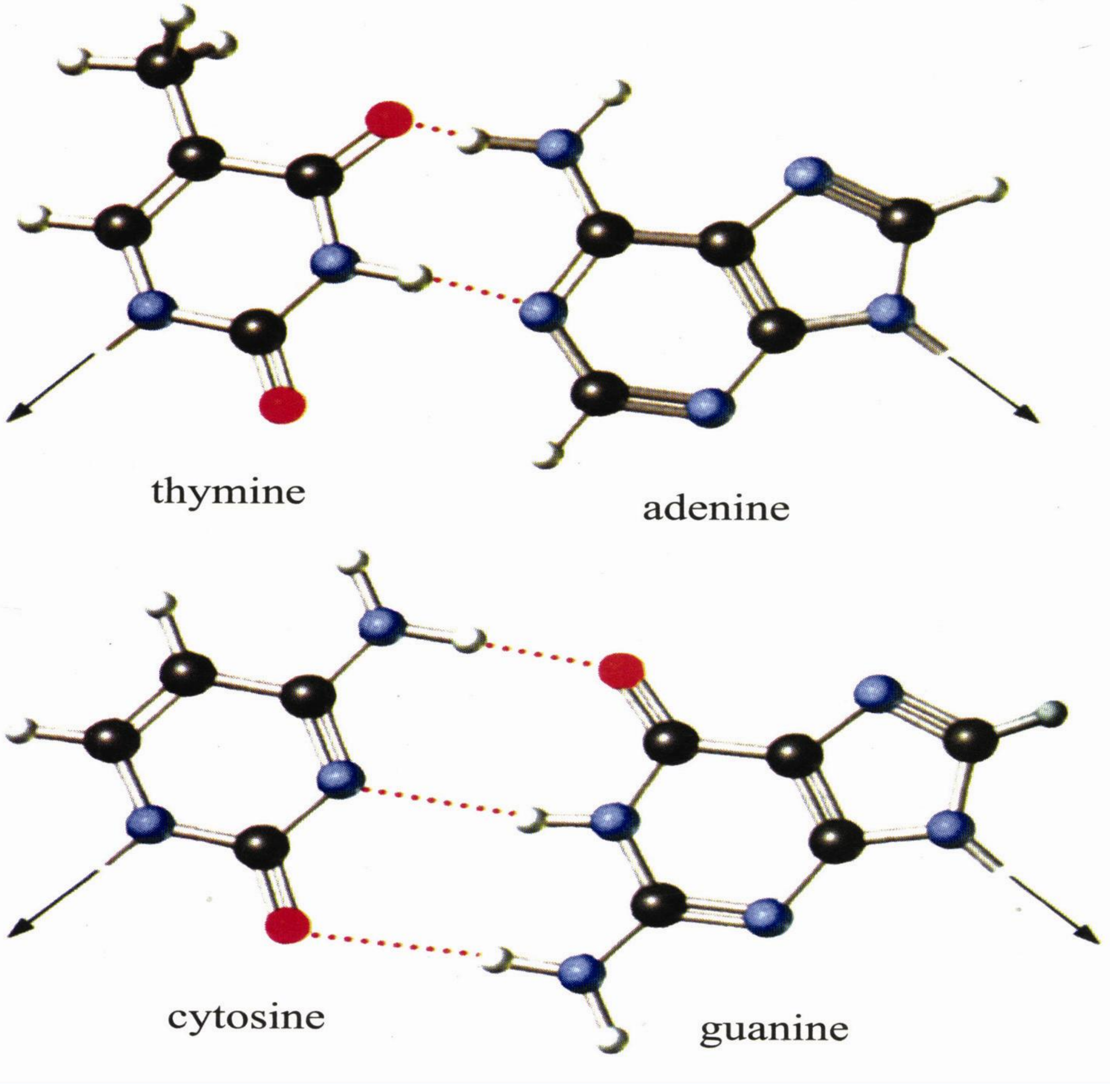
COLLEGE CHEMISTRY -II



HIMALAYA PUBLISHING HOUSE

COLLEGE CHEMISTRY-II

L. INDIRA M.Sc., M.Phil., B.Ed.,
Professor of Chemistry
Mount Carmel College, Bangalore

G.R. CHATWAL M.Sc., Ph.D.
Reader in Chemistry, Dayal Singh College,
University of Delhi, New Delhi – 111 003
Hon. Professor in Environmental Science,
I.I.E.E., New Delhi,
Member, Royal Society of Chemists (London)

Himalaya Publishing House
MUMBAI • DELHI • NAGPUR • BANGALORE • HYDERABAD

ISBN : 978-93-5024-326-8 (VOL 2)
REVISED EDITION : 2010

Published by. : Mrs. Meena Pandey
for **HIMALAYA PUBLISHING HOUSE**,
"Ramdoot", Dr. Bhalerao Marg, Girgaon,
Mumbai – 400 004.
Phone : 2386 01 70/2386 38 63 Fax : 022-2387 71 78
Email : himpub@vsnl.com
Website : www.himpub.com

Branch Offices :

Delhi : "Pooja Apartments", 4-B, Murari Lal Street,
Ansari Road, Darya Ganj,
New Delhi – 110 002.
Phone : 2327 03 92 Fax : 011-2325 62 86
Email : hphdel@ndb.vsnl.net.in

Nagpur : Kundanlal Chandak Industrial Estate,
Ghat Road, Nagpur – 440 018.
Phone : 722 12 16, Telefax : 0712-272 12 15

Bangalore : **No. 16/1 (Old 12/1), First Floor,**
Next to Hotel Highlands, Madhava Nagar,
Race Course Road, Bangalore – 560 001.
Phone : 22281541, 22385461 Telefax : 080-22286611
Email : hphblr@vsnl.com

Hyderabad : No. 2-2-1 167/2H, 1st Floor,
Near Railway Bridge, Tilak Nagar,
Main Road, Hyderabad - 500 044.
Phone : 5550 17 45 Fax : 040-2756 00 41

Printed by : Geetanjali Press, Nagpur.

Typeset by : Page Designers, Bangalore

CONTENTS

"This page is Intentionally Left Blank"

Chapter 1

Chemical Bonding

SYLLABUS

1.1 TYPES OF BONDS
1.2 IONIC BONDS
1.3 FACTORS FAVOURING FORMATION OF IONIC COMPOUNDS
1.4 PROPERTIES OF IONIC COMPOUNDS
1.5 COVALENT BOND
1.6 VALENCE BOND APPROACH (VB)
1.7 OVERLAP OF ORBITALS
1.8 BONDING IN SOME MOLECULES
1.9 CONCEPT OF RESONANCE
1.10 HYBRIDIZATION
1.11 VALENCE SHELL ELECTRON PAIR REPULSION THEORY
1.12 APPLICATIONS OF VSEPR THEORY
1.13 MOLECULAR ORBITAL THEORY (MO THEORY)
1.14 ENERGY LEVELS OF DIFFERENT MOLECULAR ORBITALS
1.15 RELATIONSHIP BETWEEN ELECTRONIC CONFIGURATION AND MOLECULAR BEHAVIOUR
1.16 MOLECULAR ORBITAL DIAGRAM OF CERTAIN HOMONUCLEAR DIATOMIC MOLECULES
1.17 COMPARISON OF VB AND MO THEORIES
1.18 POLARITY OF BONDS
1.19 PROPERTIES OF COVALENT COMPOUNDS
1.20 BOND LENGTH, BOND ANGLE AND BOND ENERGY
1.21 POLARIZABILITY
1.22 HYDROGEN BOND
1.23 VAN DER WAALS' FORCES
1.24 METALLIC BOND
1.25 CONDUCTORS, INSULATORS AND SEMICONDUCTORS
1.26 SUPERCONDUCTIVITY

The bulk of materials found in nature are compounds or mixtures of compounds rather than free elements. Since it is a rule of nature that the naturally occurring form is of the lowest energy, it follows that compounds are more stable than the free elements. A stable state has lower potential energy.

The building unit of matter is a molecule. A molecule is defined as a "small electrically neutral cluster, group or aggregate of mutually bonded atoms."

A chemical bond may be defined as an attraction which holds together the constituent atoms in a molecule.

During the formation of a chemical bond, there is necessarily a decrease in energy. Thus, when two atoms approach each other, a chemical bond is formed between them, only if potential energy of the system constituting the two atoms decreases.

1.1 TYPES OF BONDS

The formation of a bond between two atoms is due to some rearrangement of their electrons to form a more stable arrangement. The noble gases have monoatomic molecules and their atoms do not enter into chemical combination. Prior to 1962, no compounds of noble gases were known. Except helium, they all have eight electrons in their valence shell. It was suggested by Kossel and Lewis in 1916 that this octet arrangement was responsible for the stability and inertness of the noble gases. Thus *when elements form compounds they either lose or gain, or share electrons to achieve stable electron configurations similar to the nearest noble gas in the periodic table.* This simple idea forms the basis of electronic theory of bonding.

Elements may be divided into –

(i) electropositive elements, whose atoms readily give up one or more electrons.
(ii) electronegative elements whose atoms accept electrons.
(iii) elements which have little tendency to lose or gain electrons.

Depending upon the nature (electropositive or electronegative) of the element, three different types of bonds are observed.

Electropositive + *Electronegative* → *ionic bond*
Electronegative + *Electronegative* → *covalent bond*
Electropositive + *Electropositive* → *metallic bond*

The above type of classification of bonds is a broad one and a large number of intermediates between these extremes are present. In fact, only few of the bonds are purely ionic, covalent or metallic. Most of them are intermediate between these three and generally show some characteristics of all the three or at least two.

1.2 IONIC BONDS

An ionic bond is formed by the transference of one or more electrons, from one atom to the other. One of the atoms loses one or more electrons and acquires a stable octet configuration. Another atom gives one or more electrons in order to acquire a stable octet configuration. Positive and negative ions are formed. *The oppositely charged ions are held together by electrostatic forces of attraction called the ionic bond.* The attractive force tends to decrease the potential energy so that the potential energy of the molecule is less than that of the combining atoms. In the formation of sodium chloride, sodium loses an electron to form sodium ion Na^+ and acquires the stable inert gas configuration of neon. Chlorine on the other hand gains an electron to form chloride ion Cl^- thereby acquiring the stable inert gas configuration of argon.

$$\begin{array}{ccc}
\text{Na} & \xrightarrow{-e} & \text{Na}^+ \\
(1s^2 2s^2 2p^6 3s^1) & & (1s^2 2s^2 2p^6) \\
\text{Cl} & \xrightarrow{+e} & \text{Cl}^- \\
(1s^2 2s^2 2p^6 3s^2 3p^5) & & (1s^2 2s^2 2p^6 3s^2 3p^6) \\
\text{Na}^+ + \text{Cl}^- & \longrightarrow & \text{Na}^+\,\text{Cl}^-
\end{array}$$

Compounds containing ionic bonds are called ionic or electrovalent compounds.

1.2.1 Lattice Energy

In the process of the gaseous ions forming the solid crystal, a large amount of energy is released thus stabilising the compound formed. This is known as the *lattice energy* of the compound. The overall stability of a solid ionic compound depends on the interaction of all the ions present in a crystalline lattice rather than the mere interaction of a single cation with a single anion.

Lattice energy, U is defined as *the enthalpy of formation of a mole of an ionic solid from free gaseous ions brought from infinity to their respective equilibrium sites in their crystalline lattice under standard conditions.* It may also be defined as the *change in energy that occurs when an ionic solid is separated into isolated ions in the gas phase.*

For example, $Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g) \quad \Delta H = +770 \text{ kJ mol}^{-1}$

This means that when ions come together to form solid sodium chloride the energy released is 770 kJ mol^{-1}. Lattice energy of NaCl is -770 kJ mol^{-1}. The net change in energy when gaseous sodium and chlorine atoms form solid sodium chloride is -629 kJ/mol. The negative sign indicates a stable bond formation.

The following steps are assumed to be involved in the formation of solid NaCl.

$$\begin{array}{llll}
\text{Na(s)} & \xrightarrow{\Delta H_s} & \text{Na(g)} & \Delta H_1 = 108\,\text{kJ} \\
\frac{1}{2}\text{Cl}_2\text{(g)} & \xrightarrow{1/2\Delta H_d} & \text{Cl(g)} & \Delta H_2 = 121.5\,\text{kJ} \\
\text{Na(g)} & \xrightarrow{I} & \text{Na}^+\text{(g)} & \Delta H_3 = 496\,\text{kJ} \\
\text{Cl(g)} & \xrightarrow{E.A.} & \text{Cl}^-\text{(g)} & \Delta H_4 = -355\,\text{kJ} \\
\text{Na}^+\text{(g)} + \text{Cl}^-\text{(g)} & \xrightarrow{U} & \text{Na}^+\text{Cl}^-\text{(g)} & \Delta H_5 = U \\
\text{Na(s)} + \frac{1}{2}\text{Cl}_2\text{(g)} & \xrightarrow{\Delta H_f} & \text{Na}^+\text{Cl}^-\text{(s)} & \Delta H_f = -399.5\,\text{kJ}
\end{array}$$

1.2.2 Born-Haber Cycle

Unfortunately, lattice energies cannot be determined directly. *A cyclic process devised by Born and Haber (1919) now called the Born-Haber cycle relates the crystal energy to other thermochemical quantities.* Born and Haber applied the Hess's law to the enthalpy of formation of an ionic bond. For the formation of an ionic crystal of sodium chloride from the elements, the Born-Haber cycle may be written as –

$$\begin{tikzcd}
\text{Na (g)} \arrow[rrr, "\text{I} \quad 496\ \text{kJ}", "\text{step 3}"'] & & & \text{Na}^+\text{(g)} \\
& & & + \\
& & \text{Cl(g)} \arrow[r, "\text{E.A. } -355\ \text{kJ}", "\text{step 4}"'] & \text{Cl}^-\text{(g)} \arrow[d, "\text{step 5} \ U"] \\
\text{Na (s)} \arrow[uuu, "\text{step 1} \ \Delta H_s \ 108\ \text{kJ}"'] & + & \frac{1}{2}\text{Cl}_2\text{(g)} \arrow[u, "\text{step 2} \ \frac{1}{2}\Delta H_d \ 121.5\ \text{kJ}"'] \arrow[r, "\Delta H_f\ -399.5\ \text{kJ}", "\text{Direct route}"'] & \text{Na}^+\text{Cl}^-\text{(s)}
\end{tikzcd}$$

$$\Delta H_f = \Delta H_s + I + \frac{1}{2}\Delta H_d + E.A. + U$$

Since all the values other than lattice energy in the Born-Haber cycle can be determined experimentally, the lattice energy for sodium chloride can be calculated.

$$U = \Delta H_f - \Delta H_s - I - \frac{1}{2}\Delta H_d - E.A.$$

$$= -399.5 - 108 - 496 - 121.5\ (-355)$$

$$\text{Latice energy} = -770\ \text{kJ/mol}$$

The magnitude of lattice energy gives an idea of the force of attraction between Na^+ and Cl^- ions in sodium chloride crystalline lattice. *Greater the lattice energy, the more stable the ionic compound.*

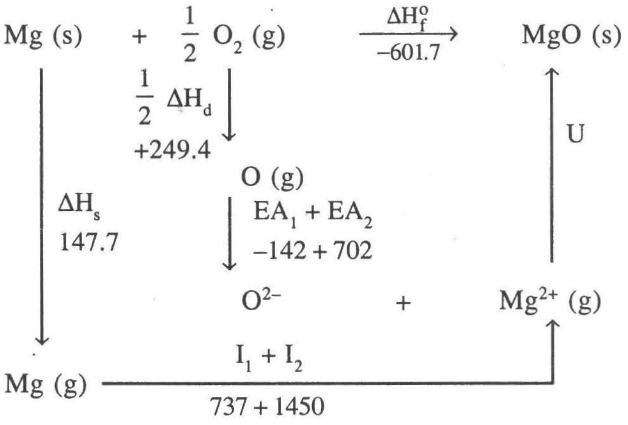
[**Note:** The actual formation of NaCl need not follow the above steps. The above steps are just a simplified and convenient way to analyse the energetics of ionic compound formation.]

Table 1.1 gives a list of lattice energies of some common compounds.

Table 1.1: Lattice Energies (kJ mol^{-1}) of some Compounds

Compound	*Lattice energy*	*Compound*	*Lattice energy*
LiF	–1012	KCl	–703
LiCl	–845	KBr	–689
LiBr	–787	KI	–632
LiI	–732	$MgCl_2$	–2527
NaCl	–770	MgO	–3933
NaBr	–736	NaI	–686

Born-Haber cycle can be set up for a compound like MgO. In magnesium oxide, magnesium is in +2 state and oxygen in –2 state. Thus one need to consider two ionisation potentials I_1, and I_2 for magnesium and two electron affinities EA_1 and EA_2 for oxygen.



Thus, $$\Delta H_f = \Delta H_s + \frac{1}{2}\Delta H_d + I_1 + I_2 + EA_1 + EA_2 + U$$

$$\begin{aligned} \text{or } U &= \Delta H_f - \Delta H_s - \frac{1}{2}\Delta H_d - I_1 - I_2 - EA_1 - EA_2 \\ &= -601.7 - 147.7 - 249.4 - 737 - 1450 - (-142) - 702 \\ &= -3745.8 \text{ kJ mol}^{-1} \end{aligned}$$

The calculation of second electron affinity of an element is made possible by constructing the Born-Haber cycle for the compound. Lattice energy for the compound is available from Born-Lande equation.

Comparing the lattice energy of NaCl with that of MgO it can be clearly seen that MgO has much stronger bonding than NaCl. This can be easily understood as in MgO, the ions involved are bivalent; assuming the distance between the ions in both solids to be roughly the same, the energy liberated will be about four times than that in NaCl according to Coulomb's law. Also, the ions in MgO are closer than in NaCl being bivalent.

1.2.3 Born-Lande Equation

Theoretical values for lattice energy may be calculated. The crystal is assumed to be made up of perfectly spherical ions. From the geometry of the crystal, the interionic distance is known. The energy of attraction between all the oppositely charged ions and the energy of repulsion between ions of same charge are calculated. The final equation obtained is *Born-Lande equation* –

$$\text{Lattice energy, } U = \frac{N_0 A z^+ z^- e^2}{A\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

N_0 – Avogadro's number (6.022×10^{23})

A – Madelung constant which depends on the crystal structure

z^+ – Charge on the cation
z^- – Charge on the anion
e – Electronic charge (1.602×10^{-19} C)
ε_o – Permitivity of medium ($8.854 \times 10^{-12}\ C^2m^{-1}J^{-1}$)
r_0 – Equilibrium interionic distance
n – Born exponent whose value depends on the type of the ion.

Calculation of lattice energy of NaCl using Born-Lande equation –

A = 1.748, r_o = 0.281 mm, n = 8

Born-Lande equation is

$$U = \frac{N_0 A z^+ z^- e^2}{A\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

For NaCl $z^+ = z^- = 1$

Substituting the values

$$= \frac{6.022\times10^{23}\times1.748\times1\times1\times\left(1.602\times10^{-19}C\right)}{4\times3.142\times8.854\times10^{-12}C^2\,m^{-1}J^{-1}\times0.281\times10^{-9}m}\left(1-\frac{1}{8}\right)$$

$$= 755.9\ \text{kJmol}^{-1}$$

Lattice energy of NaCl is – 755.9 kJ mol^{-1}

Calculation of lattice energy of MgO using Born-Lande equation

A = 1.748 r_o = 0.2106 nm, n = 7

For MgO, $z^+ = z^- = 2$

$$U = \frac{N_0 A z^+ z^- e^2}{A\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

$$= \frac{6.022\times10^{23}\times1.748\times2\times2\times\left(1.602\times10^{-19}C\right)^2}{4\times3.142\times8.854\times10^{-12}C^2\,m^{-1}J^{-1}\times0.2106\times10^{-9}m}\left(1-\frac{1}{7}\right)$$

$$= 3952.4\ \text{kJ mol}^{-1}$$

Lattice energy of MgO is –3952.4 kJ mol^{-1}

Born exponent values (n) and Madelung constants (A) are given in Tables 1.2 and 1.3.

Table 1.2: Born Exponent Values

Ion type	*Examples*	*n*	*Ion type*	*Examples*	*n*
He	Li^+, Be^{2+}	5	Kr	Rb^+, Br^-, Ag^+	10
Ne	Na^+, Mg^{2+}, O^{2-}	7	Xe	Cs^+, I^-, Au^+	12
Ar	K^+, Ca^{2+}, S^{2-}, Cl^-, Cu^+	9	Rn		14

*average values of n for the two kinds of ions are used.

Table 1.3: Madelung Constants

Crystal type	*Madelung constant*	*Crystal type*	*Madelung constant*
Zinc blende	1.638	Zinc sulphide	1.641
Sodium chloride	1.748	Rutile (TiO_2)	2.408
Caesium chloride	1.763	Fluorite (CaF_2)	2.519

1.3 FACTORS FAVOURING FORMATION OF IONIC COMPOUNDS

Ionic bonds are possible only between elements of opposite nature, i.e., one of them having a tendency to lose electrons and the other to gain electrons. Thus ionic bond formation is restricted only to most active metals (elements of group 1 and 2 and part of 13 sometimes) and the most active non-metals (elements of group 16 and 17, and nitrogen). Some transition metals also enter into ionic bond formation.

The following factors favour formation of ionic bonds –

1. Low ionization energy: One of the elements should have a low ionization energy so that it can readily form a cation. Ionization energy is a measure of the case with which atoms form cations. *Ionization energy is defined as the amount of energy required to remove the most loosely held electron from a neutral gaseous atom.* The lesser the ionization energy of an atom the greater is the ease with which an electron is lost and a cation is formed. The metals with low ionization energy values have greater tendency to form ionic bonds. Alkali (group 1) and alkaline earth metals (group 2) have relatively low ionization energies and generally form ionic compounds.

Caesium, in group I has the largest size and can lose outermost electron very easily. It forms a cation most readily. In general, cations are formed easily as we go down a group.

A very large amount of energy is required to remove a second electron from any positively charged ion. Thus, formation of a doubly charged cation Mg^{2+}, Ca^{2+} requires a large amount of energy, almost 4 times compared to that required for the removal of one electron.

Thus, alkaline earth metals (group 2) form cations (M^{2+}) with less ease compared to the alkali metals (group 1).

2. High electron affinity: The other atom forming an ionic bond must form an anion by gaining one or more electrons. This tendency of an atom to form an anion depends upon its *electron affinity. Electron affinity is defined as the amount of energy released when an electron is added to neutral gaseous atom.* Higher the electron affinity of an atom, greater is the ease of formation of anion.

