylacetylene, acetaldehyde, cyanobutadiene, and ill-defined residues. In subsequent polymerization reactions such compounds affect the rate of polymerization and may cause cross-linking or give a polymer with poor physical properties. The commercial monomer is a very pure product containing only a few parts per million of such impurities.

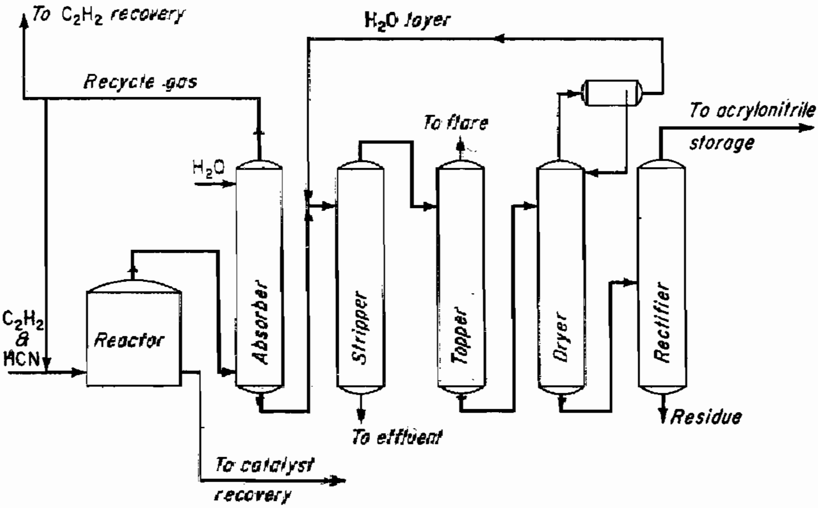

FIG. 15-41. Flow sheet for acrylonitrile manufacture.

Polymerization Techniques. Acrylonitrile is a stable monomer exhibiting little tendency toward purely thermal polymerization, but it can be polymerized readily using catalysts or various types of radiation.[2] Perox-

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[1] THURSTON, CARPENTER, and DERBENWICK, *Proc. 4th World Petroleum Congr., Rome,* 1955, Sec. IV/C, Preprint 5.

[2] "The Chemistry of Acrylonitrile," American Cyanamid Company, New York, 1951.

ides, azo compounds, ultraviolet light, x-rays, and gamma rays have been used to initiate the free radical polymerization of acrylonitrile. The alkali metals, Grignard reagents, and other basic catalysts give low-molecular-weight polymers. In the presence of water, alkalies may give partially hydrolyzed, complex products. Presence of the electron-withdrawing nitrile group makes acrylonitrile generally unsuitable for use with acidic catalysts.

Acrylonitrile is not conveniently polymerized in bulk except on a scale of only a few grams. The reaction is rapid, highly exothermic (18 kcal per mole), and difficult to control. Polymer is insoluble in the monomer, and heat is not easily removed from the resulting slurry or semisolid mass. Polymerization in homogeneous solution is limited by the fact that only a few liquids dissolve the polymer. Reactions in some of these liquids lead to polymers of low molecular weights because of chain transfer, or are objectionable because of toxicity, cost, or difficulty in solvent recovery.

Polymerization in aqueous suspension is by far the most convenient and widely used technique. The monomer is moderately soluble in water, and the polymer usually separates as a fine white floc which can be filtered easily and washed. A particular advantage of aqueous polymerization is that one can employ redox initiators such as persulfate-bisulfite or chlorate-sulfite.[1,2] These catalysts permit rapid polymerization to high conversion at relatively low temperatures, usually 20–40°C. Emulsifying agents may be present, and it is possible to prepare polymer in the form of a stable latex.[3]

Both batch and continuous methods have been used, but for large-scale production and highest uniformity of product, a continuous process is usually preferred. In a typical batch operation,[4] a stirred reactor is charged with water, and nitrogen or CO_2 is introduced to maintain an oxygen-free blanket. With the temperature maintained at 35°C, the solution is made about 1 molar in monomer and a catalyst solution containing $(NH_4)_2S_2O_8$ and $Na_2S_2O_5$ is added. Polymerization begins within 3 min, and after 4 hr the conversion to polymer is 91 per cent. The product is filtered, washed with water followed by methanol, and dried for 16 hr at 70°C.

Various techniques for continuous polymerization are described in the patent literature.[5,6] According to one process, the reactor is supplied with a high-speed agitator, inlets for the catalyst and monomer feeds, and a discharge tube for the product. The reactor is charged with an aqueous slurry

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[1] U.S. 2,751,374 (1956).

[2] Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).

[3] "Acrylonitrile in Plastics," American Cyanamid Company, New York, 1953.

[4] U.S. 2,595,907 (1952).

[5] Brit. 722,451 (1952).

[6] U.S. 2,628,223 (1953), 2,640,049 (1953), 2,748,106 (1956).

of polymer, prepared in a previous run, and monomer and catalyst are introduced at a rate calculated to give an average residence time of about two hours and a polymer concentration in the reactor of 25–35 per cent. The overflow is a relatively fluid slurry which is filtered, washed, and dried as in the batch operation. In all these polymerizations, oxygen is rigorously excluded because it reacts with the growing chains and prevents polymerization. Various metal ions such as Cu^{++}, Fe^{++}, and Ag^{+} affect polymerization rate and molecular weight even at a level of a few parts per million and must be excluded or kept constant. Molecular weight may be controlled by the catalyst/monomer ratio or by additives such as mercaptans.