The halogens (group 17) have the highest electron affinity among all the elements. The halogens, thus readily form ionic compounds. The elements of oxygen family (group 16) come next with high electron affinity values. However, energy is required to remove a second electron from a negative ion. Thus elements of group 16 form anions less readily than the halogens.

$$\text{Cl (g)} \xrightarrow{+e} \text{Cl}^- \text{(g)} \quad \text{EA} = -348 \text{ kJ/mol}$$

$$\text{O (g)} \xrightarrow{+e} \text{O}^- \text{(g)} \quad \text{EA} = -142 \text{ kJ/mol}$$

$$\text{O}^- \text{(g)} \xrightarrow{+e} \text{O}^{2-} \text{(g)} \quad \text{EA} = +702 \text{ kJ/mol}$$

3. High lattice energy: The formation and strength of an ionic bond depends on the electrostatic force of attraction between oppositely charged ions. Higher the lattice energy, greater is the ease of formation of the ionic compound. The magnitude of lattice energy depends upon –

(a) Size of the ions: Smaller the size of the ions, lesser is the internuclear distance and greater the interionic attraction. The lattice energy is therefore large. Since the size of the ions increase down any group, the lattice energy of similar compounds decreases down a group. Thus lattice energy of formation of NaCl is –770 kJ/mol whereas it is –703 kJ/mol for KCl.

(b) Charge on the ions: The electrostatic attraction is more for ions of higher charges. The lattice energy is large for ions of higher charges. The lattice energy for MgO (Mg^{2+} O^{2-}) is –3933 kJ/mol while the lattice energy for NaCl (Na^+Cl^-) is – 770 kJ/mol.

Thus, the conditions favourable for ionic compound formation are –

1. low ionization energy for one of the atoms
2. high electron affinity for the other atom
3. high lattice energy for the formation of the solid ionic crystal.

1.4 PROPERTIES OF IONIC COMPOUNDS

In ionic crystals, ions of oppositely charged ions are held together by strong electrostatic forces of attraction. These crystals are giant ionic structures and no single molecule exist. Some of the common properties are –

(i) Very stable, have high melting and boiling points. Large quantities of energy need to be supplied to pull away the ions from their relative positions for the solid to melt.

(ii) Hard and brittle. However, they may be cleaved in a particular plane.

(iii) Good conductors of electricity in the molten state and in aqueous solutions. Do not conduct current in the solid state as the ions present cannot move freely.

(iv) Soluble in polar solvents such as water but insoluble in non-polar solvents such as benzene. In polar solvents, the ions get easily solvated (or hydrated in water) and thus pass into solution.

(v) Chemical reactions of ionic compounds in solution are reactions of their constituent ions. These reactions are hence instantaneous.

1.5 COVALENT BOND

According to Lewis concept, a covalent bond is formed by sharing of electrons. This sharing of outer valence electrons in the formation of a molecule leads to the stability of the molecule. A covalent bond is formed between atoms of elements with same or similar electronegativity. This concept however could not explain how sharing of electrons takes place and the nature of the bonding forces. Also, it gives no information regarding the shapes of the molecules, bond length, different bond energies associated with different molecules etc.

With the advent of Schrodinger equation attempts were made to understand the nature of the covalent bond and wave mechanical theories have been formulated to explain the nature of the covalent bond.

Two important approaches are –

1. Valence Bond Theory
2. Molecular Orbital Theory

Bond formation is possible only when there is decrease of energy as the two atoms approach each other. When two atoms approach, attractive as well as repulsive forces come into play – internuclear and interelectronic repulsion; attraction of one nucleus towards the electron cloud of the other and vice versa. A covalent bond cloud results if the net effect is attraction leading to a decrease in total energy of the system.

1.6 VALENCE BOND APPROACH (VB)

This was first developed by Heitler and London in 1927 and later extended by Pauling and Slater in 1931. It is assumed that atoms complete with electrons, come together to form the molecule. The atoms retain their individuality and the bond is formed due to the interaction of valence electrons as the atoms approach each other.

Valence bond theory states that *a chemical bond can be formed by the overlap of atomic orbitals. Overlap means, the two orbitals share a common region in space.*

The total number of electrons in both the orbitals is not more than two. The covalent bond is formed by pairing and resultant neutralisation of opposite electron spins.

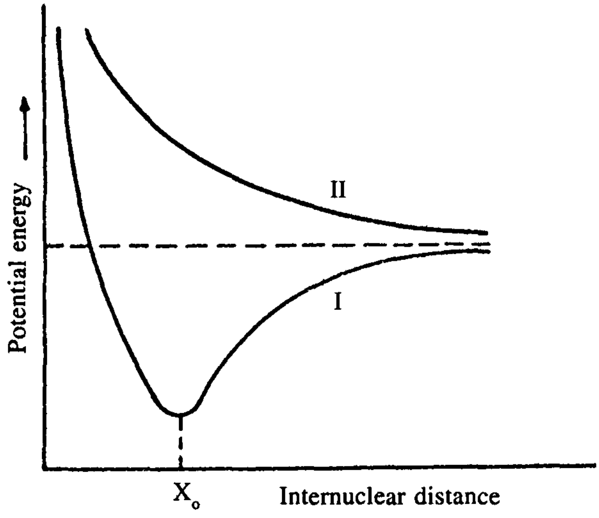


Fig. 1.1: Decrease in potential energy during the formation of a molecule

The VB approach may be illustrated considering the formation of hydrogen molecule.

The two hydrogen atoms when infinitely apart, exert no influence over each other. Although the two hydrogen atoms are identical, for convenience sake, the two electrons may be labelled 1 and 2 and the nuclei A and B.

When the hydrogen atoms are infinitely apart, the potential energy is arbitrarily set at zero. As the two atoms approach one another, the electron 1 of the atom H_A is attracted by the nucleus H_B and the electron 2 of the atom H_B is attracted by the nucleus H_A. As a result of this weak attraction, there is a decrease in the energy of the system. This attraction more than compensates for the electron-electron and nucleus-nucleus repulsions.

As the two atoms approach one another the distance between them decreases and the forces of attraction increase rapidly. Ultimately, at a certain distance x_0 between the two nuclei of the two atoms, the system has the lowest energy (curve I). The system is most stable at this point. The overlap between the two 1s orbitals is substantial and results in the formation of a stable hydrogen molecule. At this distance called the *bond distance* or the bond length, the atoms are said to be *bonded together.* If the atoms are brought closer, the forces of repulsion due to the proximity of the two nuclei sets in and there is an increase in the energy of the system (curve 1).

However, if the two electrons have parallel spins, then the energy increases continuously as the atoms come closer (curve II) and no bond is formed. Thus for bonding to occur, according to VB approach, it is *necessary that each atom must have an unpaired electron available for pairing with that of the other atom and the two electrons should be of opposite spins.*

Also as the electrons are similar and not distinguishable from each other, the electrons can exchange their positions so that electron 1 at any time is associated with nucleus B and electron 2 with nucleus A.

i.e., $H_A^1 - H_B^2$ and $H_A^2 - H_B^1$

The above two structures are indistinguishable. There is also a finite probability for both electrons to remain attached to the nucleus of one of the hydrogen atoms giving rise to following ionic configurations.

$\overline{H}{:}_A - H_B^+$ and $H_A^+ - \overline{H}{:}_B$

The bond energy calculated considering all the above possibilities is quite close to the experimental value.

The VB theory gives a clearer picture of chemical bond formation. *VB theory states that a stable molecule forms from reacting atoms when the potential energy of the system decreases to reach a minimum.* The energy changes in chemical bond formation is totally ignored in Lewis theory.

1.7 OVERLAP OF ORBITALS

When two atoms approach each other, there is partial merging of the two bonding atomic orbitals. This is known as overlapping of orbitals and results in pairing of electrons. A covalent bond is said to be formed. The strength of the bond depends upon the extent of overlapping. *The greater the overlap the stronger is the covalent bond formed.*

1.7.1 Sigma and pi bonds

Depending upon the type of atomic orbitals overlap, the covalent bonds are divided into two types, namely *sigma* (σ) *and pi* (π) *bonds.*

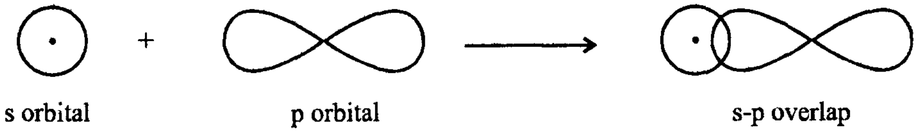
Sigma bond: Sigma bond is formed by the *end-to-end overlap of atomic orbitals along the molecular axis.* This is also known as *axial or head-on-overlap.*

A sigma bond results when there is s-s, s-p and p-p overlap along the internuclear axis.

s-s overlapping: Two half-filled s orbitals overlap along the nuclear axis as shown.

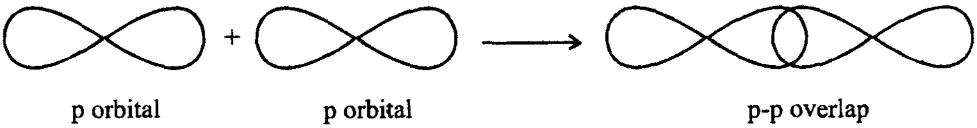
s-s overlapping is seen in the formation of H_2 and LiH molecules.

s-p overlapping: This type of overlapping occurs between a s orbital of one atom and a p orbital of the other atom along the molecular axis.



Examples include HCl, HF etc.

p-p overlapping: Two half-filled p orbitals of two atoms overlapping along the molecular axis also result in a σ bond.

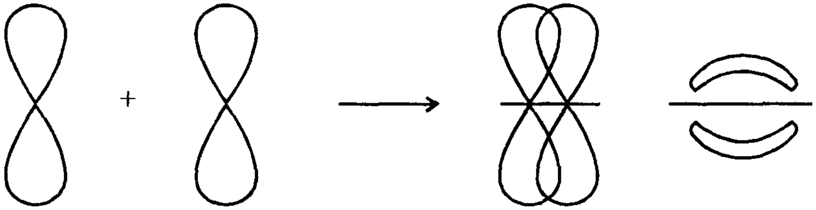


In molecules F_2, Cl_2, Br_2 etc. p-p overlap is seen.

In the case of a p orbital overlapping with s-orbital or a p-orbital, it is necessary that they be oriented along the same axis. Thus $p_x - p_x$ overlap is possible but not $p_x - p_y$ or $p_x - p_z$ or $p_y - p_z$.

Pi (π) bond: *A pi bond results by the sidewise or lateral overlap of half-filled orbitals of the atoms. The p orbitals lying perpendicular to the molecular axis overlap.*

The resultant orbital is saucer-shaped lying above and below the plane of the molecule or the bond axis.



p orbitals p-p overlap (p-bond)

The overlapping in the formation of a π bond is poor and hence the π bond is relatively weak. Whenever there are more than one bond between two atoms, only one of them is a σ bond. The rest are π bonds. Thus in oxygen molecule O = O there is one σ and one π bond between the atoms.

Table 1.4: Comparison of σ and π Bonds

Sigma (σ) bond	*Pi (π) bond*
1. A σ bond is obtained by the end-to-end overlap of atomic orbitals	A π bond is obtained by the lateral overlap of atomic orbitals.
2. The overlap is large and the bond is a strong bond.	The overlap is relatively small and the bond is therefore weak.
3. It is symmetrical about the bond axis	It is not symmetrical about the bond axis
4. A molecule may have only σ bonds but no π bonds.	The bond is formed only where there is a σ bond already present between the two atoms.
5. s orbitals can participate in the formation of a σ bond.	s orbitals cannot participate in the formation of a π bond.
6. There is free rotation of atoms about the σ bond.	There is no free rotation of atoms when a π bond is present.
7. The direction of the bond is determined by the σ bond.	The π bond plays no role in determining the direction of the bond.

1.8 BONDING IN SOME MOLECULES

Fluorine molecule (F_2): Each fluorine atom has one electron less than the octet as can seen from electron configuration $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2 2p_z^1$. The two half-filled p_z orbitals of the two fluorine atoms overlap resulting in a σ bond between the two atoms.

Hydrogen fluoride molecule (HF): While fluorine atom needs one more electron in its valence shell to complete its octet, hydrogen atom also requires one more electron to acquire a stable configuration. The s orbital of H atom and the p_z orbital of F atom overlap forming a stable HF molecule.

Oxygen molecule (O_2): Oxygen atom has the electronic configuration $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. There are two half-filled p orbitals. One of the p orbitals of the same symmetry say p_y orbitals from each oxygen atom overlap along the bond axis and a σ bond is formed. The other half-filled p_z orbital on each oxygen atom which are in a direction perpendicular to the bond axis overlap laterally. A pi bond is thus formed. A double bond (σ and π) exists between the two oxygen atoms in a molecule of oxygen.

Nitrogen molecule (N_2): Nitrogen atom has the electron configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. There are three half-filled p orbitals. As in the formation of oxygen molecule one of the p orbitals on each N atom of same symmetry overlap along the bond axis forming a σ bond. The other two half-filled orbitals on each N atom overlap laterally to form two pi bonds. Thus a triple bond (one σ and two π) is present between two N atoms in a molecule of nitrogen.

Pauling and Slater extended the VB theory of Heitler and London to account for the directional nature of the covalent bond. The directional nature of the covalent bond arises due to the vectorial nature of charge intensities responsible for such bonding.

The VB theory can be summarised as –

1. A covalent bond is formed when the orbital of one atom overlaps with the orbital of another atom, each of them containing one unpaired electron.
2. The two electrons involved in bond formation must have opposite spins. If these electrons have parallel spins, repulsion takes place and no bond formation is possible.
3. The overlapping orbitals must have an appropriate symmetry about the molecular axis for forming a bond.
4. A stable molecule is formed when there is a decrease in the potential energy of the molecules.
5. As the atomic orbitals of the two atoms overlap, the electrons in the orbitals begin to move about between the atoms. As they are attracted to both nuclei at the same time, they pull the atoms together. This causes an increase in the electron density between the two nuclei.
6. If the atoms have more than one unpaired electron, multiple bond formation is possible. In nitrogen molecule for example, three bonds are formed as there are three unpaired electrons.
7. The number of covalent bonds formed by 'an atom is equal to the number of unpaired electrons it has. Electrons already paired cannot obviously participate in bond formation as such. They can, however do so if they can be unpaired with only small expenditure of energy. In a general way, this is possible if the unpairing of electrons and promotion of one of them involves no change in the principal quantum number. Nitrogen, for example, with an

outer electronic configuration $2s^2\,2p_x^{\,1}\,2p_y^{\,1}2p_z^{\,1}$ shares its three unpaired electrons with three fluorine atoms to form nitrogen trifluoride NF_3; but does not form a pentafluoride since n = 2 level does not contain any other orbital to accommodate the unpaired 2s electrons. In contrast, phosphorus with its outer electronic configuration $3s^2\,3p_x^{\,1}\,3p_y^{\,1}\,3p_z^{\,1}$ can form a pentahalide as empty 3d orbitals are available.

8. The strength of the covalent bond is proportional to the extent of the overlapping of the two atomic orbitals. The greater the overlap between the atomic orbitals, the greater is the strength of the resulting covalent bond.
9. Overlapping takes place only between orbitals of those electrons which take part in bond formation. The other orbitals of the atoms are not affected. In other words, the inner orbitals of atoms are undisturbed.
10. A spherically symmetrical s-orbital does not show any preference in direction whereas p–, d– or f– orbitals tend to form a bond in the direction of maximum electron density within the orbital i.e., along their axes.

(a) s-s overlap is the same in all directions.

(b) p-p overlap leads to a strong bond when the overlap is along the axes.

(c) s-p overlap leads to a bond weaker than p-p bond along the axis but stronger than s-s bond.

1.9 CONCEPT OF RESONANCE

Many a time it is *not possible to represent a molecule by a single valence bond structure that would correctly account for the properties of the substance. In such cases it is represented as a hybrid of two or more valence bond structures.* The *molecule* is said to be a *resonance hybrid* of the various structures. By convention the *different valence bond structures called the resonating structures or canonical structures are written down with a double headed arrow in between.* Thus in the case of hydrogen molecule.

$$\mathrm{H}_{A}^{\cdot 1} - \mathrm{H}_{B}^{\cdot 2} \leftrightarrow \mathrm{H}_{A}^{\cdot 2} - \mathrm{H}_{B}^{\cdot 1} \leftrightarrow \overline{\mathrm{H}}{}^{:}_{A} - \overset{+}{\mathrm{H}}_{B} \leftrightarrow \overset{+}{\mathrm{H}}_{A} - \overline{\mathrm{H}}{}^{:}_{B}$$

The actual structure cannot be correctly depicted by any of the above 4 structures as it is a composite of these structures. The true structure is a hybrid of the above structures. The molecule has its own unique stable structure and the difficulty lies in representing the structure and not in the molecule. The resonance hybrid is more stable than any of the resonating structures. This extra stability of the actual molecule, is taken to be equal to the *difference in energy between the actual molecule and the most stable of the resonating structures.* This is called the *resonance energy.* This concept of resonance is of fundamental importance in valence bond treatment.

The different resonating structures are written down keeping the following the following rules in mind:

1. Each structure should have the same arrangement of atoms i.e., nuclear framework should be the same. Only the arrangement of electrons is different in the different structures.

2. Each structure should have the same number of unpaired electrons.
3. The contributing structures should all have similar energies.
4. The greater the number of covalent bonds, the greater is the contribution of the resonating structure to the resonance hybrid.

Resonance which was widely accepted in 1950's is now considered clumsy and inadequate. The entire phenomenon of resonance is mainly due to a restricted approach in VB theory of a bond – a localised pair of electrons between two nuclei. Delocalised bonding is a better way of viewing the situation.

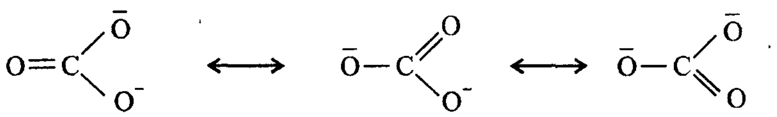
Resonance structures of some molecules:

Carbon dioxide, CO_2

$$O=C=O \longleftrightarrow \bar{O}-C\equiv\overset{+}{O} \longleftrightarrow \overset{+}{O}\equiv C-\bar{O}$$

The actual bond length is 0.115 nm. Due to the symmetrical nature the contribution by the first structure is more.

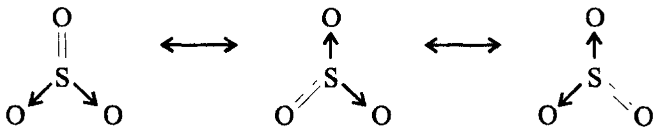
Structure of CO_3^{2-}



The observed bond length is 0.131 nm.

Structure of SO_3

The observed bond length is 0.143 nm.



1.10 HYBRIDIZATION

The concept of atomic orbital overlap when extended to polyatomic molecules must account for molecular geometry as well. To explain observed molecular geometry in polyatomic molecules, VB theory uses the concept of hybridization. *It is the phenomenon of mixing of the atomic orbitals of nearly equal energy in an atom resulting in orbitals of equal energy.* The new orbitals formed are called *hybrid orbitals.* The following rules are observed during hybridization.

1. The concept of hybridization is used to explain the bonding scheme in a molecule and not to isolated atoms.
2. Only orbitals of similar energies belonging to the same atom can undergo hybridization.
3. The number of hybrid orbitals formed is always equal to the number of orbitals mixed. Hybrid bonds are stronger than the single non-hybridized bonds of comparable energy.

4. The shapes of hybrid orbitals are different from pure atomic orbitals.
5. Once an orbital has been used to build a hybrid it is not available any longer to hold electrons in its pure form.

Most set of hybrid orbitals are equivalent and symmetric, for example, four sp^3 hybrid orbitals directed to the four corners of a regular tetrahedron, six $d^2sp^3(sp^3d^2)$ hybrid orbitals to the six corners of a regular octahedron etc. However, in the case of dsp^3 (sp^3d) hybridization the resulting hybrid orbitals are not equivalent. In the trigonal pyramidal arrangement, three orbitals directed trigonally form one set of equivalent orbitals (these may be considered as sp^2 hybrids) and two orbitals directed linearly (perpendicular to the plane of the first three) form a set of equivalent orbitals (these may be considered dp hybrids). The former set is known as *equatorial orbitals* and the latter set is called *axial orbitals*. Because of the difference in the nature of the orbitals involved, bonds formed from the two are intrinsically different and have different properties even when bonded to identical atoms. It has been found that equatorial hybrid orbitals are capable of forming stronger bonds than axial hybrids and are shorter by 0.015 nm. PCl_5 is a very good example where P undergoes sp^3d hybridization.

The hybrid orbitals generally have s or p character (even d-) which roughly depends upon the number of such pure orbitals involved in its formation.

Both pure s and pure p orbitals provide relatively inefficient overlap compared with that of hybrid orbitals. The relative overlap of hybrid orbitals is given in Table 1.5.

Table 1.5: Approximate Strengths of Bonds Formed by Various Orbitals

Orbitals	*Relative bond strength*
s	1.0
p	1.73
sp	1.93
sp^2	1.99
sp^3	2.00

Table 1.6: Types of Hybridization and Shapes of Molecules

Number of outer orbitals	*Shape*	*Hybridization*	*Bond angle*
2	Linear	sp ($BeCl_2$, C_2H_2)	180°
3	Plane triangular	sp^2 (BCl_3, C_2H_4)	120°
4	Tetrahedral	sp^3 (CH_4, CCl_4)	109.5°
5	Trigonal bipyramidal	dsp^3 (PCl_5)	90° & 120°
6	Octahedral	d^2sp^3(SF_6)	90°

1.10.1 sp Hybridization

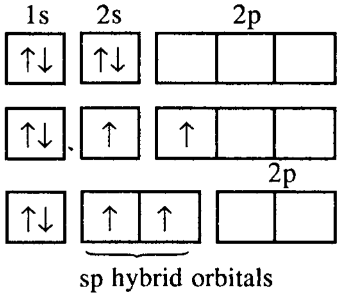
The mixing of a *s* and *p* orbital to form two orbitals of equal energy is called *sp hybridization*, The two hybrid orbitals are oriented at an angle 180° in order the repulsion be at its minimum. Each hybrid orbital has two lobes, a bigger one pointing in one direction and the other a smaller one pointing in the opposite direction. It is a common practice to show only the bigger lobe which overlaps with another atomic orbital to form a bond. The overlap is therefore more effective than the overlap of a pure atomic orbital; also, the bond formed is stronger.

The structure of beryllium chloride is linear with a bond angle 180°. The central atom beryllium undergoes sp hybridization and determines the shape of the molecule formed.

Ground state configuration of Be atom $1s^2\ 2s^2$

Excited state of Be atom $1s^2\ 2s^1\ 2p^1$

sp hybridization



The sp hybrid orbitals then overlap with 3p orbitals of two chlorine atoms to form beryllium chloride.

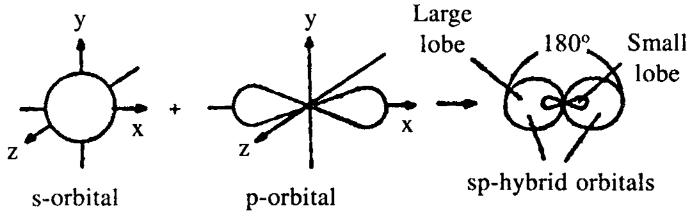


Fig. 1.2: Formation of sp hybrid orbitals

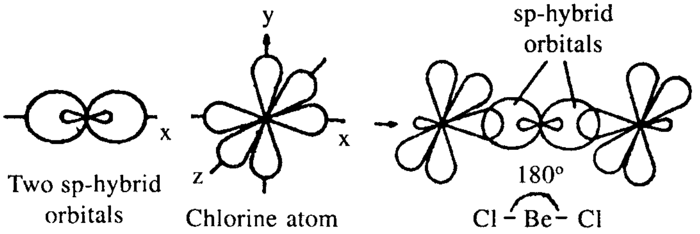


Fig. 1.3: Formation of linear $BeCl_2$ molecule

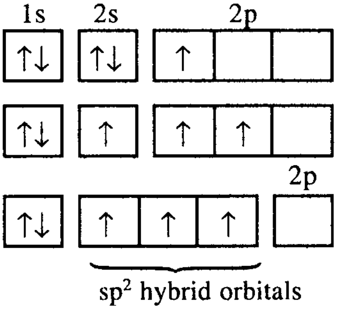
1.10.2 sp² Hybridization

To explain the planar trigonal structure of boron trichloride with a bond angle 120°, the central boron atom is said to be sp^2 hybridized. The sp^2 hybrid orbitals are obtained by the hybridization of s and two p orbitals. The three sp^2 hybrids lie in a plane and the angle between any two of them is 120°. Each B–Cl bond is formed by the overlap of an sp^2 hybrid orbital of boron with a p orbital of chlorine atom.

Ground state configuration of boron atom $1s^2\ 2s^2\ 2p^1$

Excited state of B atom $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1$

sp^2 hybridization



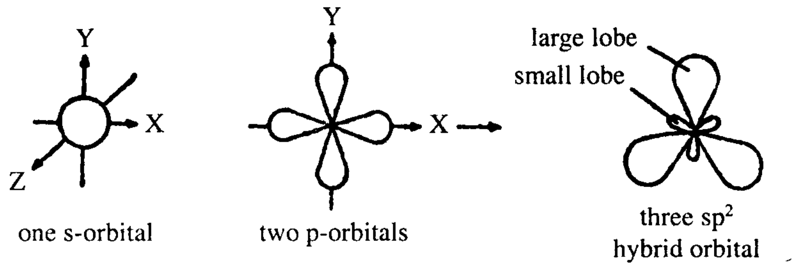


Fig. 1.4: Formation of sp^2 hybrid orbitals

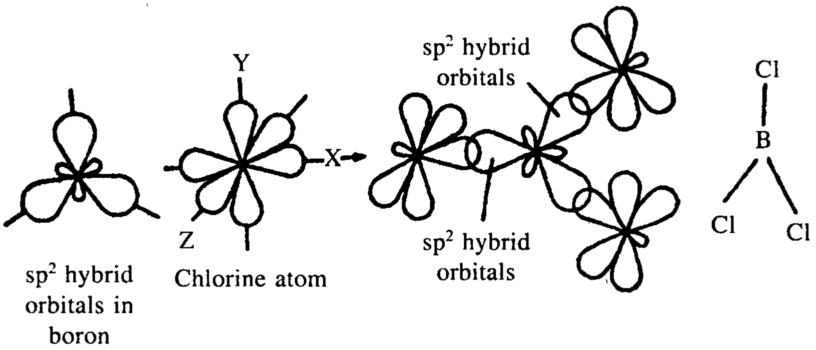


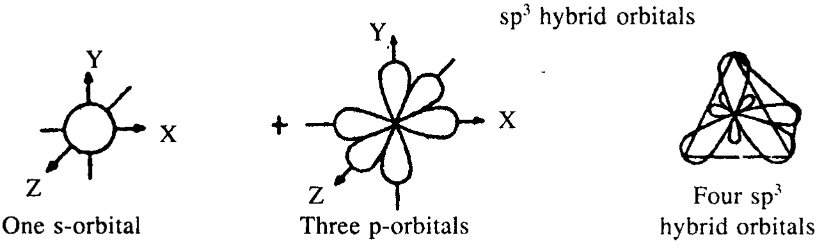
Fig. 1.5: Formation of BCl_3 molecule

1.10.3 sp^3 Hybridization

The electronic configuration of silicon in its ground state is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ with two unpaired electrons. To explain the tetravalency of silicon, sp^3 hybridization of the 3s and three 3p orbitals is proposed. For minimum repulsion of the hybrid orbitals, the four hybrid orbitals are distributed about the silicon atom at an angle 109.5° and pointing in tetrahedral directions. Each of the four Si-Cl bond is obtained by the overlapping of sp^3 hybrid orbital of the silicon atom with 2p orbital of Cl atoms. The bonds are arranged tetrahedrally.

	3s	3p		
Outer shell configuration of silicon $3s^2\ 3p^2$	↑↓	↑	↑	
Excited state of Si atom $3s^1\ 3p_x^{\ 1}p_y^{\ 1}p_z^{\ 1}$	↑	↑	↑	↑
sp^3 hybridization	↑	↑	↑	↑

sp^3 hybrid orbitals



One s-orbital

Three p-orbitals

Four sp^3 hybrid orbitals

Fig. 1.6: Formation of sp^3 hybrid orbitals

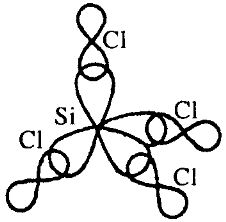


Fig. 1.7: $SiCl_4$ molecule

1.10.4 sp^3d Hybridization

The bonding in phosphorous pentachloride PCl_5, may be described considering the hybridization of 3s, 3p and 3d atomic orbitals of phosphorous as shown. This is a case of sp^3d hybridization

	3s	3p			3d				
Valance shell configuration of P atom in the ground state	↑↓	↑↓	↑						
Excited configuration of P atom $3s^1\ 3p^3\ 3d^1$	↑↓	↑	↑	↑	↑				
sp^3d hybridization	↑	↑	↑	↑	↑				

sp^3d hybrid orbitals 3d

The five hybrid orbitals combine with p orbitals of five chlorine atoms giving phosphorous pentachloride. As discussed earlier (1.10), in this case, the five hybrid orbitals are not equivalent. The geometry of the molecule has trigonal bipyramidal structure. The structure being unsymmetrical is not stable. PCl_5 is therefore a very active molecule.

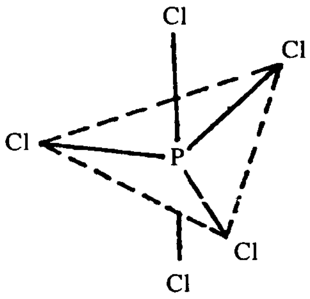


Fig. 1.8: PCl_5 molecule

1.10.5 sp^3d^2 Hybridization

The mixing of 3s, three 3p and two 3d orbitals as in sulphur atom in the molecule sulphur hexafluoride SF_6 is an example of sp^3d^2 hybridization.

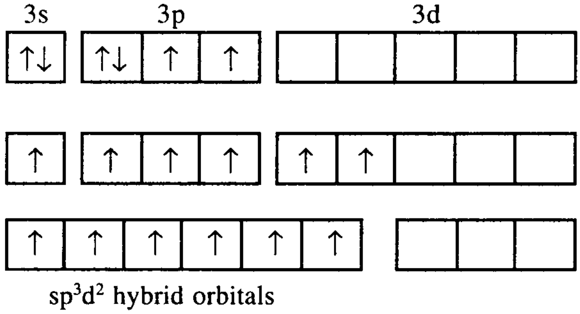
The six hybrid orbitals are directed towards the corners of a regular octahedron. Each S-F bond is formed by the overlap of a hybrid orbital (sp^3d^2) of sulphur atom with a p orbital of fluorine atom.

Valance shell electron configuration of S atom in ground state

Excited configuration of S atom

$3s^1$ $3p^3$ $3d^2$

sp^3d^2 hybridization



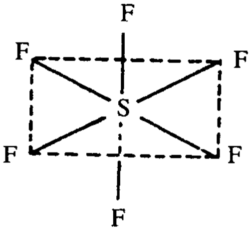


Fig. 1.9: SF_6 molecule

1.11 VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Molecular geometry is the general shape of a molecule as determined by the relative positions of the various atomic nuclei. A number of physical properties such as melting point, boiling point, density and a number of chemical properties are based on the molecular geometry. A very useful model to predict the general shape of a molecule was developed by Gillespie and Nyholm in 1957. The theory called the *Valence Shell Electron Pair Repulsion* (VSEPR pronounced as vesper) theory is an extremely powerful model for predicting the shapes and bond angles of polyatomic molecules. The theory however does not explain chemical bonding.

According to this theory, the geometry of a molecule depends upon the number of valence-shell electron pairs around its central atom. The *electron pairs* (bonding as well as non bonding) *arrange themselves in such a way that there is a minimum repulsion between them. The molecule thus has minimum energy and maximum stability.* Since there can be only one orientation of orbitals corresponding to a minimum energy, a molecule of a given substance has invariably a definite geometry. This approach to the study of molecular geometry is called the VSEPR theory. In short, in this model, the valence-shell electron pairs are arranged about each atom such that electron pairs are kept as far away from one another as possible thereby minimising electron pair repulsion.

The following simple rules are followed –

1. Electron pairs around the central atom in a molecule stay as far apart as possible. The shape of the molecule is determined by repulsions between the electron pairs present in the valence shell.
2. The central atom hybridizes suitably to accommodate both bonding and non-bonding electron pairs.
3. A non-bonding or a lone pair of electrons takes up more room on the surface of the atom than a bonding pair.
4. Double bonds cause more repulsion than single bonds and triple bonds cause more repulsion than a double bond.

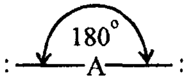
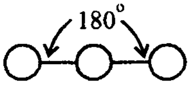
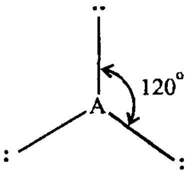
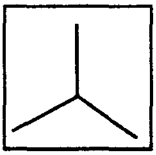
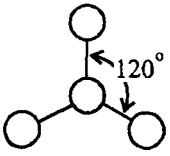
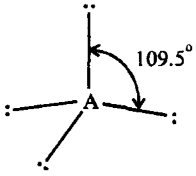
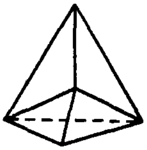
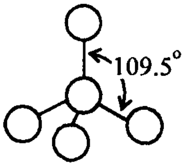
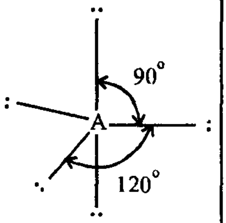
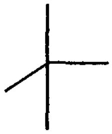
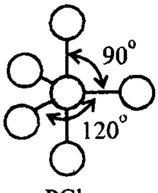
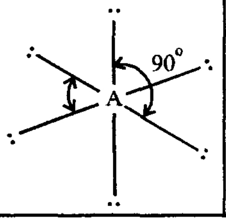
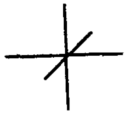
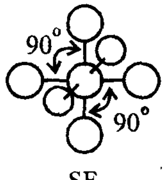
1.12 APPLICATIONS OF VSEPR THEORY

The geometry of molecules can be predicted in a systematic manner using VSEPR model. The molecules can be divided into two categories, according to whether the central atom has lone pairs of electrons or not.

1.12.1 Geometry of molecules in which the central atom has no lone pairs

When the central atom in a molecule is surrounded only by bonded electron pairs (not by lone pairs) the molecule has a regular geometry or shape which depends on the number of bonded electron pairs. Referring to the molecule as AB_x, (for convenience sake, the molecule is made up of only two elements A and B) where A is the central atom and x has integral values 2, 3 etc. Table 1.7 gives the arrangement of bonded electron pairs about a central atom and the geometry of some simple molecules.

Table 1.7: Geometry of Some Simple Molecules

Number of bonded electron pairs	*Arrangement of electron pairs*	*Bond angle*	*Molecular geometry*	*Examples*
2		180°	Linear	 $BeCl_2$
3		120°	Planar 	 BF_3, BCl_3
4		109.5°	Tetrahedral 	 CH_4, $SiCl_4$, CCl_4
5		90° & 120°	Trigonal bipyramidal 	 PCl_5
6		90°	Octahedral 	 SF_6

1.12.2 Geometry of molecules with the central atom having lone pairs of electrons

Determining the molecular geometry becomes complicated when the central atom has both lone pairs and bonded pairs. Three types of unequal repulsive forces are present in such molecules. In general, the order of repulsive forces as predicted by VSEPR theory is

lone pair-lone pair repulsion > lone pair-bonded pair repulsion > bonded pair-bonded pair repulsion

While electrons in a bond are held by the attractive forces exerted by two nuclei, the lone pair of electrons being associated with only one nucleus tend to occupy a greater angular volume.

Four equivalent bonding electron pairs

Three bonding electron pairs repelled by a nonbonding pair of electrons

Fig. 1.10: Bonding and non-bonding electron pairs around a central atom

A distinction between the overall arrangement of the electron pairs and geometry of the molecule need to be made in cases where the central atom has one or more lone pairs of electrons. While the overall arrangement of electron pairs refers to the arrangement of all the electron pairs on the central atom, the geometry of a molecule considers the arrangement of its atoms involving only the bonding pairs of electrons. *When lone pairs are present, the bond angles are smaller than predicted as per regular geometry.* Furthermore, if given a choice, the lone pair tend to occupy a position where it can expand most readily. For example, equatorial site in trigonal bipyramidal.

Ammonia: In NH_3, molecule, the central N atom has four electron pairs in the outer shell. A regular tetrahedral configuration with a bond angle 109° 28' is expected. However the actual bond angle is only 107°.

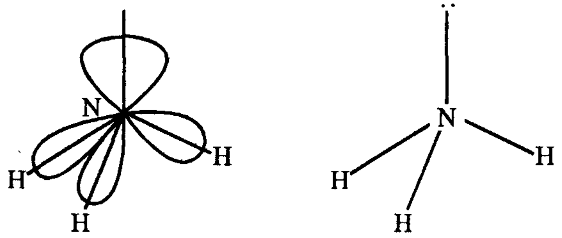


Fig. 1.11: Ammonia molecule

One of the orbitals has a lone pair of electrons. According to VSEPR theory, the force of repulsion between a lone pair and bonded pairs is more than the force of repulsion between two bonded pair of electrons. This results in the lone pair causing the three bonded pairs to be pushed closer together, thereby decreasing the bond angle from 109.5° to 107°. The shape of the molecule is thus pyramidal in which the nitrogen atom lies at the centre, the three H atoms form the base while the lone pair forms the apex of the pyramid.

Water: In H_2O molecule, the central oxygen atom has a ground state electronic configuration $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. The unpaired electrons in the p_y and p_z orbitals may be paired with electrons on two hydrogen atoms to give H_2O. But the actual bond angle is 104.5° in water molecule which is much closer to a tetrahedral angle.

In water molecule the central oxygen atom has four pairs of electrons in the outer shell. The four orbitals contain two lone pairs of electrons in two of the orbitals. The other two orbitals each have a bonded pair of electrons [bonding with 2H atoms].

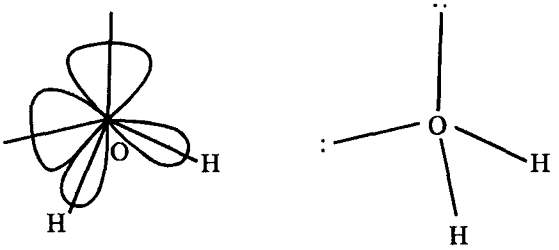


Fig. 1.12: Water molecule

The repulsive force between the two lone pairs of electrons being the greatest followed by that between a lone pair and a bonded pair which in turn is greater than that between two bonded pair of electrons, the normal tetrahedral bond angle is reduced to 104° 27°. Thus water molecule is V shaped or bent. The series CH_4 (no lone pairs, bond angle = 109.5°), ammonia (one lone pair, bond angle = 107°) and water (two lone pairs, bond angle = 104.5°) illustrates an isoelectronic series in which the increasing requirements of the lone pairs reduce the bond angle.

Bromine triflouride, BrF_3 : The central atom bromine has seven electrons in its valence shell. Three electrons form bonds with three fluorine atoms while four of them do not participate in bonding. In bromine trifluoride molecule there are a total of five electron pairs in the outer shell. The structure is a trigonal bipyramid. There are three bond pairs and two lone pairs.

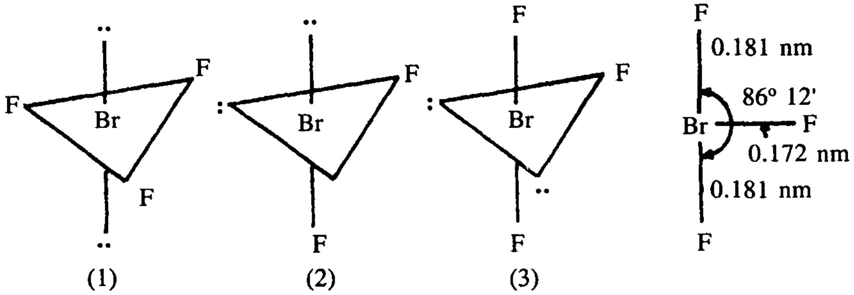


Fig. 1.13: Bromine trifluoride molecule (three possible arrangements)

The trigonal bipyramid is not a regular shape as the bond angles are different. Of the five centers, three are occupied by bonded pairs and two by lone pairs. The different arrangements as shown are possible.

Of these, the actual structure will be the one with a lowest energy, where the repulsion between the five orbitals is at its minimum. Since the bond pair – bond pair repulsion is the least, followed by bond pair – lone pair repulsion and the strongest being between lone pair-lone pair, and also groups as at 90° to each other repel strongly while the groups at 120° to each other repel much less, structure 3 is most probable of the above three arrangements. The lone pairs on bromine atom occupy two of the equatorial positions. The observed bond angle is 86° 12'. The slight distortion from 90° is due to the presence of the two lone pairs. The molecule is T-shaped with the bromine atom at the intersection of the "T". All the four atoms of the molecule lie in one plane. The bond lengths are 0.181 nm and 0.172 nm.

Polyhalide ions ICl_2^- and ICl_4^- : The structure of these ions can be explained considering the iodine atom to be the central atom.

In $IC1_2^-$, ion, iodine enters into a covalent bond with a chlorine atom and the other is a coordinate bond with chloride ion $[Cl - I \leftarrow Cl]^-$. There are a total of five electron pairs in the outer shell of the iodine atom in ICl_2^- ion and trigonal bipyramid is the predicted shape. Of the five corners, three equatorial positions are occupied by lone pairs while the two axial positions are occupied by the two chlorine atoms. The structure is therefore linear.

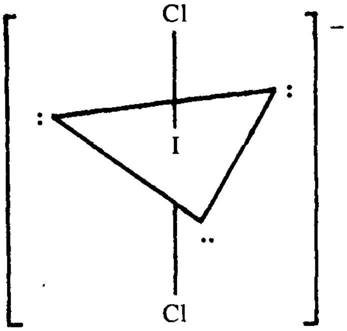


Fig. 1.14: Structure of ICl_2^- ion

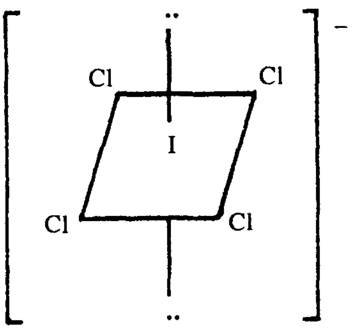


Fig. 1.15: Structure of ICl_4^- ion

Similarly, in $IC1_4^-$ ion, iodine forms three covalent bonds and one coordinate bond with three chlorine atoms and a chloride ion respectively. There are six pairs of electrons in the outer shell of iodine atom in $IC1_4^-$ ion and the predicted geometry is octahedron. The two lone pairs occupy two corners and the structure of $IC1_4^-$ ion is square planar.

1.13 MOLECULAR ORBITAL THEORY (MO THEORY)

According to the VB theory, a bond is formed between two atoms when they are brought together close enough for the atomic orbitals to overlap. Further even though the two atoms are bonded together they retain their individuality to a large extent – only the outer atomic orbitals of the bonded atoms lose their identity. Though the VB theory satisfactorily describes bonding in most of the molecules, it is found to be unsatisfactory in some cases. According to VB theory any molecule with an even number of electrons should be diamagnetic with all paired electrons. However some molecules exhibit paramagnetic behaviour which cannot be explained by VB theory.

In the molecular orbital theory, developed by Mulliken, Hund and Huckel, a molecule is considered to be quite different from the constituent atoms. MO theory describes covalent bonds in terms of molecular orbitals, which are formed from orbitals of the bonding atoms and are spread over the atoms of the entire molecule.

All the electrons belonging to the atoms constituting a molecule are considered to be moving along the entire molecule under the influence of all nuclei. A molecule is supposed to have orbitals in the same way as an isolated atom. The quantized molecular orbitals of varying energy levels surround all the nuclei of the molecule. Each molecular orbital in a molecule has discrete amount of energy described by a wave function ψ. These orbitals are essentially polycentric and not monocentric, as in atoms, Similar to the s, p, d, f orbitals determined by various sets of quantum numbers in an atom, there are σ (sigma), π (pi), δ (delta) ..... orbitals in a molecule and filling of electrons in these orbitals follows the aufbau order. Pauli's exclusion principle and Hund's rule of maximum multiplicity are also obeyed in these molecular orbitals as in atomic orbitals.