Copolymers containing mostly acrylonitrile are made in much the same manner as described for the homopolymer. If acrylonitrile is present as a minor component, the copolymer may be soluble in the monomer mixture. This is the case in preparation of acrylonitrile-styrene molding compounds containing 25–30 per cent acrylonitrile, and in this event, it may be advantageous to copolymerize the monomers in bulk or as beads. As the amount of acrylonitrile in a copolymer is reduced, it usually becomes easier to carry out typical emulsion or suspension (pearl) polymerization.

Monomer reactivity ratios have been determined for copolymerization of acrylonitrile with most of the common monomers.[1] These constants make it possible to predict the composition of copolymer forming from any given monomer mixture. When these ratios are unavailable, one may apply the Alfrey-Price theory and accept Q and e values of about 0.6 and +1.2, respectively. Usually, the composition of the product differs from that of the starting mixture, and in order to obtain a homogeneous product, it is necessary to reduce the rate of addition of the more active monomer. Several hundred monomers have been proposed for use with acrylonitrile, but only a few of these copolymers are used commercially.

Mechanism of Reaction. The mechanism of acrylonitrile polymerization is intriguing and has been much studied in recent years. Bulk polymerization exhibits unusual kinetic features attributable to the fact that polymer is insoluble in the monomer.[2] This leads to enrichment of the remaining monomer with respect to catalyst and to interference with the normal processes of chain growth and termination. Some of the growing radicals become buried in the solid phase, and their presence can be detected by physical means or by their subsequent activity in radical reactions. If the reaction is carried out in homogeneous solution[3] (e.g., in di-

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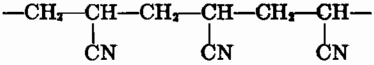
[1] Mayo and Walling, *Chem. Rev.*, **46**, 191 (1950).

[2] Bamford and Jenkins, *Proc. Roy. Soc. (London)*, **A216**, 515 (1953); *ibid.*, **228**, 220 (1955); *J. Polymer Sci.*, **20**, 405 (1956); Thomas and Pellon, *ibid.*, **13**, 329 (1954); Magat, *ibid.*, **19**, 583 (1956); **16**, 491 (1955); Prevot-Bernas and Sebban-Danon, *J. chim. phys.*, **53**, 418 (1956).

[3] Thomas, Gleason, and Pellon, *J. Polymer Sci.*, **17**, 275 (1955); Onyon, *Trans. Faraday Soc.*, **52**, 80 (1956).

methylformamide), these peculiar effects largely disappear, though chain transfer to solvent may now introduce a complication. Polymerization in aqueous medium[1] has many features of a typical emulsion polymerization. Polymerization rate is influenced not only by the rate of radical generation and monomer content, but also by agitation, electrolyte concentration, and the presence of emulsifying or suspending agents.

Polyacrylonitrile is usually represented as a linear chain with nitrile groups on alternate carbon atoms:



$$-CH_2-\underset{CN}{\underset{|}{C}H}-CH_2-\underset{CN}{\underset{|}{C}H}-CH_2-\underset{CN}{\underset{|}{C}H}-$$

In common with other vinyl polymers, polyacrylonitrile made in different ways varies in respect to average molecular weight, molecular-weight distribution, and extent of branching. Under typical conditions, polymer made in bulk may have an average molecular weight of 500,000–1,000,000. Polymer made in aqueous suspension is usually in the 50,000–100,000 range, and the molecular weight of polymer made in chain-transfer solvents like dimethylformamide is much lower, often only a few thousand. In general, polyacrylonitrile has a wide molecular-weight distribution, especially when made in bulk or in emulsion. If the polymerization temperature is much above room temperature, the polymer may be branched.[2] These considerations apply as well to copolymers where the additional possibility of graft or block structures exists. Polymer properties, especially solution viscosity, are related to structural details in a complex way, and thus the behavior of a polymer in a given application depends to an important degree on the method of preparation. Weight-average molecular weight (M_w) can be estimated from intrinsic viscosity ([η]) in dimethyl formamide by the relationship given by Cleland and Stockmayer:[3]

$$[\eta] = 2.33 \times 10^{-4} M_w^{0.75}$$

Number-average molecular weight (M_n) measured osmotically is usually much lower than M_w, and the ratio M_w/M_n gives an indication of the molecular-weight distribution.

Polymer Properties. As soon as the molecular weight of polyacrylonitrile exceeds a few hundred, the polymer is hard, insoluble in most liquids, and relatively infusible. These properties are attributed to hydrogen bonding through the strong, compact CN group. Only highly specific liquids are

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[1] THOMAS, GLEASON and MINO, *J. Polymer Sci.*, **24**, 43 (1957); MORGAN, *Trans. Faraday Soc.*, **42**, 169 (1946); BENSASSON and PREVOT-BERNAS, *J. chim. phys.*, **53**, 93 (1956).

[2] MILLER, BUTTON, STAMM, RAPOPORT, and GLEASON, paper presented Mar. 16, 1956, at the Meeting-in-Miniature of the New York Section, American Chemical Society.

[3] CLELAND and STOCKMAYER, *J. Polymer Sci.*, **17**, 473 (1955).

able to solvate the nitrile groups and thus bring the chains into solution. Among the best solvents are dimethylformamide, dimethylacetamide, dimethylsulfoxide, ethylene carbonate, and concentrated aqueous solutions of such salts as sodium thiocyanate and sodium perchlorate. By way of contrast, polymethacrylonitrile dissolves in many organic solvents.