Of the various methods of approximating the correct molecular orbitals, only the linear combination of atomic orbitals (LCAO) is discussed. Consider two atoms A and B whose atomic orbitals are described by wave functions ψ_A and ψ_B. When these orbitals approach each other, the electron clouds of the two orbitals overlap and the wave function ψ_{AB} of the molecular orbital is given by a linear combination of atomic orbitals (LCAO).

$$\psi_{\text{symmetric}} \text{ or } \psi_{\text{bonding}}\, \psi_b = \psi_A + \psi_B$$

$$\psi_{\text{antisymmetric}} \text{ or } \psi_{\text{antibonding}}\, \psi_a = \psi_A + \psi_B$$

(**Note:** The contribution = $\psi_B - \psi_A$ does not represent a third MO, but is another form of ψ_a).

The two molecular orbitals formed ψ_b and ψ_a are called *bonding molecular orbital and antibonding molecular orbital respectively.*

In bonding molecular orbital the signs of the wave functions are the same while in antibonding molecular orbital the signs of the two wave functions are different.

Note: When wave functions of the same sign overlap, there is reinforcement of the waves resulting in larger waves. On the other hand, when wave functions of different signs overlap the waves are out of phase and cancel each other by destructive interference. (The signs + and – correspond to signs of wave functions in those directions and have nothing to do with electronic charges).

In bonding molecular orbital, the electron density between the nuclei is increased. A bonding molecular orbital has lower energy by an amount Δ. It has greater stability than the atomic orbitals from which they are formed. Δ is known as *stabilisation energy.* In antibonding molecular orbitals the electron density between the nuclei is decreased. An antibonding molecular orbital has greater energy by the same amount Δ and lower stability than the atomic orbitals from which they are formed.

Electrons when placed in a bonding molecular orbital give rise to a stable covalent bond.

Electrons when placed in antibonding molecular orbitals result in an increase in the energy of the molecule and no stable chemical bond can be formed.

Overlap of atomic orbitals along the axis joining the nuclei produce σ molecular orbitals and sideways or lateral overlap of atomic orbitals produce π molecular orbitals. The subscript (1s, 2p etc.) indicate the atomic orbitals from which they are formed.

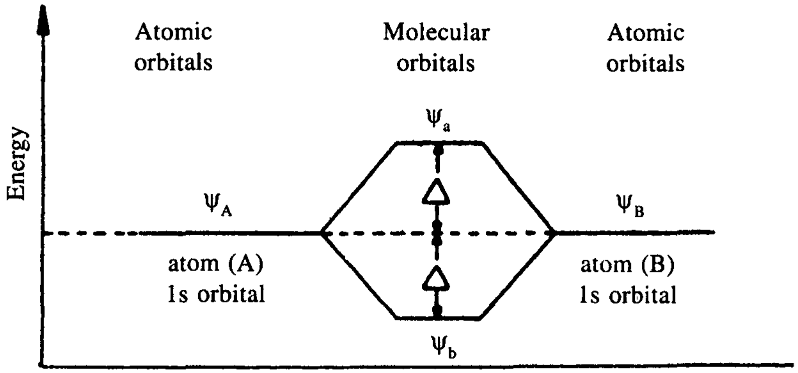


Fig. 1.16: Energy levels of s-s atomic and molecular orbitals

1.13.1 Combination of s-orbitals

When two s-atomic orbitals combine, σ molecular orbitals result.

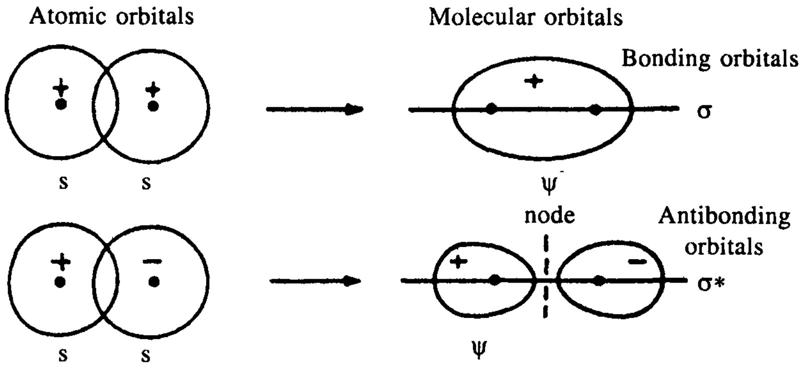


Fig. 1.17: s-s Combinations of atomic orbitals

1.13.2 Combination of s-p orbitals

The combination of s and p orbitals give rise to σ orbitals

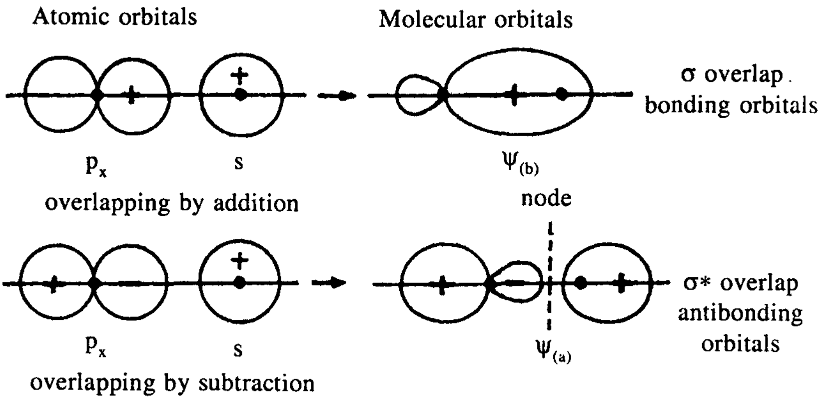


Fig. 1.18: s-p Combination of atomic orbitals

1.13.3 Combination of p-orbitals

The p orbitals can overlap and combine either end-on or sideways to form σ and π molecular orbitals.

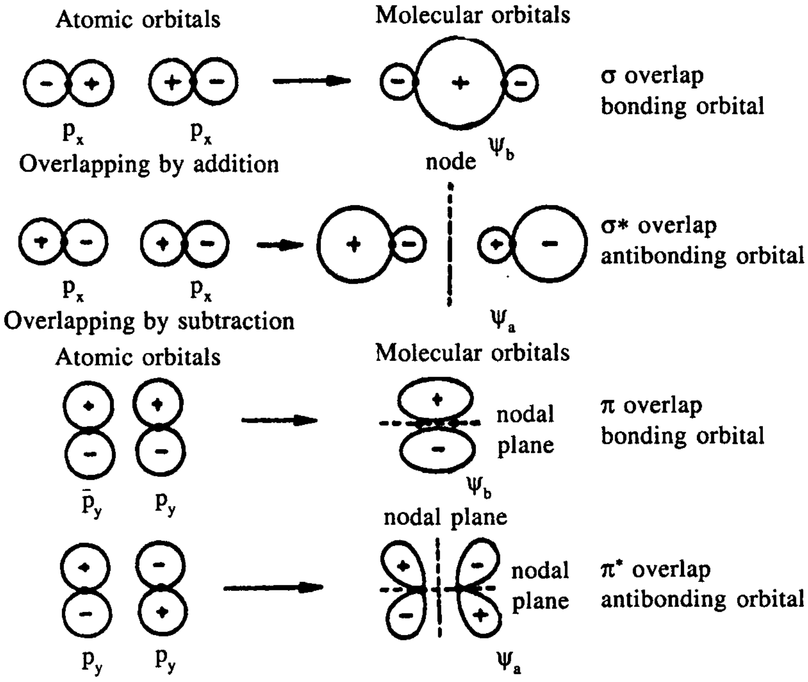
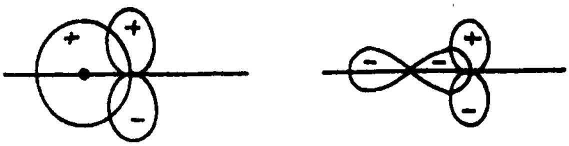


Fig. 1.19: p-p Combination of atomic orbitals

The s– and p– orbitals combine effectively under the following conditions.

1. The atomic orbitals should have comparable energies. Thus in the formation of homonuclear diatomic molecule, the 1s orbital of one atom does not combine with 2s or 2p orbital of another atom of the same element. Similarly, 2s orbital will not combine with 2p orbitals. However, in heterodiatomic molecules this may not be true.
2. The atomic orbitals combine only if they overlap to a considerable extent.
3. The combining atomic orbitals should have the same symmetry about the molecular axis.

This means that s-orbital or p_x of one atom cannot combine with p_y or p_z orbital of another atom. The molecular axis is along x axis while p_y and p_z are at right angles. This is called non-bonding situation.



s and p_y (p_z) p_x and p_y (p_z)

no bonding is possible

Difference between Bonding and Antibonding Molecular Orbitals

Bonding	*Antibonding*
1. Formed by addition overlap of atomic orbitals	Formed by subtraction overlap of atomic orbitals.
2. Has lower energy than atomic orbitals from which formed.	Has higher energy than the atomic orbitals from which formed.
3. Electron density between the nuclei is high, accounts for its stability.	Electron density between the nuclei is very low, hence not stable.

1.14 ENERGY LEVELS OF DIFFERENT MOLECULAR ORBITALS

The energy of a molecular orbital depends on (i) the type of atomic orbitals from which it is formed and (ii) the extent of overlap of the atomic orbitals forming the molecular orbital.

The energy levels of the various molecular orbitals have been determined experimentally from spectroscopic data. It may be written as (σ1s), (σ*1s), (σ*2s) (σ^*2p_x), (π^*2p_y) and ($\pi 2p_z$), ($\pi 2p_y$) and (π^*2p_z), (σ^*2p_x).

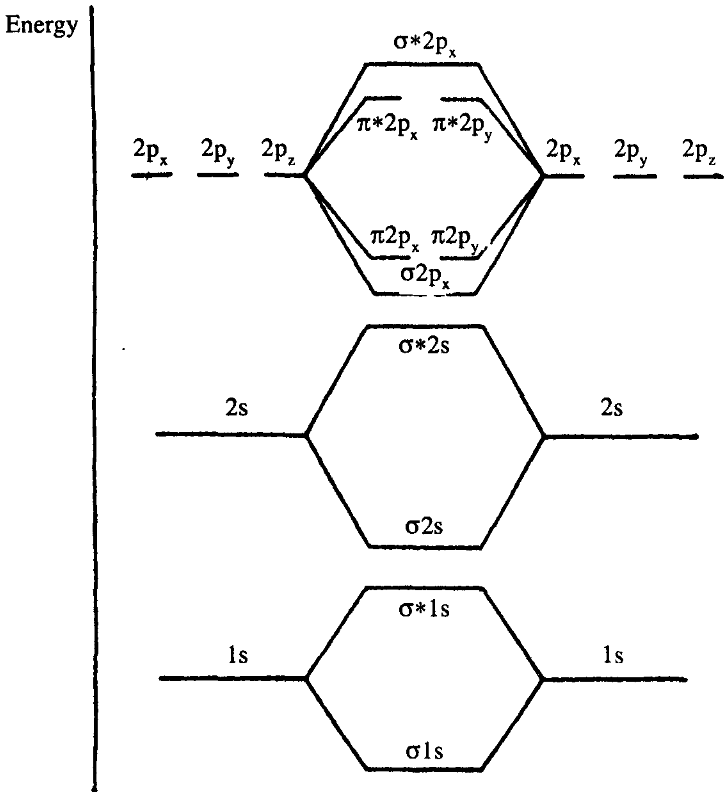


Fig. 1.20: The molecular orbital energy diagram for homopolar diatomic molecules such as H_2, O_2, F_2

It is to be noted that

1. The number of molecular orbitals formed is always equal to the number of atomic orbitals combining.
2. The more stable a bonding molecular orbital, the less stable the corresponding antibonding molecular orbital.

Molecular Electron Configuration

The molecules are built up by adding electrons to available molecular orbitals, just in the same way as the filling up of electrons in atomic orbitals according to the principles of aufbau, Pauli and Hund's. These may be summed up as –

1. The molecular orbital with the lowest energy is filled first.
2. The maximum number of electrons a molecular orbital can hold is two and with opposite spins. (Pauli's exclusion principle).
3. If there are two molecular orbitals at the same energy level, electrons will occupy separate orbitals, leading to unpaired electron spins (Hund's rule)

1.15 RELATIONSHIP BETWEEN ELECTRONIC CONFIGURATION AND MOLECULAR BEHAVIOUR

1. Bond order: The term bond order refers to the number of bonds existing between two atoms. While electrons in the bonding molecular orbitals help in the formation of covalent bonds, those in antibonding molecular orbitals oppose it. *Bond order is defined as one half of the difference between the number of electrons in the bonding molecular orbitals N_b and the number of electrons in the anti-bonding molecular orbitals N_a.*

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

Bond order need not be an integer.

2. Stability of the molecules: Bond order is a measure of the stability of the molecule. Higher the bond order greater is the stability of the molecule. Thus,

if (i) $N_b > N_a$, the molecule will be stable.

(ii) $N_b < N_a$ the molecule will be unstable.

(iii) $N_b = N_a$, the formation of the molecule does not take place. This is because the effect of anti-bonding electrons is somewhat stronger than that of bonding electrons.

3. Bond length: Bond length is inversely related to bond order. The higher the bond order, the smaller the bond length.

4. Paramagnetic or diamagnetic character of molecules: A molecule in which all electrons are paired is diamagnetic in nature while a molecule having one or more unpaired electrons is paramagnetic in nature.

1.16 MOLECULAR ORBITAL DIAGRAM OF CERTAIN HOMONUCLEAR DIATOMIC MOLECULES

Hydrogen molecule, Two 1s electrons from the two atoms of hydrogen combine and are placed in σ_{1s} molecular orbital, with paired spins. It is written as $(\sigma 1s)^2$.

$$\text{Bond order} = \frac{2-0}{2} = 1$$

This means that two hydrogen atoms are bonded together by a covalent bond.

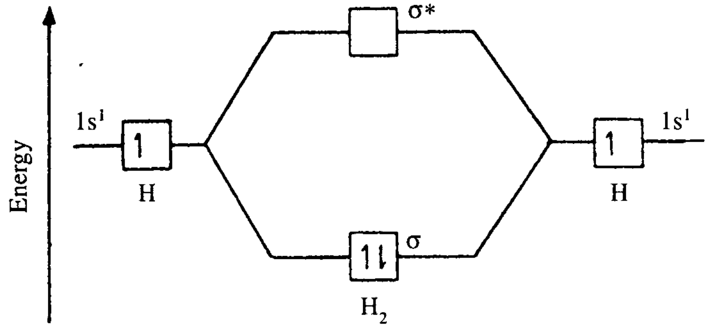


Fig. 1.21: Formation of hydrogen molecule

Since there are no unpaired electrons, the molecule is diamagnetic.

Bond length = 0.074 nm.

Helium molecule ion, He_2^+ : the helium molecule ion is considered as a combination of a helium atom and a helium ion He^+. It has three electrons in all. This molecule has the electron configuration $(\sigma 1s)^2$ $(\sigma^* 1s)^1$

$$\text{Bond order} = \frac{2-1}{2} = \frac{1}{2}$$

This molecule ion can exist and has been observed spectroscopically. It is however not very stable.

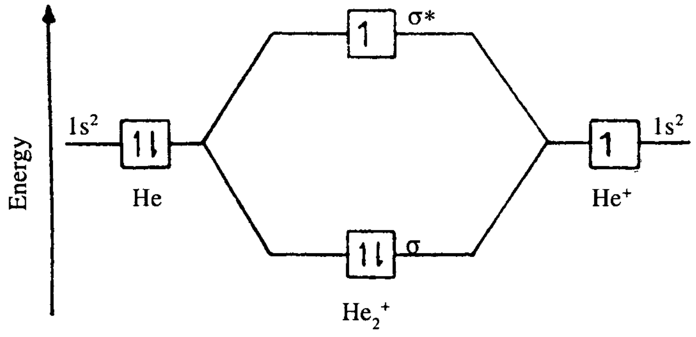


Fig. 1.22: Formation of He_2^+ molecule ion

The presence of an unpaired electron indicates it to be paramagnetic in nature.

Beryllium molecule, Be_2

The configuration of Be atom being $1s^2\ 2s^2$, in Be_2 molecule there are a total of 8 electrons. These may be arranged in molecular orbitals as

$$(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2 \text{ or } KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2 \text{ bond order} = \frac{2-2}{2} = 0.$$

It is obvious that the effects of the bonding $\sigma 2s^2$ is cancelled by the anti bonding $\sigma^* 2s^2$. There is no stabilization and Be_2 molecule therefore is not expected to exist.

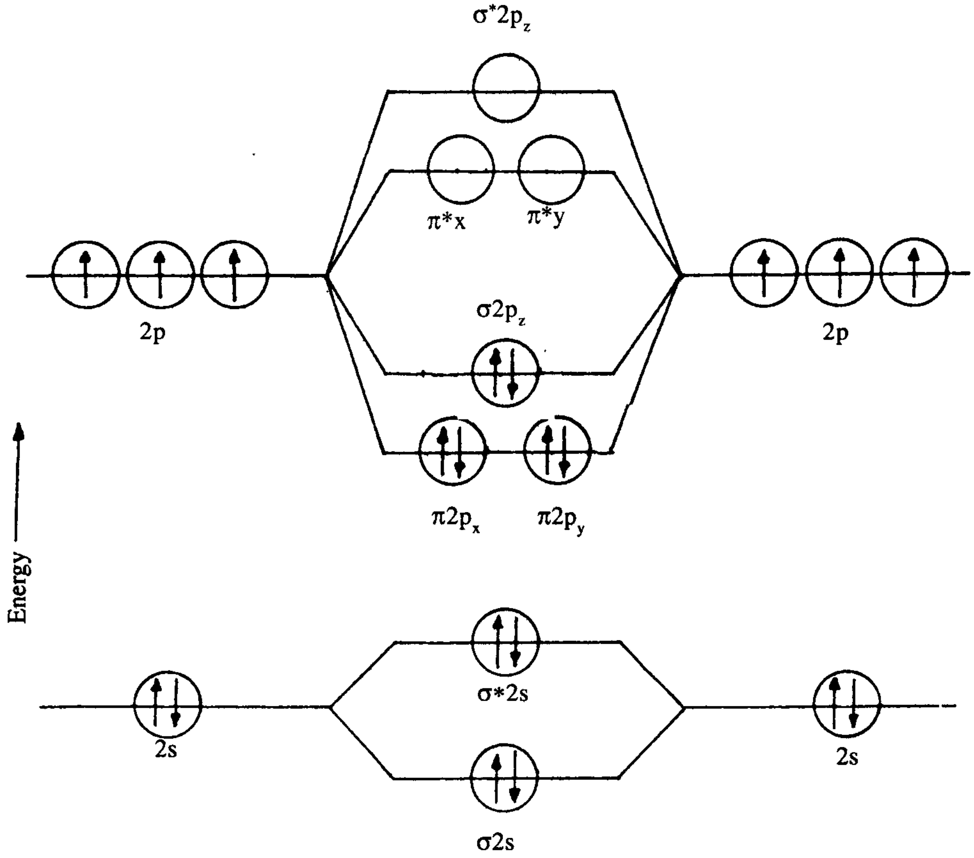


Fig. 1.23: Molecular orbitals for nitrogen

Nitrogen molecule, N_2: The nitrogen molecule has 14 electrons. Four of these lie in the σ1s and σ*1s orbitals, which cancel and may be thus ignored. This is generally abbreviated as KK meaning 1s shell of each of the nitrogen atom. The next four occupy the σ2s and σ*2s orbitals and again contribute nothing to the net bonding. The remaining six electrons form a σ bond and 2π bonds. The electronic configuration is written as:

$$KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_y)^2 = (\pi 2p_z)^2\ (\sigma 2p_x)^2$$

$$\text{Bond order} = \frac{1}{2}(8 - 2) = 3$$

Thus nitrogen molecule has 3 bonds between nitrogen atoms.

Bond length is 0.1098 nm.

The resulting molecule is a very stable one with 1σ and 2π bonds. This is in good agreement with the experimentally observed large dissociation energy 942 kJ mol^{-1}. It is diamagnetic.

In N_2, molecule, the order of energies of molecular orbitals is different from the usual arrangement i.e., π2p orbitals are lower in energy than the $\sigma 2p_x$. The arrangement of molecular orbitals obtained from 2s and 2p orbitals is energetically different in the case of nitrogen molecule (N_2, B_2, and C_2). This arises due to a possibility of the mixing of $\sigma(2s)$ and $\sigma(2p_z)$ as well as $\sigma^*(2s)$ and $\sigma^*(2p_z)$. This is possible because of a small energy difference between 2s and 2p atomic orbitals.

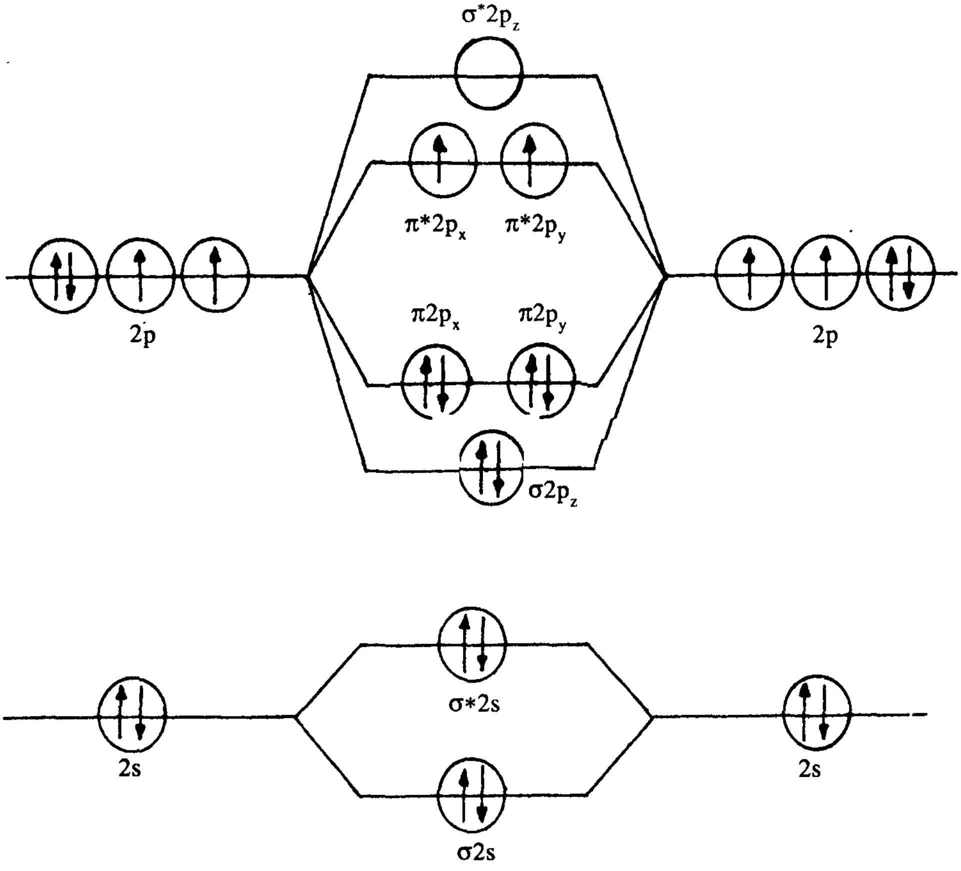


Fig. 1.24: Molecular orbitals for oxygen

Oxygen molecule O_2: In O_2 molecule 16 electrons are to be accommodated. Since 4 electrons fill σ1s and σ*1s orbitals and do not contribute to bonding, only 12 electrons remain to be accommodated in σ2s, σ*2s etc., orbitals. The structure can be written as

$$O_2 = KK\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\sigma 2p_x)^2\ (\pi 2p_y)^2 = (\pi 2p_z)^2\ (\pi^*2p_y)^1 = (\pi^*2p_z)^1$$

Two electrons occupy the antibonding p molecular orbital singly as predicted by Hund's rule.

$$\text{Bond order} = \frac{1}{2}\ (8 - 4) = 2$$

i.e., O_2 molecule has 2 covalent bonds (one σ and one π). It is less stable than N_2 as it has 4 antibonding electrons. It has bond energy 493.59 kJmol^{-1} and a bond length 0.1207 nm.

Since *there are two unpaired electrons in a molecule of O_2, the molecule is paramagnetic.* The simple *VB theory predicts, all electrons in O_2 molecule to be paired and is not able to account for the paramagnetic behaviour of O_2 molecules.* The MO theory is able to explain this phenomenon and was the first success of MO theory.

1.17 COMPARISON OF VB AND MO THEORIES

According to Leonard-Jones, there is a little difference in the two approaches of covalent bonds. In the real sense, each approach has a different utility under a given set of circumstances. Both theories can be compared by considering their similarities and differences.

Similarities

1. Both theories consider the formation of covalent bond to be due to overlap or combination of atomic orbitals.
2. In both the theories the essential requirement is that the atomic orbital which overlap or combine should have nearly equal energies.
3. Charge cloud is assumed to reside between the two nuclei or a large concentration of electron density between the two nuclei is assumed.
4. Directional character is explained by both theories.

Differences

1. In MO theory, the atomic orbitals lose their individuality whereas in VB theory, the inner atomic orbitals retain their individualities and only the outer orbitals are involved in bonding.
2. Molecular orbitals are polycentric while atomic orbitals are monocentric.
3. In VB theory an atomic orbital with paired electrons does not even take a chance to form a bond. On the other hand, the MO theory permits a combination of atomic orbitals only to be dissolved completely.
4. VB theory fails to account for the paramagnetic character of oxygen while MO theory offers a satisfactory explanation.

5. While resonance plays an important role in VB theory, it has no place in MO theory.

1.18 POLARITY OF BONDS

A covalent bond is formed by the sharing of a pair of electrons between two atoms. The electron pair is shared equally when the atoms are alike as in H_2 molecule.

A bond between two identical atoms is a nonpolar bond and the molecule is non polar.

When the two bonding atoms are different, the sharing is unequal, as in molecules of HF, HCl, H_2O. One of the atoms which has a greater electronegativity attracts the shared electron pair more towards itself. For example, in HCl the electron pair is closer to Cl atom and the chlorine end of the molecule has a slight negative charge. The hydrogen end has a slight positive charge. These are represented as δ^+ and δ^- meaning small charges.

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

i.e., the unsymmetrical distribution of electrons leads to charge separation. Such *molecules having two oppositely charged poles are called polar molecules and the bond is said to be a polar covalent bond.* The bonding electrons spend more time near one of the atoms than the other. The polar covalent bond has therefore partial ionic character. The molecules are also called *dipoles*. A polar covalent bond is intermediate between a nonpolar covalent bond and ionic bond.

Greater the difference in the electronegativities of the atoms forming the bonds, greater is the charge separation and greater will be the polarity.

The degree of polarity of a bond is usually expressed in terms of *dipole moment* which is defined as the *product of the magnitude of the charges and the distance between them.*

Mathematically,

Dipole moment $\mu = \delta \times d$

where δ is the magnitude of the charge and d is the distance separating the two charges δ^+ and δ^-.

Dipole moments are measured in debyes (D).

In SI system, the unit of dipole moment is coulomb metre and

$$1\ D = 3.34 \times 10^{-30}\ Cm.$$

Each bond dipole is a vector quantity and often indicated by an arrow drawn parallel to the line joining the two charges and pointing towards the negative end.

$$\overrightarrow{H - F}, \quad \overrightarrow{H - Cl}$$

1.18.1 Dipole Moment and Diatomic Molecules

A diatomic molecule is polar if the bond formed between them is polar. The dipole moment of the molecule is the same as that of the individual bond. Thus dipole moment of HCl molecule is 1.03 D which is same as that of the single H – Cl bond. In simple molecules the dipole moments are related to the difference in the electronegativities of the atoms.

1.18.2 Dipole Moment and Polyatomic Molecules

In triatomic and polyatomic molecules i.e., molecules containing more than one polar bond, the molecular dipole moment is made up of the dipole moments of all the individual polar bonds. Its magnitude depends not only on the values of the individual dipole moments but also on the spatial arrangement of all the atoms in the molecule.

For example, the molecular dipole moment of water molecule is 1.84D which is the resultant of the two polar O – H bonds. Since the dipole moment of each O – H bond is 1.60D, the angle between them should be 104.5 so that the molecular dipole moment of H_2O is 1.84D. The value of the angle H – O – H has been confirmed by X–ray analysis. Similarly, the molecular dipole moment of NH_3 is 1.49D.

On the other hand, CO_2 and a zero dipole moment even though the C = O bond is a polar bond and has dipole moment. The zero dipole moment of the molecule indicates that the individual dipole moments cancel out each other being equal in magnitude but opposite in direction. This is possible only if CO_2 molecule is linear.

$$\overset{\longleftarrow}{O=}C\overset{\longrightarrow}{=O}$$

Similarly, BF_3 molecule has zero dipole moment as also CH_4, CCl_4 molecules. In all these cases, the individual dipole moments are all equal in magnitude and oriented in such a way that the net sum is zero. In BF_3, the three flourine atoms are at the vertices of an equilateral triangle and the boron atom is at its center. In CH_4, the C atom is at the center of a regular tetrahedron while the four atoms bonded are at the vertices.

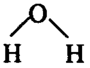
Thus in *a molecule containing more than one polar bond, the dipole moment of the molecule is given by vectoral addition of the dipole moments of the individual bonds. The dipole moment is zero in a symmetrical molecule.*

In other words, a symmetrical molecule is nonpolar even if it contains polar bonds.

The dipole moment of 1,4 dichlorobenzene is zero while that of 1,2 dichlorobenzene is 2.25D. In fact, measurement of dipole moments gives valuable information about the structure of molecules.

Relationship between dipole moment and molecular geometry is given in table 1.8.

Table 1.8: Dipole Moment and Molecular Geometry

Formula	*Molecular Geometry*	*Example*	*Dipole Moment (D)*
AX	Linear		Non Zero
		HF	1.91
		HCl	1.08
AX_2	Linear	O = C = O	zero
	Bent		1.85
AX_3	Trigonal planar	BF_3	zero
	Trigonal pyramidal	NH_3	1.47
AX_4	Tetrahedral	CH_4, CCl_4	zero
	Square planar	XeF_4	zero
AX_6	Octahedral	SF_6	zero

1.19 PROPERTIES OF COVALENT COMPOUNDS

1. Most covalent compounds are liquids or gases at room temperature and pressure. Only large molecular weight compounds are solids at room temperature.
2. Depending upon the type of forces holding them together, they may be soft and easily fusible or hard and brittle.
3. The molecules are held together by weak van der Waals' forces (exception being those compounds which exist as giant molecules). Their melting and boiling points are generally low.
4. They are poor conductors of electricity in the fused state or in aqueous solutions. This is because there are no free ions in the compounds to carry the electricity. Graphite is an exception.
5. They are soluble in non-polar solvents such as benzene, ether etc., and are generally insoluble in water.

1.20 BOND LENGTH, BOND ANGLE AND BOND ENERGY

A bond is formed by the overlap of atomic orbitals of two constituent atoms. This overlap occurs at a certain distance between the two nuclei. This distance between the two nuclei is called the *bond length*. Since the atoms in a molecule are in a state of constant vibrational motion, *bond length is defined as the average distance between the two nuclei*. The bond distance between any two given atoms is generally a constant even in different molecules, i.e., C–H distance is the same in methane, ethane etc. There are some exceptions, however.

In general, a single bond is longer than a double or a triple bond. The double bond length is longer than a triple bond length.

Bond lengths are determined experimentally using X-ray diffraction or molecular spectroscopy. In many instances, the bond length A–B is close to the average of A–A and B–B bond distances. Thus the bond length C–Cl is the average of the C–C and Cl–Cl bond distances. The sum of covalent radii gives the bond length in simple molecules.

Bond angle may be defined as the *internal angle between the orbitals containing electron pairs in the valency shell of the central atom in* a *molecule*

Bond angle is also *defined as the angle formed between two imaginary lines drawn from the nucleus of the central atom to the nuclei of the other two atoms bonded to it.*

The bond angle in water molecule is 104.5°, in ammonia molecule it is 107°.

Bond angle depends on two important factors –

1. presence of lone pairs and bonded pairs around the central atom,
2. the electronegativity of the central atom.

Bond angle thus gives an idea of the distribution of the orbitals in the three dimensional space around the central atom in the molecule and an idea of the shape of the molecule.

Bond energy is a *measure of energy required to break Avogadro number of bonds*, which is an indication of the strength of the bond. The larger the bond energy, the stronger the bond.

It is *defined as the energy (kJ/mol) required to break one mole of bonds of that type in a substance in gaseous state.* i.e., energy required to break

$$A - B(g) \longrightarrow A^{\circ}(g) + B^{\circ}(g) \text{ (free radicals)}$$

which is also the dissociation energy for the molecule AB or the enthalpy change for a gas phase reaction in which a bond breaks.

Bond energies for diatomic molecules (both homo– and hetero) are easily determined

$$H_2(g) \longrightarrow 2\,H(g) \qquad \Delta H^{\circ} = 436.4 \text{ kJ}$$
$$Cl_2(g) \longrightarrow 2\,Cl(g) \qquad \Delta H^{\circ} = 242.7 \text{ kJ}$$
$$HCl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H^{\circ} = 431.9 \text{ kJ}$$
$$O_2(g) \longrightarrow 2\,O(g) \qquad \Delta H^{\circ} = 498.7 \text{ kJ}$$

A similar determination in polyatomic molecules is complicated. For instance the energy needed to break the first O–H bond in water is slightly different from that needed to break the second bond.

$$H_2O(g) \longrightarrow H(g) + O - H(g) \qquad \Delta H^{\circ} = 502 \text{ kJ}$$
$$OH(g) \longrightarrow H(g) + O(g) \qquad \Delta H^{\circ} = 427 \text{ kJ}$$

The difference arises due to a change in the environment of the remaining atoms after an atom has been removed from a molecule. Generally the average value of the complete process is given as the bond energy. In the above example O–H bond energy is given as 464.5 kJ. Similarly the bond energy of C–H is given as one-fourth the dissociation energy of methane molecule.

i.e., $$CH_4\,(g) \longrightarrow C\,(g) + 4\,H\,(g) \qquad \Delta H = 1656.0\text{ kJ}$$

$$C - H \text{ bond energy is } \frac{1}{4}\,(1656.0) = 414.0\text{ kJ/mol}$$

Table 1.9: Some Bond Dissociation Energies

Bond	*Bond energy kJ/mol*	*Bond*	*Bond energy kJ/mol*
H – H	436.4	C – H	414
H – N	393.0	C – C	347
H – O	464.0	C = C	620
H – F	568.2	C ≡ C	812
H – Cl	431.9	C – N	276
N – N	191.0	C – O	351
N ≡ N	941.4	C = O	745
O – O	142.0	F – F	156.9
O = O	498.7	Cl – Cl	242.7
Br – Br	192.5		

Triple bonds are stronger than double bonds which in turn are stronger than single bonds.

Bond energies are of great importance in understanding the relative stabilities of compound.

1.21 POLARIZABILITY

When an ion or a polar molecule is brought near an atom (or a nonpolar molecule), the electron distribution of the atom gets distorted by the force exerted by the ion or the polar molecule. This kind of distortion brought about in the electron distribution is called polarization.

Polarizability is the *ease, with which the electron distribution in the atom (or molecule) can be distorted.* The larger the number of electrons in the atom or the molecule and the more diffuse the electron cloud, greater is the *polarizability.*

When a positive ion is brought near a negative ion, besides the attraction between the two species, there is also repulsion between the positive ion and the nucleus of the negative ion which distorts or polarises the negative ion. If the degree of polarizability is small, a bond which is largely ionic is formed. On the other hand, if the degree of polarization is large, electrons are pulled towards the positive ion from the negative ion. This leads to an increased electron density between the two nuclei and the bond formed is largely covalent.

Though the polarising of a positive ion by a negative ion is quite probable, the phenomenon is much less pronounced as the anions are large and cations are small so that the effect of a large ion on a small ion is very small. Also, large negative ions are more polarizable than small negative ions.

Fajans put forth a set of rules which summarises the factors favouring polarization and hence covalency.

1. *A small positive ion favours covalency*

In a small positive ion, the charge density is more and the ion is highly polarizing and very good at distorting the negative ion.

2. *A large negative ion favours covalency*

In a large negative ion, the outermost electrons are shielded from the nucleus by the inner core of electrons and are highly polarizable.

3. *Large charge on either or both ions favours covalency*

A high charge increases the extent of polarization.

4. *Polarization, and hence covalency is favoured when the positive ion does not have noble gas configuration.*

This is because the noble gas configuration is most effective in shielding the nuclear charge and hence ions without the noble gas configuration have high charges at their surfaces and are thus highly polarizing.

A number of transition metal ions such as Cr^{3+}, Mn^{2+}, Cu^{+}, Ti^{3+} and a few main group ions such as Pb^{2+}, Bi^{3+} are examples of ions not having a noble gas configuration.

In short, a small cation and a large anion favours covalency.

1.22 HYDROGEN BOND

For many years there has been evidence that in certain cases a H-atom is able to link two electronegative atoms. This was first considered by T.S. Moore and T.F. Winmill (1912) and by P. Pfeiffer (1913) and its wide applicability was realised by W.M. Latimer and W.H. Rodebush (1920). In more recent years the concept of hydrogen bond has received general acceptance.

Consider a molecule of type X – H where X is highly electronegative in nature. The shared electron pair, lies far away from H atom so that the atom X carries a partial negative charge and the atom H a partial positive charge i.e., $^{\delta-}X - H^{\delta+}$.

In other words, the molecule X – H is polar and behaves as a dipole. Due to the high polarity, the H atom is able to attract another electronegative atom.

It is an instance where the monovalent H atom is linked to two electronegative atoms, to one by means of a pure covalent bond and to the other by purely electrostatic forces called the hydrogen bond. This may be illustrated as follows –

$$\mathrm{F}\underset{\substack{\downarrow\\ \text{covalent}}}{-}\mathrm{H}\text{ - - - }\mathrm{F}-\mathrm{H}\overset{\substack{\text{hydrogen bond}\\ \uparrow}}{\text{ - - - }}\mathrm{F}$$

The H bond is generally represented by a dotted line.

The essential requirements for an H bond are:

(a) a hydrogen atom linked to a small highly electronegative atom.

(b) an unshared pair of electrons on the electronegative atom.

The attractive force which binds hydrogen atom of one molecule with another small highly electronegative atom (N, O or F) of another molecule is known as hydrogen bonding.

1.22.1 Nature of Hydrogen Bond

Hydrogen bond is purely electrostatic in nature formed between the positive end of one molecule (dipole) and negative end of another molecule (or even same molecule). It can be considered as a special case of strong dipole-dipole attraction. The strength of hydrogen bond is about 10-40 kJ mol^{-1} which is much less than that of a pure covalent bond (400 kJ mol^{-1}).

Formation of H bond does not involve sharing of electrons. Thus it is quite different from a covalent bond. The positive charge of the thinly shielded H nucleus in one molecule is attracted strongly by the negative charge of the electronegative atom of another molecule.

Hydrogen bond can form a link only between two atoms which are small in size and highly electronegative like F, O and N and to some extent Cl. Though Cl has the same electronegativity as N, because of its larger size hydrogen bonding involving Cl atom is not very common.

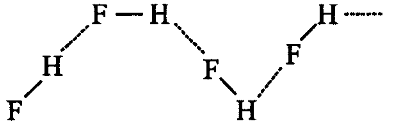
Hydrogen bond length is found to be more than covalent bond length. Thus the proton does not lie exactly at the mid point of the electronegative atoms.

1.22.2 Types of Hydrogen Bond

Two types of hydrogen bonds are known namely *intermolecular* and *intramolecular.*

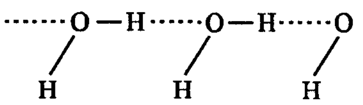
Intermolecular H bonding: A linking together of number of different molecules by hydrogen bond is known as intermolecular H bonding. The association may involve a large number of molecules as in HF, H_2O or only a limited number as in KHF_2, carboxylic acids.

(1) $(HF)_n$

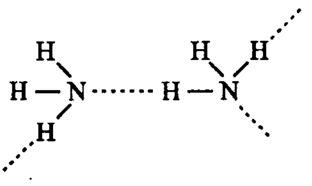


Bond angle is found to be 140°.

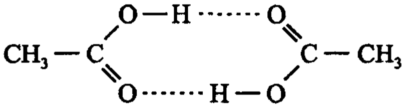
(2) $(H_2O)_n$



(3) NH_3

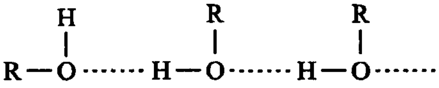


(4) Carboxylic acids RCOOH : In carboxylic acids the association is restricted to two molecules.



Ethanoic acid

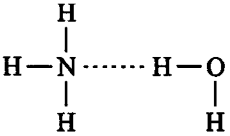
(5) Alcohols ROH



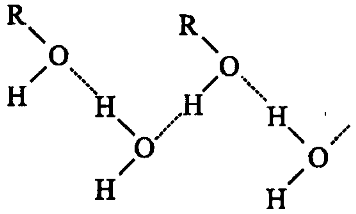
(6) KHF_2 or $K(HF_2)$ – i.e., $[F......H - F]^- K^+$

Chlorine, bromine and iodine are not as highly electronegative as fluorine and are larger in size and the tendency to form H bond in these cases is therefore, less. This explains the non-existence of compounds like $KHCl_2$, $KHBr_2$ and KHI_2.

Sometimes H bonding may occur between molecules of different substances.



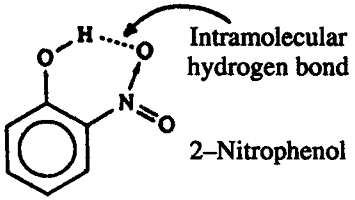
NH_3 and H_2O



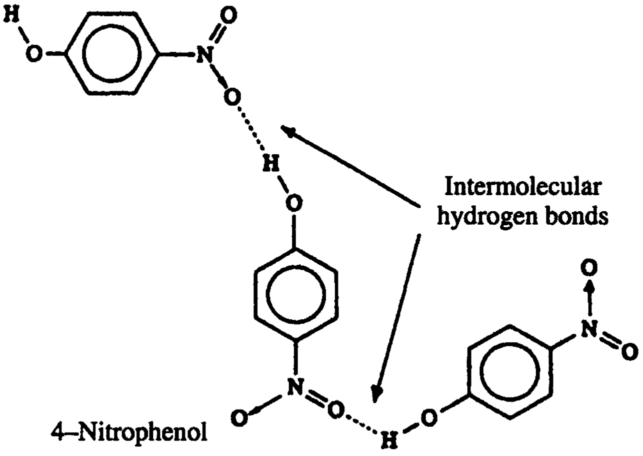
ROH and H_2O

Intramolecular H bonding: This type of bond arises due to *electrostatic forces of attraction between H and an electronegative element present in the same molecule. This results in ring formation or chelation.* In intramoleculer H– bonding, the hydrogen bond occurs within the molecule. For intramolecular H bonding it is necessary that the molecule be planar and also contain two groups such that one group contains H atom linked to a highly electronegative atom and another group containing an electronegative atom linked to a lesser electronegative atom.

2-nitrophenol, 2-chlorophenol, salicylaldehyde and acetoacetic ester are common examples. In 2-nitrophenol and also in 2-chlorophenol intramolecular H bonding is observed. This is as shown in the figure.

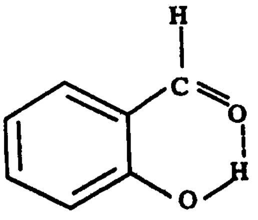


2–Nitrophenol

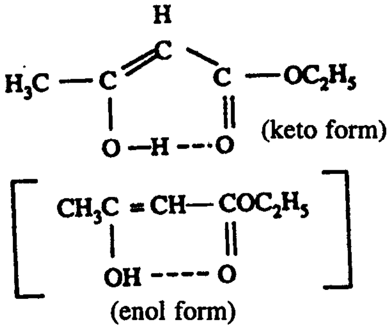


4–Nitrophenol

In 4–(or p–) and 3–(or m–) nitrophenols as well as in 4– (or p–) and 3– (or m–) chlorophenols intermolecular H bonding is possible and not intramolecular H bonding. This obviously is due to larger distances between the two groups. Due to intermolecular H bonding there is association of molecules resulting in high boiling point in p- and m- nitro- and chloro-phenols. Intramolecular H bonding on the other hand, causes a decrease in boiling point so that 2– and 4– chlorophenols and 2– and 4– nitrophenols can be easily separated by steam distillation. While the 2– isomer is steam volatile the 4– isomer is steam non-volatile.



Salicyladehyde



Acetoacetic ester (enol form)

It has been found that the enol form of acetoacetic ester has lower boiling point than the keto form.