Polyacrylonitrile can be made to undergo many of the reactions of simple nitriles, but in common with most reactions on polymers, these procedures give mixtures that are difficult to purify. A useful product can be made by heating the polymer above about 80°C with a fairly concentrated alkali. Part of the nitrogen is liberated as ammonia, and the product is essentially a copolymer of acrylamide and acrylic acid. It is useful as a soil-stabilizing agent and for control of water loss in drilling muds.

Polyacrylonitrile is not a typical thermoplastic. It is quite stable to heat below about 130°C, but at higher temperatures it begins to yellow, and above 200°C complex rearrangements occur. These are thought to involve formation of pyridine-type structures. Yellowing is more rapid in the presence of alkali. Monomer cannot be obtained by pyrolysis of the polymer. Polymer exhibits an apparent transition in the range of 80–90°C but has no true melting point.[1] These thermal properties make it difficult to mold the homopolymer, but simple shapes can be made by careful compression molding.

Applications of Acrylonitrile Polymers. Clear, rather brittle films can be cast from solutions of polyacrylonitrile, but the unmodified polymer is not widely used in films or in molded form. The homopolymer has been suggested for use in flatting agents for varnishes and lacquers,[2] and it can be spun into fibers or filaments. So far, a completely satisfactory external plasticizer has not been developed. One therefore relies on comonomers to provide the plasticity or special properties that may be required.

A very large use for acrylonitrile polymers is in synthetic fibers.[3] In this country there are at present six commercial or semicommercial fibers containing substantial amounts of acrylonitrile; at least an equal number are under development in Europe, Russia, and Japan. If the acrylonitrile content is in excess of 80–85 per cent, the fiber retains most of the properties of the homopolymer but may be improved in respect to spinability and dye receptivity. Acrylic fibers are spun from solvents, either by direct evaporation or by use of a coagulating bath. Principal uses are in suits and other woven fabrics, in jersey knit goods, in sweaters, and in blankets. Acrylics have outstanding resistance to sunlight, insects, and chemicals. They have high sticking temperatures, warm feel, good dimensional stability, and low

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[1] Ham, *Textile Research J.*, **24**, 597 (1954); Kolb and Izard, *J. Appl. Phys.*, **20**, 570 (1949).

[2] U.S. 2,534,717 (1950).

[3] Koch, *Modern Textiles Mag.*, January, 1956, p. 46.

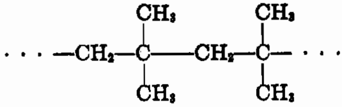
moisture absorption. They can be used alone, as in sweaters, but are often blended with wool or with rayon.

Acrylonitrile is used as a comonomer in plastics to impart one or more of the following properties: higher heat-distortion temperature, superior resistance to chemicals, greater surface hardness, good impact strength, higher flexural strength, and superior outdoor durability. One of the most promising applications is in copolymers with styrene or methyl styrene.[1] The acrylonitrile content is usually about 30 per cent. These copolymers exhibit better heat resistance, toughness, and chemical and craze resistance.

One of the largest uses of acrylonitrile copolymers continues to be nitrile rubbers. They contain 20–50 per cent acrylonitrile, the remainder being butadiene, and have superior resistance to oil and chemicals along with good properties as elastomers. In addition to their use as rubbers, they are valuable for blending with polystyrene, with polyvinyl chloride, or with phenolic resins. The blend with polystyrene is a thermolplastic molding compound with up to ten times the impact strength of polystyrene alone.

Copolymers of acrylonitrile have been proposed for a large variety of other industrial applications. These include adhesives, electrical insulation, coatings for leather, paper, and textiles, impregnating agents for paper, and components of surface coatings.

POLYISOBUTYLENE



$$\cdots -CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}- \cdots$$

The catalytic dehydration of tertiary or isobutyl alcohol results in the formation of isobutylene in satisfactory yield. Isobutylene, a gas (bp, −6°C), is polymerized in bulk, and the temperature and catalyst conditions of the reaction influence decisively the characteristics of the polymer. Polymerizations carried out at room temperature lead only to low-molecular-weight products. The average degree of polymerization increases as the temperature of the reaction decreases. At a temperature of −78°C, using boron trifluoride, tin tetrachloride, or aluminum chloride as catalyst, high polymers of an average polymerization degree of 3,000–4,000 can be obtained. These products are characterized by a high degree of rubberlike elasticity, whereas lower polymers, of an approximate polymerization degree of 1,000, show considerably more plastic flow. Finally, low-molecular-weight polymers of an average polymerization degree of 50–100 have the consistency of viscous oils.

The polyisobutylenes, consisting of saturated hydrocarbon chains, show excellent electrical properties and chemical stability. Combined with these

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[1] Melchore, *Modern Plastics*, **33**, 163 (1956).

characteristics are their elastic and plastic properties, which can be regulated by the proper choice of the average molecular weight of the polymer or by copolymerization of isobutylene with other olefins or dienes. A copolymerization product of isobutylene with a small amount of a diene, e.g., isoprene, has the added advantage of possible vulcanization through the residual double bond of the diene component. Such products are on the market under the name of butyl rubber and often have better aging and ozone-stability characteristics than natural rubber.

Polyisobutylenes have found manifold applications in the rubber and cable industry; they are also used as lubricating oils, as textile finishing and impregnating agents, and for the preparation of self-supporting films and coated fabrics.

ALLYL POLYMERS

By N. G. Gaylord[1]

Allyl compounds polymerize with considerably more difficulty than analogous vinyl compounds. The most characteristic feature in allyl polymerization is the formation of stable allylic radicals, only a fraction of which participate in further polymerization. They are generally produced by the abstraction of a hydrogen atom by the catalyst radical [reaction (1)] or by a chain transfer.

$$R^{*} + CH_2{=}CHCH_2X{-}\begin{cases}\longrightarrow RH + CH_2{=}\dot{C}HCHX & (1)\\ \longrightarrow R{-}CH_2\dot{C}HCH_2X & (2)\end{cases}$$

The abstraction takes place mostly on the carbon atom alpha to the double bond, although in alcohols and esters other radicals may also be formed. If produced by chain transfer, they terminate the propagation of a chain; if produced by a catalyst radical, they destroy a potential polymerization initiator and reduce the effective catalyst concentration. These reactions compete with the normal addition polymerization [reaction (2)], and the over-all result is a slow rate of polymerization and the formation of low-molecular-weight polymer.

Allyl alcohol is converted to a viscous polymer of low molecular weight by heating to 100°C in the presence of air, oxygen, hydrogen peroxide, or benzoyl peroxide. However, in order to obtain reasonable conversions of monomer to polymer, these catalysts must be replenished frequently during the long reaction period. Allyl chloride is converted, in high yield, to a polymer containing six monomer units per molecule by heating at 80°C in the presence of benzoyl peroxide. Whereas allyl bromide is polymerized in

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[1] Interchemical Corporation.

the presence of acetyl peroxide, no polymer is obtained in the presence of benzoyl peroxide.

The polymerization of allyl esters of saturated monobasic acids, e.g., allyl acetate and allyl laurate, yields linear thermoplastic polymers containing 5–20 monomer units per molecule. These homopolymers and copolymers with vinyl monomers such as vinyl acetate, vinyl chloride, and vinylidene chloride have been used as thermoplastic adhesives and plasticizers.

Whereas monoallyl derivatives yield thermoplastic polymers, allyl esters containing two or more unsaturated groups yield thermosetting resins. Thus, monoallyl esters of unsaturated acids, e.g., allyl acrylate, allyl methacrylate, allyl crotonate, and allyl itaconate, and diallyl esters of dibasic acids, e.g., diallyl oxalate, diallyl phthalate, and diallyl itaconate, yield thermoset resins which generally combine solvent resistance, toughness, hardness, transparency, and heat resistance. The cross-linking tendency of the allyl esters makes them useful in copolymerization wherein they impart these properties to normally linear polymers.

In the polymerization of a polyfunctional monomer such as a diallyl compound, the resin generally passes through a soluble, fusible stage before conversion to the insoluble, infusible thermoset polymer. If the polymerization is stopped short of gelation by dilution with a solvent which is a precipitant for the polymer, a "prepolymer" may be isolated. This material may later be converted to the thermoset condition, under the influence of a catalyst and heat. Under controlled conditions, the copolymerization of a polyallyl compound may be stopped at a thermoplastic stage. The resulting resin may be utilized in the form of a surface coating which becomes infusable and insoluble by heating in the presence of air or a catalyst.

One of the major uses of diallyl esters is in the preparation of reinforced plastics. In this application, a woven fabric or mat prepared from glass or other fibers is saturated with a liquid resin or monomer containing a peroxide catalyst. The liquid resin may be a diallyl ester, a mixture of an unsaturated polyester resin and a vinyl or allyl monomer, or a mixture of monomer and prepolymer. The resin-monomer-fiber combination is placed in a mold and under the influence of heat and pressure is converted to a thermoset reinforced material. The steps are outlined in Fig. 15-42.

Diallyl phthalate is used as a monomer as well as in prepolymer form in the preparation of reinforced plastics. Diallyl itaconate is also used as a cross-linking agent for unsaturated polyester resins as well as in cross-linking of vinyl copolymers.

Diethylene glycol bis(allyl carbonate) is used to form clear castings which have excellent thermal stability as well as scratch and abrasion resistance. The polymers and copolymers with methyl methacrylate are used in optical applications such as lenses and windows as well as in the preparation of cross-linked polyesters.

Diallyl phenyl phosphonate is used in the preparation of thermoset resins with improved transparency and flame resistance. Diallyl isobutenyl phosphonate is also used to impart flame resistance.

Triallyl esters impart a greater degree of cross-linking than diallyl esters and are therefore used as hardening agents. Triallyl cyanurate forms extremely stable cross-links that result in excellent chemical and thermal resistance. Triallyl citrate is also used to give extremely hard, infusible, insoluble polymers.

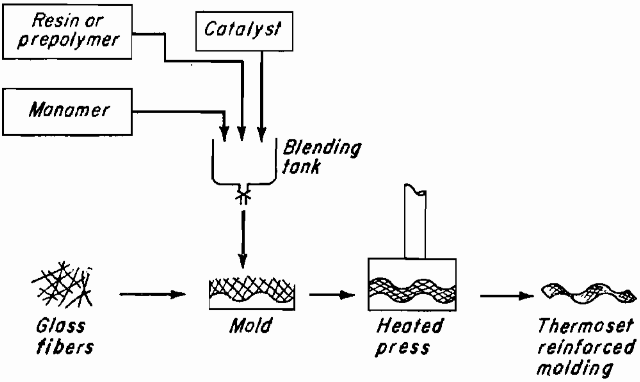


FIG. 15-42. Preparation of glass fiber-reinforced plastics.