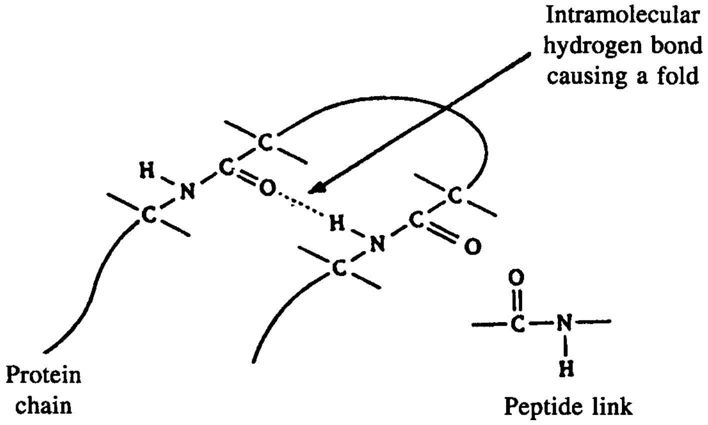


Fig. 1.25: Intramolecular hydrogen bonds can occur along a protein chain. The fold in a peptide chain can be produced by hydrogen bonds between different peptide links.

1.22.3 Hydrogen Bonding in Biological Molecules

Proteins are large molecules containing polypeptides. The manner in which a polypeptide chain twists and folds into a particular form is decided largely by hydrophobic interactions; the shape is further stabilised by H–bonds. One of the most common configuration of a polypeptide is the α-helix. In the α-helix, the polypeptide backbone coils as a right-handed screw with all its side chains sticking to the outside of the coil. The H-bonds in α-helix extend from the hydrogen atoms of the polar NH groups to oxygen atoms of polar carbonyl groups four residues farther along the backbone.

In the case of proteins occurring as fibres, strands of protein molecules are held together by hydrogen bonds.

DNA (deoxyribonucleic acid) is another example where H-bonding plays a major role. DNA exists as two interwined helices. The two strands of the double helix are held together by means of H-bonds between the sidechain bases. The sidechain bases have functional groups so arranged geometrically that they fit to each other by means of H-bonds. This phenomenon is known as *base-pairing*. The arrangement is such that only certain base pairs can exist. In DNA, G and C always form a pair and, A and T form another pair. G or C never pairs with A or T.

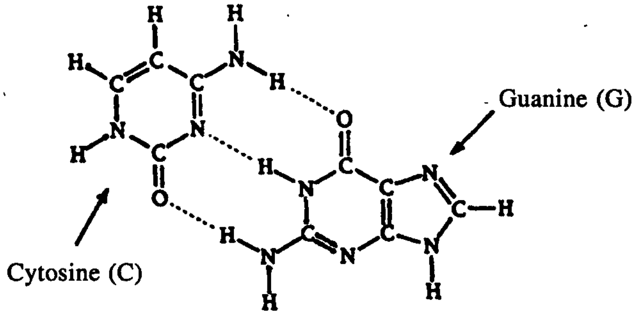


Fig. 1.26: Pairs of organic bases like guanine and cytosine have exactly the right shape to be held together by hydrogen bonds

1.22.4 Consequences of Hydrogen Bonding

1. *High melting and boiling points:* It is found that association of molecules by H bonding results in higher melting point and boiling point. This is because more energy is needed to break the H bonds before the molecules could be separated sufficiently to undergo melting or boiling. This is obvious in the case of HF, H_2O, NH_3 molecules (Fig. 1.26 & 1.27). These have abnormally high melting point and boiling point compared to the hydrides of the other elements in respective groups.

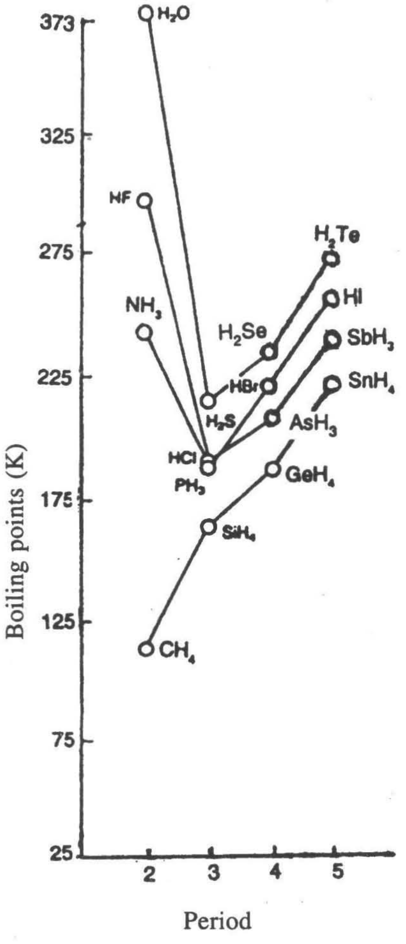


Fig. 1.27: Boiling points of hydrides

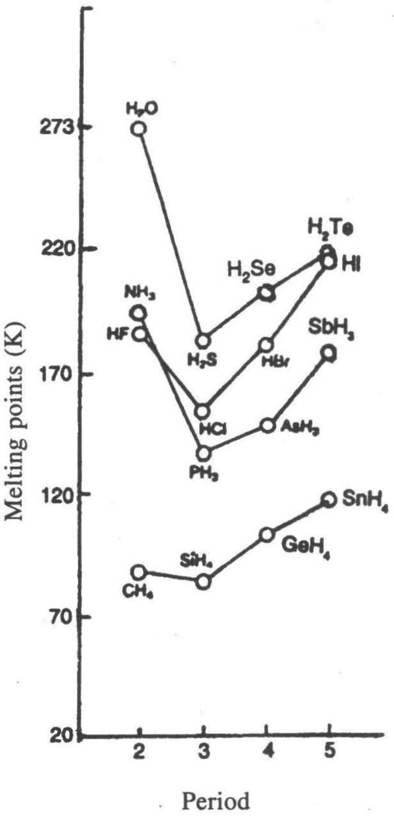


Fig. 1.28: Melting points of hydrides

2. *Dielectric constants:* These compounds have abnormally high dielectric constants and high dipole moment.
3. *Viscosity:* The increased association of molecules in H bonded systems decreases the freedom of molecular motion causing more entanglements between molecules and an increased viscosity.

Table 1.10: Boiling Points of Hydrides of Groups 15, 16 and 17

Group V			*Group VI*			*Group VII*		
Formula	*Molar mass*	*B.P. K*	*Formula*	*Molar mass*	*B.P. K*	*Formula*	*Molar mass*	*B.P K*
SbH_3	125	256	H_2Te	130	271	HI	127.9	269
AsH_3	78	218	H_2Se	81	231	HBr	80.9	206
PH_3	34	189.5	H_2S	33	213	HCl	36.5	188
NH_3	17	240	H_2O	18	373	HF	20.0	292.4

1.22.5 Anamolous Properties of Certain Molecules

Hydrogen Fluoride: In crystalline HF long zig-zag chains of the type F .... H – F with bond angle 140° are found. These chains persist to a large extent in liquid and gaseous phases. The number of molecules associated in the vapour phase is comparatively small, about 6 only. This is because heating breaks down H – F bonds.

In aqueous solution, H – F ionises not to yield F^- ion but HF_2^- ion and salts of the type KHF_2 are known. It is seen that in HF_2^- ion the H atom is equidistant from the two F nuclei (generally H bond is longer than covalent bond). It is believed HF_2^- ion is a resonance hybrid of

$$F^- \text{----} H - F \leftrightarrow F - H \text{----} F^-$$

This is not common in H bonding.

Water: Water exists as a high boiling liquid because of hydrogen bonding.

The oxygen atom of the water molecule can form, two H bonds in addition to two covalent bonds with two H atoms. It has been shown by spectral studies that each O atom is bonded tetrahedrally to 4 H atoms, two of them being covalently bonded and two others by H bonds. The water molecules are joined together in an extensive three dimensional network. The three dimensional network is unique to water molecule. In ice, the H bonding between water molecules is more extensive than in liquid water. Each O atom is surrounded tetrahedrally by 4 H atoms as in liquid water and the basic unit in the crystalline lattice is hexagonal. H bond being weaker is longer than the covalent bond. Ice, as can be seen, has open cage structure with a large empty space. The molecules are thus not closely packed and density of ice is thus low.

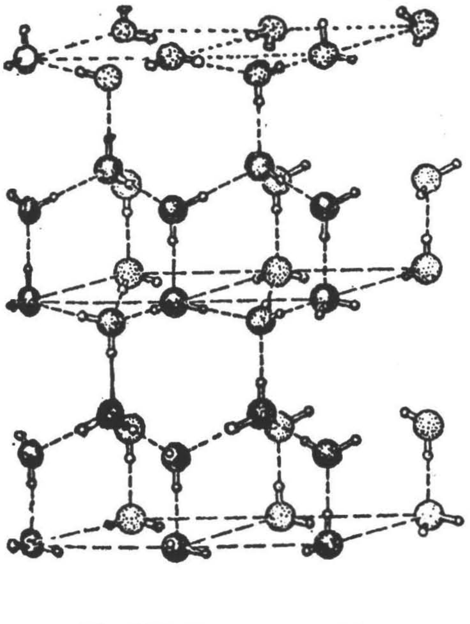


Fig. 1.29: The structure of ice

When ice is heated, some H bonds are broken and the open cage structure also breaks down. The molecules come closer to one another causing a decrease in volume and a sharp increase in density. The density of liquid water is therefore higher than that in ice.

As water is heated from 0°C to 4°C, hydrogen bonds continue to be broken and the molecules come closer and closer to one another. The volume goes on decreasing i.e., water contracts between 0° and 4°C. At the same time there is also expansion of water due to an increase in temperature. At 4°C, contraction due to H bonding predominates and the contraction is maximum. The density of water at 4°C is thus the maximum. Above 4°C the normal expansion effect predominates and there is continual increase in volume with increase of temperature.

1.22.6 Importance of H Bonding

1. But for H bonding, H_2O would have existed as a gas like H_2S and no life would have been possible.
2. H bonds are important in biological systems. Proteins contain both CO– and NH_2– groups and H bonds can be formed as a link between O and N atoms. Thus the structure and the properties of proteins depend on the existence of H bonds.
3. It plays an important role in making wood fibres more rigid thereby increasing its utility as an article of housing, furniture etc.
4. Cotton, silk or synthetic fibres owe their rigidity and tensile strength to hydrogen bonding.
5. The stickiness of glue or honey is again due to H bonding. Most of our food materials also consist of H bonding – proteins, carbohydrates etc.

1.23 VAN DER WAALS' FORCES

Chemical forces or interatomic forces (bonding) existing between atoms, ions etc, are responsible for the formation of molecules. Similarly, the molecules, specially in a liquid or solid state is held together by forces known as *cohesive forces* or *van der Waals' forces.*

These are:

(i) physical forces much weaker than chemical forces;

(ii) short range forces of attraction;

(iii) electrostatic in nature much weaker than ionic and covalent bonds (of the order of 25 kJ/mol).

(iv) known to exist between all kinds of atoms, molecules and ions.

Different types of van der Waals forces are known

Dipole – dipole interactions : *These exist between polar molecules which have a permanent dipole moment.* As the molecules come nearer, they orient themselves in such a way that the positive end of the dipole attracts the negative end of another molecule. The dipole - dipole attraction holds the molecules together.

These are the strongest among the different types of van der Waals' forces.

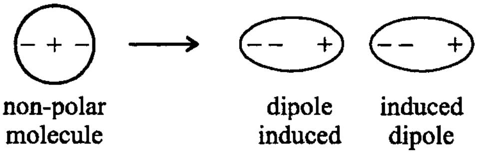
Their magnitude depends on the dipole moments of the molecules concerned. The larger the dipole moment, the greater is the dipole - dipole attraction.

Such interactions are seen in $CHCl_3$, $C_6H_5NO_2$, CH_3COCH_3 molecules.

Dipole – induced dipole interactions : The *attractive interactions between polar and nonpolar molecules are due to dipole - induced dipole interactions.* A polar molecule when brought near a nonpolar molecule, polarises the nonpolar molecule. The positive end of polar molecule attracts the electron cloud of the nonpolar molecule and induces a polarity in it. This results is an attraction between the molecules. The magnitude of this type of interaction depends on the polarizability of the nonpolar molecule and the dipole moment of the polar molecule.

Induced dipole – induced dipole interactions : These are also known as *London forces.* These *are forces existing between nonpolar molecules.* Monoatomic rare gases like helium, neon, argon etc, and other gases like nitrogen, oxygen and halogens condense to liquids at sufficiently low temperature and high pressures. This proves the existence of inter molecular forces of attraction in them.

Since the electrons in a molecule are in continuous motion, the electron charge cloud around the molecule will not be symmetrical. This results in the concentration of the negative charge at any one region of molecule. An instantaneous electric dipole is thus formed. This dipole induces an electric dipole in the neighbouring molecule. The arrangement will be such that the positive end of the original dipole is pointing towards the negative end of the induced dipole. Thus a weak induced dipole - induced dipole attraction exists between the molecules. These induced dipoles are continually forming and disappearing as a result of continuous motion of electrons. These are very weak forces and exist between all types of molecules.



This kind of interaction increases with increase in the number of electrons in the molecule. Thus, larger the molecular size, greater is the induced dipole - induced dipole interaction.

This phenomenon explains the increased boiling points in the cases of halogens, inert gases etc, with increasing molar masses.

Gas	He	H_2	Ne	N_2	O_2	Ar	F_2	Cl_2
Number of electrons	2	2	10	14	16	18	18	34
B.P (K)	4	13	27	77	90	87	85	238

1. van der Waals' forces have been extremely useful in understanding the behaviour of real gases i.e., deviation from ideal gas behaviour.
2. These forces are responsible for the condensation and liquefaction of rare gases, halogens etc.

3. In molecular crystals both of polar (ice) and nonpolar molecules (sulphur, phosphorus, solid carbon dioxide) the molecules are held together by weak van der Waals' forces. This explains their softness and easy compressibility.

In graphite, the layers of hexagonally arranged carbon atoms are held together by van der Waals' forces. These forces being weak causes the layer to slide over one another on the application of slightest pressure. Graphite is thus soft and acts as a solid lubricant.

1.24 METALLIC BOND

A metal is characterised by the following physical properties –

(i) exceptionally good conductor of electricity and heat,
(ii) possesses a bright appearance called metallic lusture
(iii) crystallizes with a close packing arrangement in which a central atom has as many as 8 to 14 neighbours.
(iv) is malleable and ductile.

On the basis of the above properties, it can be said that,

(i) A metallic bond cannot be ionic in nature since an ionic bond is formed between atoms of different electronegativity. In a metal, the bonding is between identical atoms.
(ii) van der Waals' forces are too weak to explain the nature of the bonding in metals since metals possess high melting points.
(iii) Covalent bond is again not possible as the number of valence electrons available for bonding are not sufficient for mutual sharing with 8 to 14 neighbouring atoms. Other than transition metals, all metals have only one to four valence electrons.

It is obvious that the conventional type of bonding cannot explain the nature of the metallic bond.

According to the *electron sea model* proposed by Lorentz, the metal is regarded as a close packing arrangement of positive ions surrounded by a sea of valance shell electrons. These electrons are free to move around the lattice. The *metallic bond* is defined as the *attractive force between the mobile electrons and the positive ion binding the metal atoms together.*

1.24.1 Molecular Orbital Theory or Band Theory

This quantum mechanical approach was proposed by Bloch, Sommerfeld and others.

The metals are electron deficient crystals and the electrons in a metal are considered to belong to the crystal as a whole and not to any individual atom. As discussed earlier, when two atomic orbitals combine, two molecular orbitals are formed (one bonding and the other antibonding), One of the molecular orbital has lower energy than the combining atomic orbitals while the other has higher energy than the combining atomic orbitals.

On the same lines, if three orbitals combine three molecular orbitals are obtained. Thus for n atomic orbitals combining belonging to n different atoms, n molecular orbitals can be expected. Half of these (n/2) are of lower energy called bonding molecular orbitals and the other half are of higher energy than the combining atomic orbitals called antibonding. The value of n is very large for metallic crystal, of the order 10^{23} and thus a very large number of molecular orbitals are obtained,

In Li_2, molecule where two atoms of Li combine six electrons are accommodated as shown.

$$(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2$$

$\sigma 2s$ bonding orbital is full while the corresponding antibonding orbital is empty. The outer shell electrons occupy the bonding orbitals. In Li_3 molecule involving three 2s atomic orbitals, three molecular orbitals – one bonding, one nonbonding and one antibonding are formed. The three electrons occupy bonding and nonbonding molecular orbitals as shown in Fig. 1.30.

The nonbonding molecular orbital has an energy intermediate between bonding and antibonding molecular orbitals.

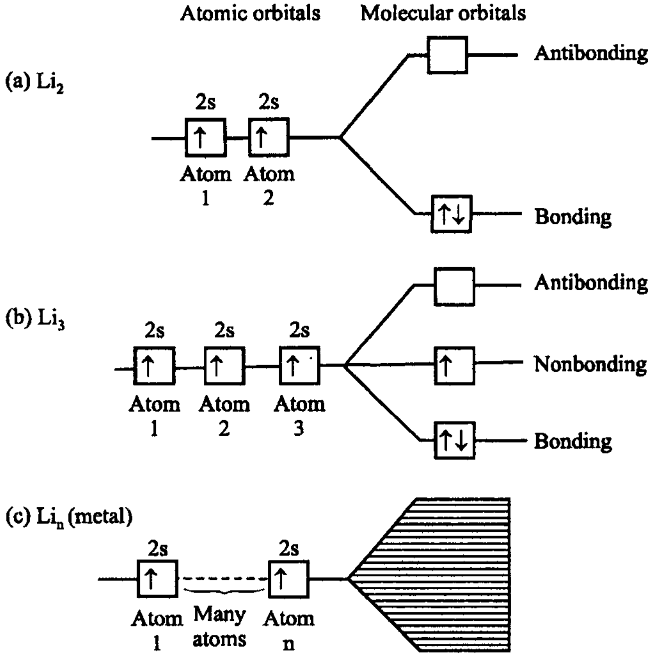


Fig. 1.30: Development of molecular orbitals into bands in metals

By extending this to n lithium atoms, n molecular orbitals result, half (n/2) of them are bonding and the other half are antibonding. The spacing between the various energy orbitals becomes very less and these molecular orbitals are very close to one another and form an energy band. Each molecular orbital can accommodate a maximum of two electrons. The upper half is empty. This, of course is true at absolute zero. As the temperature is increased a few of the electrons acquire sufficient kinetic energy and get promoted to the upper half of the band and may be only singly occupied. (A few unpaired electrons are found to be present in any metallic crystal above K) The molecular orbitals extend in three dimensions over all the atoms in the crystal. The electrons have a high degree of mobility and account for the high electrical and thermal conductivity of the metals.

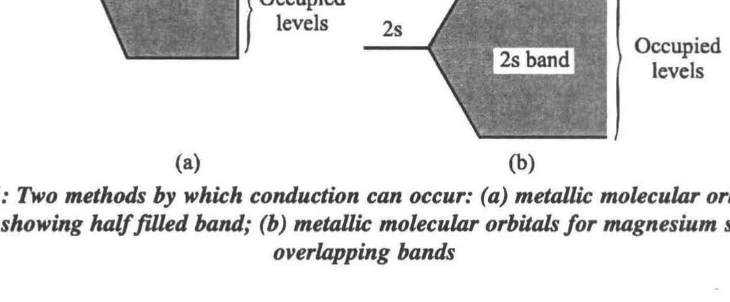
In a similar way, it might be possible to combine 2p, 2s, 3p orbitals etc, to form energy bands in a crystal. In the metallic crystal therefore, the nuclei are surrounded by a series of energy bands. The electrons may be found in these bands which are called *"permitted" energy bands* or *Brilloiun zones*. Between these permitted energy bands are gaps or empty bands where electrons are not found. Such gaps are therefore *called forbidden bands*. Large amount of energy is required to cross these energy bands. Some energy bands in a solid may overlap and in such a case there is a continuous distribution of allowable energies for its electrons.

1.25 CONDUCTORS, INSULATORS AND SEMICONDUCTORS

The band in which the valence electrons are present is called the *valence band.* This may be partly or completely filled. There may be an outer band which is empty and is called the *conduction band.* The two are separated by a *forbidden zone* and for an electron to jump from valence band to conduction band some energy is needed. The extent of filling of these bands, the width of the forbidden zone determine whether a substance is a conductor, insulator or a semiconductor.

1.25.1 True Metal or Conductor

The true metal is characterized by excellent conductance but showing increased resistance with rise in temperature. The distinctive feature is either a partially filled band (alkali metals) or an occupied band overlapping an empty conduction band (alkaline earth metals). In sodium, the electrons in inner shells 1s, 2s, 2p of constituent atoms are present in the lower bands. In these bands there are just enough orbitals to accommodate all the available electrons (i.e., 1s, 2s, 2p) so that these bands are completely filled. The 3s band on the other hand, is only half filled with electrons and all the electrons possess the same spin.



(a) (b)

Fig. 1.31: Two methods by which conduction can occur: (a) metallic molecular orbitals for lithium showing half filled band; (b) metallic molecular orbitals for magnesium showing overlapping bands

These electrons belong to the metallic crystal as a whole and are mobile. On application of an electric potential across the metal, the mobile electrons are set into motion and as all the energy levels are delocalised, current is easily conducted through the metal.

Magnesium has an outermost orbital with 2 electrons i.e., $3s^2$ and is thus expected to have a completely filled 3s band. However, in this case, the 3s and the 3p bands are sufficiently close to overlap and a number of empty orbitals are made available. Thus an unfilled band with free electrons is obtained making it a good conductor. Infact this overlap of ns and np bands takes place in the case of alkali metals also.

The conductance of metal decreases with an increase in temperature. This is due to the fact that vibratory motion of atoms increases with temperature which interfere with the free movement of electrons.

1.25.2 Insulators

In an insulator all low energy bands i.e., valence bands are completely occupied. The energy gap between this band and the next conduction band is too large and even on heating, electrons are not able to jump the forbidden zone and move into the conduction band. Thus they are not able to conduct electricity.

1.25.3 Semiconductors

Semiconductors comprise that class of solids whose electrical properties are intermediate between insulators and good metallic conductors. In a semiconductor the energy gap between the filled valence band and the next conduction band is rather low. For example, in diamond it is 589 kJ/mol whereas for silicon (a semiconductor) it is 105 kJ/mol and in germanium it is 69 kJ/mol. At low temperatures the energy is not sufficient to cross the forbidden zone and the material remains a poor conductor or insulator. As the temperature is increased a few electrons acquire sufficient energy to cross over the forbidden zone and occupy the empty conduction bands. Thus the substance is able to conduct current.