The presence of a multiplicity of allyl groups in a polymer results in a thermosetting composition. Thus, the various drying oil alkyds, containing side chains derived from dehydrated castor oil and linseed oil, are cross-linked by polymerization of allylic double bonds. Allyl starch and allyl sucrose are extremely interesting materials prepared by treatment of the polyols with allyl chloride in the presence of base. Coatings prepared from these compounds are readily cross-linked by the application of heat.

Two monoallyl ethers have recently become commercially available and offer the possibility of cross-linking by post-reactions. In addition to its use in a copolymer by polymerizaton through the allyl group, glycerol α-allyl ether can be used in place of a glycol in the preparation of polyester resins by reaction with a dibasic acid such as phthalic acid. These linear polymers are thermoset through polymerization of the side-chain allyl groups. Allyl glycidyl ether can be polymerized through the allyl group to yield a polymer with epoxide side chains. This polymer can be cross-linked by polymerization through the epoxide groups. Conversely, polymerization of the monomer through the epoxide group yields a resin which can be cross-linked through the allyl groups.

SYNTHETIC DIENE ELASTOMERS

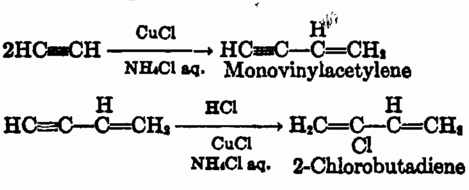
By P. G. Carpenter and C. A. Uraneck[1]

The creation of a synthetic rubber industry in the United States was a cooperative endeavor of many petroleum, chemical, and rubber companies. On a war-emergency basis between 1941 and 1944, elastomer production increased from 8,100 to 790,000 tons per year. This major technological accomplishment had much significance of a political and economic nature. By 1957, production capacity of the industry had increased to over 1,200,000 tons per year.

Many hundreds of diene polymers were investigated for their suitability as elastomers. Only three of these have achieved widespread commercial acceptance: butadiene-styrene copolymers, butadiene-acrylonitrile copolymers, and poly-2-chlorobutadienes. Other essentially non-diene elastomers such as butyl rubber from isobutene, Thiokol from ethylene dihalides and polysulfides, and silicones have become important for special applications.

The first attempts to prepare synthetic rubber were made with isoprene, which was known to be a building unit of the natural products, hevea, gutta percha, and others. The difficulty of producing isoprene economically, the poor properties of the early polyisoprene, and finally the realization that a successful synthetic rubber, unlike other natural substitutes, would not necessarily be an exact duplication of the natural product encouraged research with other monomers. Some of the first synthetic diene polymers produced commercially, the Neoprenes, a class of poly-2-chlorobutadienes, were superior to natural rubber in resistance to aging, chemical attack, and wear.[2]

Syntheses of Dienes. The original process for preparing monovinylacetylene from acetylene[3] is still used as the first step in the manufacture of 2-chlorobutadiene. Monovinlyacetylene is then reacted with hydrogen chloride to form the 2-chlorobutadiene according to the process described by Carothers. The two steps are illustrated as follows:



$$2HC\equiv CH \xrightarrow[\text{NH}_4\text{Cl aq.}]{\text{CuCl}} HC\equiv C-\overset{H}{C}=CH_2$$

Monovinylacetylene

$$HC\equiv C-\overset{H}{C}=CH_2 \xrightarrow[\substack{\text{CuCl}\\ \text{NH}_4\text{Cl aq.}}]{\text{HCl}} H_2C=\underset{Cl}{C}-\overset{H}{C}=CH_2$$

2-Chlorobutadiene

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[1] Phillips Petroleum Company.

[2] Whitby, "Synthetic Rubber," chap. XXII, John Wiley & Sons, Inc., New York, 1954; "Collected Papers of Wallace Hume Carothers on High Polymeric Substances," Interscience Publishers, Inc., New York, 1940.

[3] Nieuwland, Calcott, Downing, and Carter, *J. Am. Chem. Soc.*, **53**, 4197 (1931).

Historically, the high cost of poly-2-chlorobutadiene precluded the use of this synthetic elastomer in competition with natural rubber. The search for a low-cost monomer eventually led to butadiene. This diene can be readily produced and has been manufactured on a large scale from various starting materials,[1] notably ethanol (in Russia and in the United States on a war-emergency basis) and 2-butyne-1,4-diol, obtained from acetylene and formaldehyde (in Germany). The most economical production has been the dehydrogenation of *n*-butenes which are large-volume by-products as well as intermediates in the petroleum industry.

The process employed for the production of butadiene is determined by the availability of *n*-butenes, which in turn is determined by the feedstocks, the catalytic cracking processes employed, and the need of *n*-butenes for the production of gasoline. When sufficient *n*-butenes are not available, a four-step process is used: (1) catalytic dehydrogenation of butane or cracking of feedstocks to *n*-butenes and higher and lower boiling fractions, (2) separation of *n*-butenes from the high and low fractions, (3) dehydrogenation of *n*-butenes to butadiene and higher and lower boiling products, and (4) separation of butadiene from step 3 by extractive distillation. The flow sheet in Fig. 15-43 illustrates the four-step process for preparing butadiene from butane. Various catalysts have been used in the first-step dehydrogenation of butane to butenes, and a chromia-alumina catalyst has proved particularly effective.[2] An iron oxide catalyst promoted with a potassium compound[3] is a type used for the dehydrogenation of *n*-butenes in step 3. Research on catalysts for the dehydrogenation steps is continuing. New and improved types can be expected. A chromium oxide–stabilized calcium–nickel phosphate catalyst for butene dehydrogenation is an example of recent developments.

Polymerization and Copolymerization of Dienes. Diene monomers can be polymerized to elastomers by bulk, solution, suspension, or emulsion processes. In commercial practice virtually all the diene elastomers are, however, prepared by the emulsion process. Some basic recipes used for preparing various types of synthetic rubber are shown in Table 15-17.

As seen from the lists in Table 15-17, many ingredients comprise a modern polymerization recipe used for the production of synthetic rubber. Many of these exert minor influences such as pH and viscosity control but are still necessary for commercial production. The main ingredients are, however, (1) the monomers, (2) the emulsifier, (3) the modifiers, and (4) the initiator system.

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[1] Marchionna, "Butalastic Polymers," Reinhold Publishing Corporation, New York, 1946.

[2] Pitzer, Owen, and Clark, *Ind. Eng. Chem.*, **46**, 1541 (1954).

[3] Kearby, *Ind. Eng. Chem.*, **42**, 295 (1950).

Research sponsored by the government and private corporations has contributed much to the understanding of fundamentals that govern the complex process of emulsion polymerization. Emulsifiers play the triple role of emulsifying the monomers, furnishing micelles which are the sites of polymer initiation, and stabilizing the latex during the polymerization and afterward.[1] To obtain satisfactory rates of polymerization at low temperatures, redox couples such as those given in the last two recipes of Table 15-17 are employed. Polymerizations in the emulsion systems occur by free-radical mechanisms. The initiating radical is generated by a reaction of the oxidant and reductant, which are solubilized in the separate hydrocarbon and aqueous phases. The initiating reagents must have the proper solubility in the different phases, the proper rate of diffusion, and the proper oxidation-reduction potentials; the initiating free radical must have the proper reactivity.[2] Despite the tremendous amount of research done on initiating systems, even the simplest redox couple is not completely under-

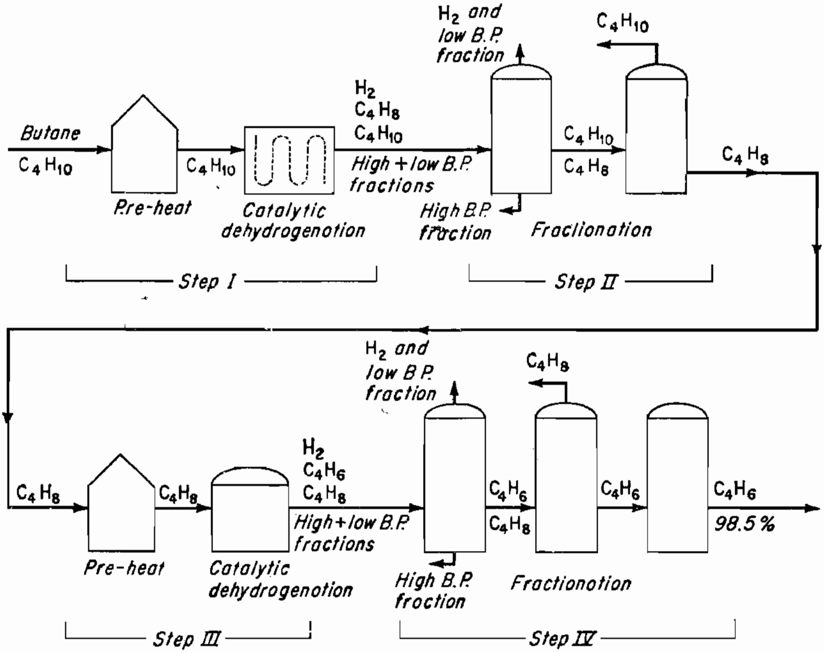

FIG. 15-43. Flow diagram for production of butadiene from butane.

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[1] HARKINS, *J. Polymer Sci.*, 5, 217 (1950).

[2] BOVEY, KOLTHOFF, MEDELIA, and MEEHAN, "Emulsion Polymerizations," chap. III, Interscience Publishers, Inc., New York, 1955.

TABLE 15-17. BASIC RECIPES FOR DIENE POLYMERIZATIONS

Ingredient	Polychlorobutadiene	"Hot" persulfate recipe	"Cold" iron pyrophosphate recipe	"Cold" sulfoxylate recipe
2-Chlorobutadiene	100			
Butadiene	.....	75	75	75
Styrene	.....	25	25	25
Water	150	180	180	180
Emulsifier	4.0	4.7	4.7	4.5
Dispersion agent	0.7	.....	0.15	0.15
Electrolyte	0.8	....	0.5	0.5
Dodecyl mercaptan	.....	0.5	0.18	0.18
Sulfur	0.6			
Potassium persulfate	0.6	0.3		
p-Menthanehydroperoxide	.....	.....	0.08	0.06
Ferrous sulfate, $FeSO_4 \cdot 7H_2O$	.....	.....	0.16	0.018
Potassium pyrophosphate	.....	.....	0.19	
Sodium ethylenediamine tetraacetate	.....	.....	......	0.027
Sodium formaldehyde sulfoxylate	.....	.....	......	0.07
Temperature, °C	40	50	5	5