There are two types of semiconductors: intrinsic and extrinsic.

Intrinsic semiconductors: These substances are poor conductors or insulators at low temperatures. Their conductivity increases rapidly with increase in temperature. *Conduction increases in these cases by thermal excitation of electrons enabling them to cross the forbidden zone.* The number of electrons shifted from the valence band to conduction band is not very high and hence the conductivity is not as high as in a metal. Si, Ge, Se are all intrinsic semiconductors.

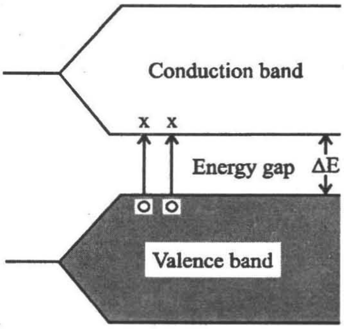


Fig. 1.32: Thermal exictation of electrons in an intrinsic semiconductor. The x's represent electrons and the o's holes.

Extrinsic semiconductors: These are also known as *impurity semiconductors*. The presence of certain impurities like As, P, B, Ga improve their conductivity which are normally insulators. The filled valence band and the conduction band which are separated by a small energy gap is bridged by the energy states of the impurities added.

n-type extrinsic semiconductors

Here silicon or germanium is impregnated (or doped) with an impurity like P, As (group 15) which has more valence electrons (5) than the parent insulator. Each of the impurity atom contributes one more electron. This extra electron occupies an energy state well above the valence band. It is called the *donor state* or *donor level.* At room temperature the energy gap is quite close enough to excite the extra electron from the donor state to the conduction band and thus can conduct electricity. *Such semiconductors in which current flow is due to the movement of electrons from donor state to conduction band is called n-type (negative electrons) semiconductors.*

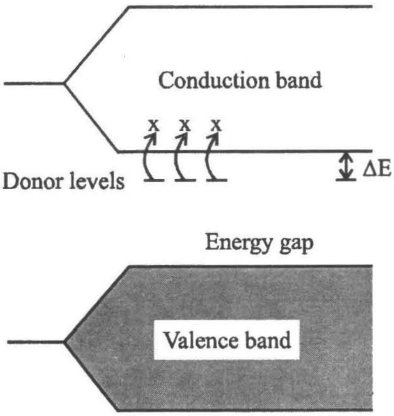


Fig. 1.33: Conduction by electrons in donor or n-type semiconductor

p-type extrinsic semiconductor

In this type, an impurity is added to the semiconductor which has less valence electrons than the parent insulator. Addition (or doping) of Ge, Si with Al, B, Ga (group 13) results in p-type semiconductors. Each of the impurity atom contributes only three electrons rather than the requisite four to keep the band filled. The energy levels of the impurity lie very close to the valence band of the semiconductor and are called the *acceptor states* or *acceptor levels.* At room temperature few electrons from top of the valence band are excited to the acceptor states of impurity atoms.

Thus positive holes are left behind in the valence band, and as electrons move into these positive holes, they appear to migrate. *Thus the conduction is due to the movement of positive holes and hence the name p-type extrinsic semiconductor.*

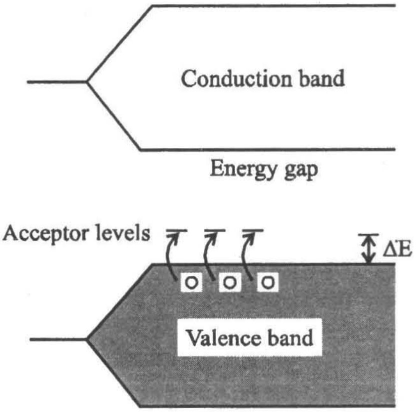


Fig. 1.34: Conduction by holes in acceptor or p-type semiconductor

Various imperfections can lead to semiconductivity in analogous ways. The range of possibilities for semiconductors is very great and the applications to the operation of transistors and related devices has revolutionized the electronics industry.

1.26 SUPERCONDUCTIVITY

Even the best of metallic conductors of electricity (Cu, Al), show some electrical resistance which decreases with decrease in temperature. In 1911 the Dutch scientist Heike Kamerlingh Onnes discovered that mercury suddenly loses all its resistance to an electric current when cooled to a temperature close to that of liquid helium (– 4K). *A material that has zero or almost close to zero electrical resistance is called a superconductor.* A superconductor is a *material that abruptly loses its resistance to an electric current when cooled to a definite characteristic temperature. The temperature at which the resistance drops sharply and superconducting occurs* is called *the critical temperature*, Tc. A superconductor can carry current without losing energy. These very low temperature superconductors requiring liquid helium are of little practical use.

Another important property associated with *superconductors* is that they *do not allow a magnetic field to penetrate their bulk.* This was discovered by Meissner and Oshsenfeld and is now called the *Meissner effect.* They also give rise to *'levitation'*. Levitation occurs when objects float in air. This is achieved due to mutual repulsion between a superconductor and a permanent magnet.

In 1950s certain alloys of niobium and titanium with a T_C in the range of 20-30K were discovered. Attempts to make wires of these materials for constructing superconducting magnets were made.

The first non-metallic superconductor was found in 1964. In 1986, George Bednorz and Alex Muller of IBM, Switzerland discovered that certain copper oxide materials become superconducting at 30K. Similar materials with high T_C values were reported soon after. The compound is a mixed oxide with a formula $La_{(2-x)}Ba_xCuO_{(4-y)}$ where x is 0.15 - 0.20 and y is a very small quantity. This compound has a perovskite structure and is slightly oxygen deficient. Similar compounds with Sr^{2+} or Ca^{2+} replacing Ba^{2+} were reported. Critical temperature as high as 50 K was possible. Bednorz and Muller were awarded the Noble Prize in physics in 1987.

Another significant development was the superconducting system of a mixed oxide of yttrium reported by Wu, Chu and co-workers. The compound has a formula $YBa_2Cu_3O_x$, where x is between 6 and 7 and a T_C 93 K which means that the expensive liquid helium can be replaced by cheap liquid nitrogen (77 K). For simplicity, the above system is called the 1-2-3 system based on the ratio of the metals present. This also has a perovskite structure. Similar compounds substituting yttrium by other lanthanides like europium, samarium etc., are known. These are called *warm superconductors.* A lot of research to obtain high T_C are going on and superconductors with T_C as high as 164 K have been reported.

1.26.1 Applications of Superconductors

1. Electrical power transmission using a superconducting material can be very economical. A very fine wire made of superconducting material has effectively zero resistance and the wire does not get heated up. Since there is no current loss, current can flow in the coil indefinitely once it starts.

2. Superfast computers called supercomputers can be built. Heat problems faced in using miniature computer chips will be dramatically reduced. Superconductors will also lead to faster chips.
3. Powerful electromagnets with high electromagnetic fields are possible. They find extensive use in medical magnetic resonance imaging. Powerful particle accelerators, efficient devices for nuclear fusion can also be built.
4. The levitation effect can be used to construct fast, quiet and smooth trains riding above the tracks. These operate on superconducting materials.

The only difficulty lies in fabrication of these superconducting materials into wires of durability.

IMPORTANT POINTS

- A chemical bond is defined as an attraction which holds together the constituent atoms in a molecule.
- Ionic bond is formed by the transference of one or more electrons from one atom to the other.
- The oppositely charged ions are held together by electrostatic forces of attraction called the ionic bond.
- Lattice energy is the enthalpy of formation of a mole of ionic solid from free gaseous ions brought from infinity to their respective equilibrium sites in their crystalline lattice under standard conditions.
- Born-Haber cycle is a cyclic process which relates lattice energy to other thermochemical quantities.
- Greater the lattice energy, the more stable is the ionic compound.
- Low ionization energy for one of the elements, high electron affinity for the other element and high lattice energy favour the formation of ionic compounds.
- Ionic compounds are held together by strong electrostatic forces of attraction and are very stable. They are hard, brittle, possess high melting and high boiling points.
- Ionic compounds are soluble in water and in polar solvents. They are good conductors of electricity in fused state and in aqueous solutions.
- A covalent bond is formed by the sharing of electrons by the two atoms.
- When two atomic orbitals share a common region in space there is said to be an overlap of orbitals.
- According to valence bond theory, a chemical bond can be formed by the overlap of atomic orbitals.
- For bonding to occur each atom should have an unpaired electron and of opposite spins.
- When there is more than one unpaired electron, multiple bond formation is possible.
- A stable molecule is formed when there is a decrease in the potential energy of the molecule.
- The strength of the covalent bond depends upon the extent of overlapping. The greater the overlap, the stronger is the covalent bond formed.

- Sigma bond results due to end-to-end or axial overlap of atomic orbitals along the molecular axis.
- Pi bond results by the sidewise or lateral overlap of atomic orbitals. s orbitals cannot form pi bonds.
- Sigma bond is a stronger bond than pi bond.
- When a molecule cannot be represented by a single valence bond structure it is considered as a hybrid of two or more structures. The molecule is called a resonance hybrid.
- The difference in energy between the actual molecule and the most stable of resonating structures is called the resonance energy.
- The phenomenon of mixing of the atomic orbitals of nearly equal energy in an atom resulting in orbitals of equal energy is called hybridization.
- The number of hybrid orbitals is always equal to the number of orbitals mixed.
- Hybrid orbitals overlap better than pure atomic orbitals.
- The bond angles in sp, sp^2, sp^3 hybridization are 180°, 120° and 109.5° respectively.
- In sp^3d hybridization the bond angle between three of the hybrid orbitals is 120° and it is 90° in the case of the other two.
- The bond angle is 90° in sp^3d^2 hybridization.
- Electron pairs around a central atom arrange themselves such that there is minimum repulsion between them.
- Valence Shell Electron Pair Repulsion (VSEPR) Theory is useful in predicting the general shape of a molecule.
- A molecule has a regular geometry when the central atom is surrounded by only bonded pairs of electrons.
- The repulsion existing between different types of electron pair is lone pair-lone repulsion > lone pair-bonded pair repulsion > bonded pair-bonded pair repulsion.
- The bond angle is smaller than predicted by regular geometry when lone pairs of electrons are present.
- The bond angle in NH_3 is 107° and H_2O is 104.5°
- BrF_3 is T-shaped, ICl^- is linear and ICl^-_4 is square planar.
- Molecular orbital theory describes covalent bonds in terms of molecular orbitals.
- Molecular orbitals are formed by the linear combination of atomic orbitals (LCAO) of bonding atoms and spread over the entire molecule.
- When two atomic orbitals overlap, a bonding molecular orbital and an antibonding molecular orbital result.
- The bonding molecular orbital has a lower energy and the antibonding molecular orbital has a higher energy than the corresponding atomic orbitals.
- Each molecular orbital in a molecule has a discrete energy associated with it.
- Electrons belonging to the entire molecule are filled in the molecular orbitals according to the principles of aufbau, Pauli and Hund.
- Stability of a molecule depends on the bond order.
- Higher the bond order greater is the stability of the molecule.

- A molecule with no unpaired electron is diamagnetic while a molecule with one or more unpaired electron is paramagnetic in nature.
- He_2, Be_2 molecules do not exist.
- O_2 molecule is paramagnetic in nature because of the presence of two unpaired electrons in it.
- A covalent bond between two identical atoms is a nonpolar bond and the molecule is nonpolar.
- A covalent bond between two different atoms is polar. The shared electron pair is closer to the more electronegative atom. Such molecules are dipoles.
- The polarity of a bond is measured in terms of dipole moment.
- Dipole moment is defined as the product of the magnitude of the charges and the distance between them.
- A diatomic molecule is polar if the bond between them is polar.
- A polyatomic molecule may have zero dipole moment even if it contains polar bonds; this may arise due to symmetrical nature of the molecule and cancellation of individual dipole moments.
- Dipole moments of CO_2, BF_3, CH_4, CCl_4 are zero.
- Most covalent compounds are liquids or gases at room temperature. They may be soft or hard. Their melting and boiling points are low.
- They are soluble in non polar solvents such as benzene, ether and insoluble in polar solvents.
- They are poor conductors of electricity.
- Bond length is defined as the average distance between the two nuclei.
- Bond angle is defined as the angle formed between two imaginary lines drawn from the nucleus of the central atom to the nuclei of the other two atoms bonded to it.
- Bond energy is the energy required to break one mole of bonds of that type in a gaseous substance.
- Polarizability is the ease with which the electron distribution in the atom (molecule) can be distorted. The distortion brought about in electron distribution is called polarization.
- A large degree of polarizability results in a bond which is largely covalent.
- A small cation and a large anion favours covalency.
- The attractive force which binds hydrogen atom of one molecule with another small highly electronegative atom (F, O, N) of another molecule is known as hydrogen bond.
- Hydrogen bond is weaker than a covalent bond.
- Intermolecular and intramolecular hydrogen bonding exist.
- Hydrogen bonding in compounds result in high melting and boiling points, increased viscosity etc.
- The anomalous properties of water like floating of ice in water, a maximum density at 4°C are due to hydrogen bonding.
- van der Waals forces are weak, short range forces of attraction between molecules. They are purely electrostatic in nature.

- The different types of van der Waals' forces are dipole-dipole, dipole-induced dipole and induced dipole-induced dipole interactions.
- van der Waals' forces can explain the condensation and liquifaction of inert gases, halogens etc; They explain the increase in the boiling points of these compounds with increase in molecular masses.
- van der Waals' forces explain the softness and easy compressibility of molecular crystals.
- Metallic bond is the attractive force between the mobile electrons and the positive ions binding the metal atoms together.
- The atomic orbitals of a large number of metal atoms combine together to give a large number of molecular orbitals. These molecular orbitals form an energy band.
- Electrons are found in these energy bands called permitted bands or Brillouin zones.
- The band in which valence electrons are present is called valence band. The outer empty band is called conduction band.
- The energy gap is small in a metal, very large in an insulator and intermediate in a semiconductor.
- Intrinsic semiconductors are poor conductors at low temperature but become better conductors with increase in temperature.
- Extrinsic semiconductors have traces of impurities in them. The energy states of the impurities bridge the energy gap between valence band and conduction band.
- In n-type semiconductor, impurities like P, As are added and current flow is due to the movement of electrons from donor state to conduction band.
- In p-type semiconductors, the impurities are B, Al etc., and conduction is due to migration of positive holes in the valence band.
- A superconductor has zero electrical resistance. The temperature at which resistance to flow of electricity drops to zero is called critical temperature, T_c.
- Superconductors do not allow a magnetic field to penetrate their bulk and also give rise to levitation effect.
- Certain mixed oxide systems ($YBa_2Cu_2O_x$) exhibit superconductivity around 93 K. These are called warm superconductors.
- Superconductors find application in electrical power transmission, superfast computers, powerful electromagnets etc.

Important Mathematical Relations

Born-Haber Cycle: $\Delta H_f = \Delta H_s + I + \Delta H_d + E.A. + U$

Born-Lande equation $U = \dfrac{N_o A z^+ z^- e^2}{4\pi\varepsilon_o r_o}\left[1-\dfrac{1}{n}\right]$

Bond order $= \dfrac{1}{2}\,[N_b - N_a]$

Dipole moment $\mu = \delta \times d$

EXERCISE

Short Answer Type Questions:

1. Define a chemical bond.
2. Define an ionic bond.
3. Define lattice energy.
4. Specify the compound in the following pairs which has the higher lattice energy (i) KCl and MgO (ii) NaF and NaBr. Justify your answer.
5. How is a chemical bond formed according to valence bond theory?
6. What is meant by overlapping of orbitals? How do you relate the strength of a bond in terms of extent of overlap?
7. How does valence bond theory explain the formation of a stable hydrogen molecule?
8. What is meant by resonance?
9. Write the resonance structures for hydrogen molecule.
10. Give the resonating structures of (i) carbonate ion and (ii) carbon dioxide molecule.
11. Define hybridization.
12. Give the bond angles between the hybrid orbitals in the following types of hybridization sp, sp^2, sp^3, sp^3d^2
13. Explain sp^3 hybridization with an example.
14. Explain sp^3d^2 hybridization with an example.
15. Write the structure of phosphorus pentachloride. Mention the type of hybridization involved.
16. Describe the hybridization of P in PCl_5. Give the shape of phosphorus pentachloride.
17. Give the hybridization involved and geometrical shape of BCl_3 molecule.
18. Mention the shapes of molecules with bond angles 180° and 120°.
19. Explain how boron achieves a trivalency despite having only one unpaired electron.
20. How many atoms are directly bonded to the central atom in a (i) tetrahedral (ii) octahedral (iii) trigonal pyramidal molecules. Give an example of each.
21. Predict the geometry of the following molecules using VSEPR theory (i) BF_3 (ii) CCl_4 (iii) SF_6.
22. Explain the shape of ammonia molecule on the basis of VSEPR theory.
23. What do you mean by lone pair and bonded pair of electrons?
24. Why is a lone pair expected to occupy an equatorial position than an axial position?
25. In water molecule, the H – O – H bond angle is 104.5°. On the basis of VSEPR theory discuss its structure.
26. Why are the bond angles in NH_3 and H_2O different when both of them exhibit tetrahedral geometry.
27. Define (i) bonding molecular orbital; (ii) antibonding molecular orbital.
28. Bring out the differences between bonding and antibonding molecular orbitals.
29. Define bond order.
30. Can bond order be used to compare the strengths of chemical bonds?

31. Illustrate with diagrams (i) p-p σ bond (ii) p-p π bond.
32. Write the molecular orbital configuration of
    (i) N_2 molecule
    (ii) O_2 molecule
33. Set up the molecular orbital diagram for oxygen molecule. Explain why oxygen is paramagnetic.
34. With the help of molecular orbital theory, explain the formation of nitrogen molecule.
35. Explain the paramagnetic nature of oxygen molecule on the basis of MO theory?
36. Explain why Be_2 molecule does not exist.
37. Why VB theory cannot explain the paramagnetic nature of oxygen molecule?
38. How many antibonding electrons are there in (a) He_2^+ ion (b) N_2 and (c) O_2?
39. What is a polar covalent bond? Give an example of a diatomic molecule with a polar covalent bond.
40. What are polar and nonpolar molecules? Give an example for each.
41. Define dipole moment and give its units.
42. What is dipole moment? Explain this with reference to HCl and CO_2 molecules.
43. How is it possible for a molecule to have polar bonds and yet have zero dipole moment?
44. The molecule H_2S has a dipole moment 0.97D. Is the geometry linear or bent? Justify your answer.
45. C – Cl bond is polar but the molecule CCl_4 is nonpolar. Explain.
46. What is meant by polarizability?
47. State and explain Fajan's rules of polarization.
48. Define the following terms (i) bond length (ii) bond angle (iii) bond energy.
49. Arrange the following in the decreasing order of bond length C – C, C ≡ C, C ≡ C.
50. What is hydrogen bonding? Mention the types with one example for each.
51. Write a note on hydrogen bonding.
52. Discuss the nature of hydrogen bonding in nitrophenols.
53. Write short notes on (i) intermolecular hydrogen bonding (ii) intramolecular hydrogen bonding.
54. What is the importance of hydrogen bonding?
55. What are the different types of van der Waals forces?
56. Briefly explain.
    (a) dipole-dipole interaction
    (b) dipole-induced dipole interaction
    (c) induced dipole-induced dipole interaction.
57. How do you account for the regular increase in the boiling points of rare gases? Explain.
58. Mention the type of interactions existing between the molecules of: (a) C_2H_5OH, (b) CH_3COCH_3, (c) Cl_2.
59. What is a metallic bond?

60. What is meant by a semiconductor?
61. Account for the conducting property of semiconductors based on band theory.
62. 'Metals are good conductors of electricity' – How does the band theory explain this?
63. On the basis of band theory explain the electrical conductivity of metals.
64. What is a superconductor?
65. Give an example of a superconductor which is (a) metallic (b) ceramic, in nature?
66. Explain giving reasons:
    (a) Ice floats on water
    (b) Ice has a lower density than water
    (c) HF has a higher boiling point than HCl.
    (d) Both nitrogen and chlorine have the same electronegativity. Chlorine rarely enters into hydrogen bonding.
    (e) o-Nitrophenol has a low melting and boiling point compared to p-nitrophenol.
    (f) C – O bond is polar but CO_2 molecule has zero dipole moment.
    (g) BF_3 is planar whereas NF_3 is trigonal pyramidal.
    (h) Both CCl_4 and CH_3Cl have a tetrahedral geometry. CCl_4 has zero dipole moment while CH_3Cl has a net dipole moment.
    (i) Phosphorous forms PCl_5 but nitrogen does not form NCl_5.
    (j) $BeCl_2$ is linear but water is not.
    (k) Ionic compounds are soluble in water whereas covalent compounds are not.

Essay Type Questions:

1. Discuss the factors influencing the formation of ions.
2. Define lattice energy. How does it influence the stability of an ionic compound?
3. Set up Born-Haber cycle for $Na + 1/2\ Cl_2 \rightarrow NaCl$ and explain how lattice energy of NaCl be calculated using Born-Haber cycle.
4. Using Born-Haber cycle, how do you calculate the lattice energy of potassium chloride.
5. Write the Born-Lande equation and explain the terms involved.
6. Write a note on the properties of ionic compounds.
7. Draw the potential energy diagram for the formation of a diatomic molecule and explain.
8. Briefly summarise VB Theory.
9. Explain the terms:
    (a) resonance
    (b) resonance energy
    (c) resonating structures.
10. Does hybridization always form equivalent hybrid orbitals? If not, which are the exceptional cases? Explain taking an example.
11. Explain why the repulsion decreases in the order –
    lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.
12. Discuss the structure of BrF_5 molecule.

13. Discuss the structure of ICl_2^- and ICl_4^- ions.
14. Mention any two common features and any two differences between VB and MO theory.
15. What is molecular orbital theory? How does it differ from VB theory?
16. Compare the properties of ionic and covalent compounds.
17. Covalent compounds have low melting and low boiling points while ionic compounds have high melting and boiling points. Why?
18. Elements A and B have atomic numbers 11 and 17, respectively. Write their electronic configuration. What would be the type of bond formed when A and B combine to form a compound?
19. A, B and C are three consecutive elements in the periodic table. If the electronic configuration of the middle element is [Ne] $3s^2 3p^6$, state with reason what type of linkage would you expect between the atoms of C and A?
20. Define bond dissociation energy? Why are bond energies of polyatomic molecules an average value?
21. State Fajan's rule and explain.
22. What type of bonding is expected in the following cases? Explain giving reasons.
    (a) a small cation and a large anion
    (b) atoms having a large difference in electronegativities
    (c) atoms of the same element.
23. What is hydrogen bonding? What are the different types of hydrogen bonding? Explain with an example.
24. How does hydrogen bonding influence the properties of molecules?
25. Write a note on the anamolous properties of water.
26. What are van der Waals' forces? What properties of molecules are explained by these forces?
27. Discuss the band theory of metals.
28. Using the band theory of metals, differentiate between a metal, an insulator and a semiconductor.
29. Write notes on (a) n type semiconductor and (b) p type semiconductor.
30. Explain why the electrical conductivity of a metal decreases with increase in temperature, whereas it increases in the case of semiconductors.
31. Write a note on semiconductors.
32. What is superconductivity? What potential uses are there for superconductors?