stood. The modifiers must also satisfy these important requirements: proper solubility, proper rate of diffusion, and proper reactivity.[1] An ideal modifier would be one with the water solubility of a octyl mercaptan and with a transfer constant of one. With this type of modifier, the rate of its disappearance should exactly parallel the rate of polymerization. The relationship between the number of particles in an emulsion system and the rate of polymerization has been explained by a theory devised by Smith and Ewart.[2] Validity of this theory has been tested for recipes similar to those in Table 15-17.[3] Although deviations from the Smith-Ewart theory have been found for these systems, the theory serves as an excellent guide for studying the mechanism of the emulsion polymerization systems.

Stopping the polymerization at the proper conversion with short-stopping agents and protecting the isolated rubber with antioxidants are of practical importance. These steps are necessary to prevent changes in the polymer during processing and storage because of cross-linking and oxidative breakdown.

A flow sheet of a typical butadiene-styrene synthetic rubber plant is given in Fig. 15-44. A standard plant is divided into four areas: pigment

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[1] BOVEY, KOLTHOFF, MEDELIA, and MEEHAN, "Emulsion Polymerizations," chap. IV, Interscience Publishers, Inc., New York, 1955.

[2] SMITH and EWART, *J. Chem. Phys.*, **16**, 592 (1948).

[3] MORTON, SALATIELLO, and LANDFIELD, *Polymer Sci.*, **8**, 111 (1952).

(solution preparation), reactor, monomer recovery, and process (coagulation, drying, baling, storage).

Characteristics of Diene Polymers. The physical and chemical properties of polymers are the resultant contributions of the fine structure and the gross properties of the polymer. Fine structure features of diene polymers are the ratio of the *cis*, *trans*, and vinyl configurations of the butadiene units, total unsaturation, combining ratio of monomers in copolymers, and tendency to crystallize. The gross properties include the viscosity of the bulk polymer (measured as Mooney viscosity in the rubber industry), average molecular weight, molecular-weight distribution, percentage of gel, extent of branching, and others. Some typical fine and gross properties of commercial diene polymers are given in Table 15-18.

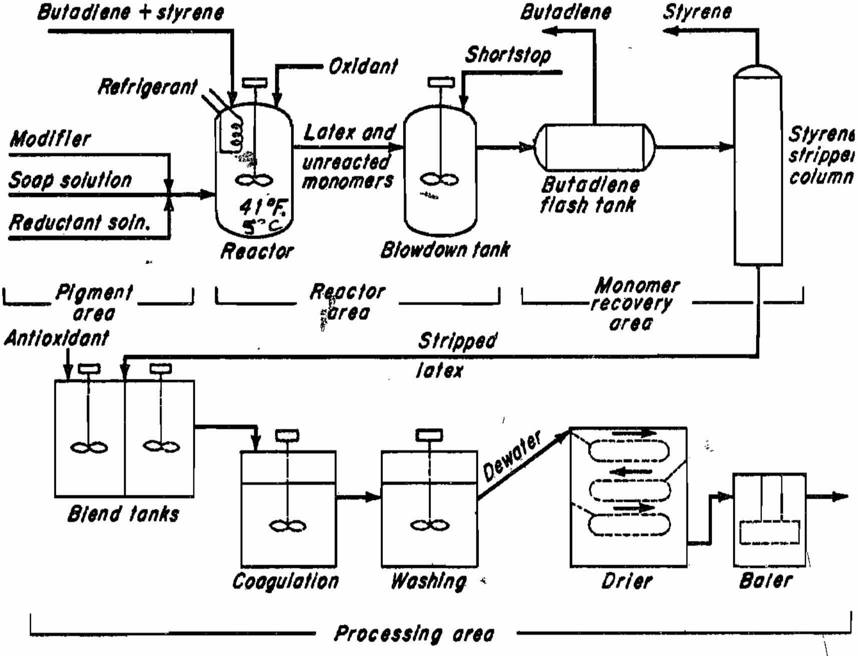

FIG. 15-44. Flow diagram for production of "cold" butadiene-styrene copolymer.

Although the differences in values for the various properties of "hot" and "cold" elastomers are small, they are importantly reflected in vulcanized products.

Increasing quantities of rubber are produced as a master batch. A master batch is produced by mixing a carbon black slurry or an oil emulsion or both with a latex and coagulating the ingredients. Thirty or more grades of butadiene-styrene synthetic rubber are commercially available which

TABLE 15-18. SOME TYPICAL PROPERTIES OF DIENE ELASTOMERS

Elastomer	Building units	Conversion, %	Total unsaturation, %	Diene addition		Diene unit configuration		Mooney viscosity, ML-4	Approx mol. wt. No. average	Density at 25°C	Glass temp, °C
				1,4-, %	1,2-, %	cis, %	trans, %				
"Hot"......	Butadiene styrene	72	76*	81	19	22	59	48	94,000	0.933	−56
"Cold".....	Butadiene styrene	60	79*	82	18	13	69	52	113,000	0.929	−52
Polychlorobutadiene	Chlorobutadiene	..	95†	94	1.6‡	10	84	65	114,000	1.229	−40

* Difference from 100 per cent represents bound styrene which is determined by original charge ratio and conversion.

† Differences from 100 per cent represents rearrangements and hydrolysis.

‡ 3,4 Addition amounts to approximately 1.0 per cent.

represent variations of monomer ratio, recipe ingredients, temperature of polymerization, conversion, and type of finishing operation. In addition, various carbon black, oil, and carbon black–oil master batches are available.

The development of highly reinforcing furnace blacks paralleled the creation of the synthetic-rubber industry. Improved "cold" butadiene-styrene elastomers reinforced with these new blacks give vulcanizates that are superior to natural rubber in tire treads.

Applications. Raw rubbers have few end uses, and the ultimate product is generally obtained by mixing the polymer with a variety of ingredients and heating this mixture at an elevated temperature to obtain vulcanization or cross-linking. Typical compounding formulations, shown in Table 15-19, are mixed in mechanical mixers such as Banbury or roll mills prior to placing in a vulcanization press.

TABLE 15-19. COMPOUNDING FORMULATION FOR BUTADIENE-STYRENE OR POLYCHLOROBUTADIENE ELASTOMERS

Ingredient	Tire tread with butadiene-styrene rubber	Wire jacket with polychlorobutadiene
Elastomer..............................	100	100
Carbon black...........................	50	50
Hard clay..............................	.....	35
Stearic acid...........................	2	
Zinc oxide.............................	3	5
Magnesium oxide........................	...	4
Softener oil...........................	10	12
Antioxidants...........................	2	2
Sulfur.................................	1.75	
Accelerator............................	1.0	0.5

Each ingredient of a compounding formulation performs one or more functions which may be summarized as follows. The elastomer is the basic ingredient of the compounding formulation. Carbon black or clay hardens and reinforces the elastomer and also serves as a diluent to reduce compound costs. The softener oil plasticizes the compound and aids in processing. The vulcanizing agent (sulfur) induces cross-linking reactions which are influenced in speed and degree by the accelerator used. Activators such as zinc oxide and magnesium oxide help to control the vulcanizing reaction. Many other ingredients may be used for special purposes, that is, to impart color, increase tackiness, or to retard deterioration caused by weathering, light, or heat.

The properties of a vulcanizate are the resultant of the inherent properties of the raw rubber and the chemical and physical changes accomplished by compounding, processing, and vulcanization. Vulcanizates prepared in accordance with the compounding recipes given in Table 15-19 would give the characteristic properties listed in Table 15-20.

TABLE 15-20. TYPICAL PHYSICAL PROPERTIES OF DIENE POLYMERS VULCANIZED IN ACCORDANCE WITH STANDARD RECIPES

Rubber	80°F			Heat build-up, ΔT, °F	Resilience, %	Crack growth resistance, flexures $\times 10^{-3}$	Shore hardness	Relative ratings		
	300% modulus, psi	Tensile, psi	Elongation, %					Resistance to chemicals	Resistance to aging	Resistance to wear
"Hot"	1,340	3,020	500	69	56	5	54	Good	Good	Good
"Cold"	1,580	4,060	555	73	59	14	60	Good	Good	Excellent
Polychlorobutadiene	2,000	2,300	340	..	..	..	..	Excellent	Excellent	Satisfactory

A balanced combination of properties is the criterion of performance. In tread-wear resistance, "cold" butadiene-styrene tires are approximately 20–30 per cent superior to natural-rubber or "hot" rubber treads. However, in tire carcass or sidewalls, natural rubber exhibits superior performance, especially in truck tires, because of lower heat build-up.

Over 30,000 products are made of rubber. In the passenger car alone, approximately 500 items in 100 different parts amounting to 170 lb of rubber are used, and greater amounts of rubber will be used in cars of the future if current trends continue. In nontransportation uses, industrial mechanical goods, sponge- and foam-rubber cushionings, heels and soles, wire and cable insulation, and footwear are the most important uses.

Trend of the Future. Research is being reported on emulsion polymerization systems which should result in the preparation of better butadiene-styrene elastomers. Polymers with more uniform molecular-weight distributions, more uniform fine structures, and better processing are desirable.

New diene copolymers can be expected. Butadiene–acrylic acid and butadiene–methylvinylpyridine copolymers have been reported. One of the former copolymers, compounded with zinc oxide, formed a vulcanizate with a tensile strength of over 8,000 psi, the highest on record.[1] The latter copolymer has been quaternized with active halogen compounds to form a new type of elastomeric material.[2]

The most significant development in synthetic-rubber research is the preparation of stereospecific polymers. With the synthesis of all *cis*-polyisoprene, the long sought after preparation of the natural rubber, hevea, has been accomplished.[3] This accomplishment, together with other stereospecific polymerization of dienes that have been announced, has opened a new field of polymerization research, the full significance of which cannot yet be foreseen. For example, polybutadiene containing a high percentage of *cis*-1,4 structure has been announced which approximates hevea in several important properties such as resilience and heat build-up.[4] These recent accomplishments portend that the rubber industry will eventually be free of the vicissitudes of the natural-rubber market.

[1] BROWN and GIBBS, *Ind. Eng. Chem.*, **47**, 1006 (1955).

[2] PRITCHARD and OPHEIM, *Ind. Eng. Chem.*, **46**, 2242 (1954).

[3] STAVELY et al., *Ind. Eng. Chem.*, **48**, 778 (1956); HORNE et al. *ibid.*, **48**, 784 (1956).

[4] *Rubber Age*, **79**, 322 (1956).