PROBLEMS

1. Calculate lattice energy of NaI from the following data:
   $\Delta H_f^o = -287.6$ kJ mol^{-1}, $\Delta H_d = +213.6$ kJ/mol, $\Delta H_s^0 = +107.3$ kJ mol^{-1}, EA = –295.2 kJ/mol, I = 496 kJ/mol.
2. Calculate the electron affinity of bromine from the data given below for KBr.
   $\Delta H_f^o = -393.8$ kJ mol^{-1}, $\Delta H_d = 223.8$ kJ/mol^{-1}, $\Delta H_s^0 = 89.2$ kJ/mol, I = 418.9 kJ mol^{-1}, U = –689.1 kJ/mol^{-1}.

❖ ❖ ❖

Chapter 2

Noble Gases – Elements of Group 18

SYLLABUS

The six elements, *helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon(Xe) and radon (Rn) comprise the noble gases* and belong *to group 18 (group zero) of the periodic table*. A new group called group zero after the seventh group, was introduced by Ramsay, the discoverer of these gases. They were earlier called 'inert gases' or 'noble gases' because of their chemical inactivity. Since the discovery of xenon fluoride in 1962, it is known that these do enter into chemical reactions under suitable conditions and the name 'noble' gases is more appropriate. The term noble implies that these gases tend to be inactive in much the same way as the noble metals and enter into very few chemical reactions. Their chemical inertness is related to their highly stable outer electronic configuration s^2p^6. (Helium is an exception with an electronic configuration $1s^2$).

They have zero electronic affinities and very high ionization energies, the highest in that particular period. Under normal conditions, the noble gases have little tendency to gain or lose electrons. The molecules of these gases are monoatomic.

2.1 OCCURRENCE

The gases except radon occur as minor constituents in the atmosphere. Radon is obtained as a product of disintegration from radium and is radioactive. The most stable isotope ^{222}Rn is a short lived isotope with a half life period of 3.8 days. Table 2.1 gives the percentage by volume of the noble gases in the atmosphere.

Table 2.1 : Abundance of noble gases in atmosphere

Element	*(% by volume)*
He	5.2×10^{-4}
Ne	1.5×10^{-3}
Ar	0.93
Kr	1.1×10^{-4}
Xe	8.7×10^{-6}

Helium occurs upto 7% in natural gas coming out of certain oil wells in USA (Kansas).

Helium is also present occluded in certain radioactive minerals, clevite, monazite, pitchblende, thorite etc. The gas is given off when the mineral is heated to 1273 K in vacuum.

2.2 DISCOVERY OF NOBLE GASES

Discovery of Argon

As early as 1785, Henry Cavendish working on the composition of air found a small portion of air, about 1/120th of the original volume, unreactive (N_2 was removed as NO_2 by sparking with excess oxygen and NO_2 formed was absorbed in sodium hydroxide solution. Excess O_2 was removed by reaction with burning sulphur). He failed to draw any conclusion about the residual gas and this important absorption was forgotten for over a century.

In 1891, Lord Rayleigh found the density of atmospheric nitrogen to be about 0.5 percent higher than nitrogen isolated from chemical sources. The discrepancy was thought to be due to the presence of some heavier gas in atmospheric nitrogen. The suggestion came from Ramsay and the two of them repeated the experiments of Cavendish. A residual gas left behind gave a spectrum which did not coincide with that of any of the elements hitherto known. The vapour density of the gas was found to be about 20 which gave the molecular mass of the gas as 40. The discovery was announced in the year 1894 and was given the name '*argon*' (*argos* in Greek means the 'lazy one') by Lord Rayleigh and Ramsay.

Discovery of Helium

In August 1868, during a total eclipse, Sir J Norman Lockyer observed in the sun's chromosphere a bright yellow line near the D_1 and D_2 lines of sodium. He called it the D_3 line and related it to the presence of a new element, *helium* (*helios* in Greek means the 'sun'). At that time it was believed that this element existed only on the sun and not on the earth. Its existence in earth was recognised only in 1895.

In 1890, William Hilderbrand obtained a gas by heating uranium minerals with strong acids. He assumed the occluded gas to be nitrogen. Ramsay repeated the experiment with clevite and analysed the gas spectroscopically. A new bright yellow line was observed. This was shown to be due to helium by Sir William Crooke, a specialist in spectroscopy. The atomic mass of the element was found to be 4.

Discovery of Neon, Krypton and Xenon

A new group to include the new elements argon and helium were introduced in the periodic table. More research to discover the remaining elements of this group was carried out by Ramsay and Morris William Travers. Careful fractination of liquid argon resulted in another new element '*neon*' (meaning 'new'). The vapour density of this gas was found to be 10.1 and hence the molecular mass 20.2. From the less volatile fraction of liquid air they isolated two other gases which are named *krypton* (meaning 'hidden') with atomic mass 80 and *xenon* (meaning 'stranger') with an atomic mass 128.

Discovery of Radon

The last member of this group was later discovered by Dorn as one of the disintegration products of radium. It was named *radon* (meaning 'ray').

2.3 ISOLATION OF NOBLE GASES FROM LIQUID AIR

Atmospheric air is the only source for the gases neon, argon, krypton and xenon. Helium is found in atmospheric air, natural gas and radioactive minerals.

Fractination of liquid air by Claude process give rise to two main fractions, one containing mainly nitrogen and the other containing mainly oxygen.

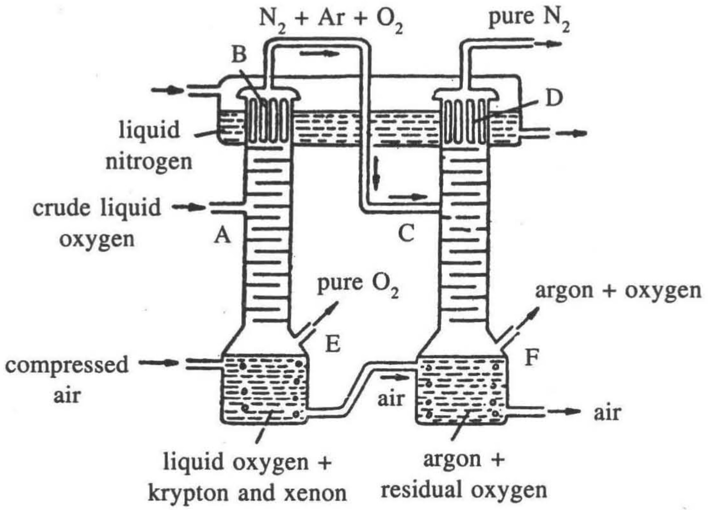


Fig. 2.1: Isolation of Argon

On the basis of their boiling points it is obvious that the more volatile helium and neon will be present in the nitrogen fraction. The oxygen fraction has the less volatile, argon, krypton and xenon. Also as the boiling points of oxygen and argon are very close, argon remains mixed with oxygen.

Table 2.2 : Boiling points of noble gases, N_2 and O_2

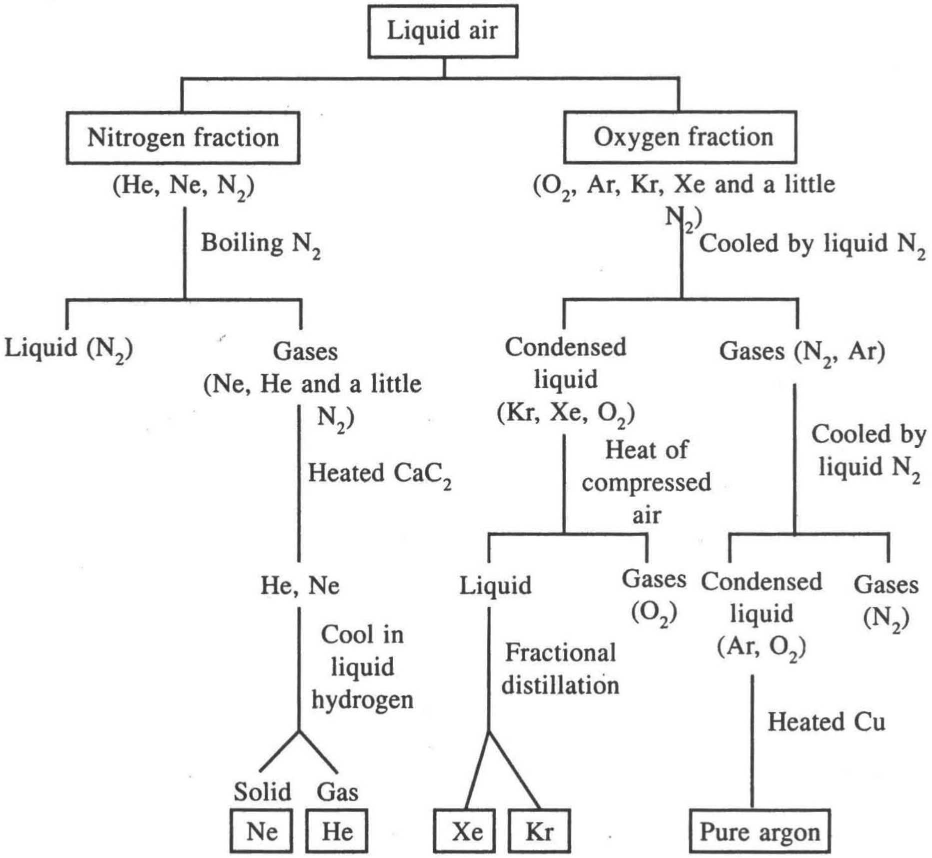
Element	*Boiling point (K)*
He	4.2
Ne	27.1
N_2	77.2
Ar	87.3
O_2	90.0
Kr	120.1
Xe	165.2

1. The oxygen fraction (Ar, Xe, Kr and a little N_2) is pumped into a fractination column (Fig. 2.1) the upper part of which is kept cooled by liquid nitrogen. O_2, Kr and Xe get condensed being less volatile (IA). The gaseous mixture of argon (47%), nitrogen (47%) and oxygen (6%) i.e. led into another column also cooled by liquid nitrogen. Nitrogen escapes as gas while argon with a little oxygen condense as a liquid. Oxygen is removed from this mixture by passing over heated copper on sparking with hydrogen. Argon is obtained in the pure form.

2. The liquid part of oxygen fraction (IA) containing Kr, Xe and oxygen accumulate at the bottom of the left column. The oxygen is evaporated by the heat of compressed air while krypton and xenon in the liquid state. The two can be separated by fractional distillation or by selective adsorption on charcoal.

3. The nitrogen fraction is passed through a spiral column surrounded by a bath of boiling nitrogen. Most of the nitrogen gets liquefied. The more volatile helium and neon escapes. Any uncondensed nitrogen is removed by passing over heated calcium carbide. The gaseous mixture of neon (75%) and helium (25%) is cooled in liquid hydrogen. Neon solidifies while helium escapes as a gas.

Flow chart of the above process is as shown:



2.4 ISOLATION OF HELIUM FROM NATURAL GAS

Natural gas contains as much as 7% of helium along with hydrocarbons, carbon dioxide and nitrogen. Carbon dioxide is removed by reaction with concentrated potash (KOH). The gases are liquefied when most of the hydrocarbons gets liquefied. The residual gas mixture consists of nitrogen, helium and a small amount of methane. The mixture is compressed to 100 atmospheres and cooled to 73 K when except helium, the other gases get liquefied, 99% pure helium is obtained. This is further purified by cooling to 3 K and passing over activated charcoal. All the gases except helium are absorbed and pure helium is obtained.

2.5 APPLICATIONS OF NOBLE GASES

The more important applications of noble gases are listed in Table 2.3

Table 2.3 : Important uses of Noble gases

Element	*Important Uses*
Helium	In air ships and weather balloons (in preference to hydrogen which is inflammable). Mixed with oxygen, as breathing gas for divers (nitrogen is replaced by helium and the risk of "bends" in blood is prevented). To provide inert atmosphere for welding of metals like Mg, Al, Ti and stainless steel. Has the lowest boiling point, hence used a refrigerant in cryoscopy, to obtain a low temperature for the study of superconductors and in lasers. As a cooling gas in some nuclear reactors.
Neon	In neon lamps (has a characteristic red glow). Neon mixed with argon or mercury can also be used (the colour of light produced varies from green to dark blue). In electronics for filling voltage stabilisers, photoelectric cells etc.,
Argon	To provide inert atmosphere for various metallurgical operations such as welding of Mg, Al, Ti, stainless steel etc. For filling in electric light bulbs to prevent oxidation of the tungsten filament at the prevailing high temperature. In growing silicon and germanium crystals for transistors. In fluorescent lamps, radio valves, in GM (Geiger–Muller) counter.
Krypton	In high efficiency filament lamps, in coloured display lamps
Xenon	In high light intensity photographic flash tubes.
Radon	Used in radiotherapy in the treatment of cancer.

2.6 COMPOUNDS OF NOBLE GASES

Any attempts to prepare compounds of noble gases were put to a halt by the success of the valency theory relating to a stable octet configuration of noble gases.

The first real compound of noble gases was made by Bartlett and Lohman at the University of British Columbia in 1962. Bartlett was studying the properties of platinum hexafluoride, an extremely powerful oxidising agent. Oxygen gets oxidised by it and the result is

$$O_2 + PtF_6 \longrightarrow O_2^+[PtF_6]^-$$

The product was isolated. Bartlett noticed that the ionisation energy of O_2 (1165 kJmol^{-1}) to be very close to that of xenon (1170 kJmol^{-1}), hence xenon was expected to react with PtF_6. He mixed equivolumes of the two and immediately a yellow solid was obtained. The product was incorrectly thought to be $Xe^+[PtF_6]^-$. The structure of the product was later proved to be wrong. However, the fact that xenon has reacted opened up a lot of research activities in that direction.

Soon after, formation of xenon tetrafluoride was reported.

The ionization energies of He, Ne and Ar are much higher than that of Xe and are not expected to form similar compounds. Kr with a slightly lower ionization energy than Xe does from KrF_2. Radon though has an ionization energy less than Xe, being radioactive provides limited scope for work. A few complexes of Rn and RnF_2 are known.

2.7 FLUORIDES OF XENON

Three fluorides of xenon namely XeF_2, XeF_4 and XeF_6 are known.

2.7.1 Xenon difluoride, XeF_2

Preparation:

1. Xenon reacts directly with fluorine. A 2 : 1 mixture of xenon and fluorine when heated in a sealed nickel vessel at 670 K forms xenon difluoride.

   $$Xe + F_2 \xrightarrow{670K} XeF_2$$

   It is contaminated with the tetrafluoride and is separated by freezing it rapidly at 225 K.
2. Xenon and fluorine are mixed together in a nickel container and is left exposed to bright sunlight (UV light).
3. It can be obtained by reaction of xenon with excess dioxygen difluoride O_2F_2.

   $$Xe + O_2F_2 \longrightarrow XeF_2 + O_2$$

Properties:

It is a colourless crystalline solid and sublimes at room temperature. XeF_2 is the least volatile of fluorides of xenon.

It melts at 400 K.

It is quite stable and can be stored indefinitiely in silica, nickel or monel containers when pure and dry.

It dissolves in liquid HF.

It is an extremely strong oxidising and fluorinating agent.

(a) It oxides hydrogen

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$

(b) It oxides Cl^- to Cl_2, I^- to I_2, Ce(III) to Ce(IV), Co(II) to Co(III)

$$XeF_2 + 2HCl \longrightarrow 2HF + Xe + Cl_2$$

$$XeF_2 + 2KI \longrightarrow 2KF + Xe + I_2$$

$$XeF_2 + Ce_2(SO_4)_3 + H_2SO_4 \longrightarrow 2Ce(SO_4)_2 + Xe + 2HF$$

(c) It fluorinates and forms complexes with fluorides like PF_5, SbF_5, IrF_5 to compounds of the type

$[XeF]^+ [MF_6]^-$ i.e., $[XeF_2] [MF_5]$,

$[Xe_2F_3]^+ [MF_6]^-$ i.e., $[2XeF_2] [MF_5]$

and $XeF_2\ 2MF_5$.

(d) It fluorinates ethane to 1, 1 and 1, 2–difluoroethane at room temperature.

$$2\ XeF_2 + CH_2 = CH_2 \longrightarrow CH_2F - CH_2F + CHF_2 - CH_3 + 2\ Xe$$

2. It is soluble in water and undergoes slow hydrolysis

$$2\ XeF_2 + 2H_2O \longrightarrow 2\ Xe + 4\ HF + O_2$$

3. The hydrolysis is rapid in presence of a base.

$$2\ XeF_2 + 4NaOH \longrightarrow 2\ Xe + 4\ NaF + 2\ H_2O + O_2$$

2.7.2 Xenon tetrafluoride, XeF_4

Preparation:

1. This was first prepared by Classen, Selig and Malon in 1962. This compound is also prepared by direct reaction between xenon and fluorine in the ratio 1 : 5 in a nickel tube at 670 K under a pressure of 6 atmospheres for about an hour and then condensing the product

$$Xe + 2\ F_2 \longrightarrow XeF_4$$

It is contaminated with small amounts of XeF_2 and XeF_6.

2. Pure XeF_4 is obtained by reaction with O_2F_2 and Xe at low temperature.

$$Xe + 2\ O_2F_2 \longrightarrow XeF_4 + 2O_2$$

Properties:

It melts at 390 K.

It is a volatile solid which sublimes on heating in a current of nitrogen forming colourless vapours.

It can be stored in dry pyrex or nickel containers.

It dissolves in liquid HF.

1. It is a fairly strong fluorinating and oxidising agent.

$$XeF_4 + 2\ H_2 \longrightarrow Xe + 4\ HF$$

$$XeF_4 + Pt \longrightarrow PtF_4 + Xe$$

$$XeF_4 + 2\ CH_2 = CH_2 \longrightarrow CH_2F - CH_2F + CH_3 - CHF_2 + Xe$$

$$XeF_4 + 2\ C_6H_6 \longrightarrow 2\ C_6H_5F + 2\ HF + Xe$$

$$XeF_4 + 2\ SF_4 \longrightarrow Xe + 2\ SF_6$$

It oxidises I^- to I_2, Cl^- to Cl_2, Ce(III) to Ce(IV) etc.,

$$XeF_4 + 4KI \longrightarrow 4\ KF + 2\ I_2 + Xe$$

$$XeF_4 + 4\ HCl \longrightarrow 4\ HF + 2\ Cl_2 + Xe$$

2. It reacts violently with water, undergoes hydrolysis and the final product is xenon trioxide.

$$6\ XeF_4 + 12\ H_2O \longrightarrow 4\ Xe + 2\ XeO_3 + 24\ HF + 3\ O_2$$

2.7.3 Xenon hexafluoride, XeF_6

Preparation:

1. Xe and F_2 in the ratio 1 : 20 is heated to about 550 K at a pressure of 55 atmospheres in a nickel vessel.

$$Xe + 3\,F_2 \longrightarrow XeF_6$$

A quantitative yield can be expected at a low pressure and a high temperature of 970 – 1070 K in presence of a nickel filament.

XeF_6 is contaminated with XeF_4. This is removed by heating with NaF for about 2 hours at 373 K when XeF_6 forms an addition compound $2NaF.XeF_6$ while the others are unaffected. The addition compound decomposes at about 400 K to give pure XeF_6.

2. It is also prepared by the action of XeF_4 and O_2F_2 at 140 K.

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

Properties:

It is a crystalline solid. It melts at 323 K and the liquid is yellow.

It is the most volatile of xenon fluorides.

It is stable at room temperature and can be stored in nickel containers.

It reacts with silica and hence cannot be stored in glass vessels.

$$2\,XeF_6 + SiO_2 \longrightarrow 2\,XeOF_4 + SiF_4$$
$$2\,XeOF_4 + SiO_2 \longrightarrow 2\,XeO_2F_2 + SiF_4$$
$$2\,XeO_2F_2 + SiO_2 \longrightarrow 2\,XeO_3 + SiF_6$$

1. It dissolves in liquid HF and forms ions in solution, The solution is therefore conducting.

$$XeF_6 + HF \rightleftharpoons XeF_5^+ + HF_2^-$$

2. It is the most powerful fluorinating agent among the fluorides of xenon. It is a powerful oxidising agent.

$$XeF_6 + 3\,H_2 \longrightarrow Xe + 6\,HF$$
$$XeF_6 + 6\,HCl \longrightarrow Xe + 6\,HF + 3\,Cl_2$$
$$XeF_6 + 8NH_3 \longrightarrow Xe + N_2 + 6NH_4F$$

3. It reacts violently with water.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2\,HF$$
$$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2\,HF$$
$$XeO_2F_2 + H_2O \longrightarrow XeO_3 + 2\,HF$$

The final product XeO_3 is a highly explosive solid.

XeF_6 can act as a Lewis acid. It reacts with the heavier alkali fluorides to form seven-coordinate anion which rearranges to form eight–coordinate species.

$$MF + XeF_6 \longrightarrow M^+ (XeF_7)^- \quad (M = Na, K, Rb, Cs)$$

$$[M^+ (XeF_7)^-] \xrightarrow{heat} M_2(XeF_8) + XeF_6 \quad (M = Rb, Cs)$$

The octafluoroxenates are the most stable xenon compounds known and are stable up to 670 K.

2.8 OXIDES OF XENON

Two oxides of xenon are known namely XeO_3 and XeO_4.

2.8.1 Xenon trioxide, XeO_3

Preparation:

Xenon trioxide is obtained by the hydrolysis of xenon tetrafluoride or xenon hexafluoride. The solution on evaporation gives solid XeO_3.

$$6\,XeF_4 + 12\,H_2O \longrightarrow 2\,XeO_3 + 4\,Xe + 3\,O_2 + 24\,HF$$

$$XeF_6 + 3\,H_2O \longrightarrow XeO_3 + 6\,HF$$

Properties:

It is a non-volatile, highly explosive solid. Simple rubbing or pressing can detonate the solid.

It is stable in slightly acidic solution.

1. It dissolves in water and gives a weakly acidic solution.

$$XeO_3 + H_2O \longrightarrow \underset{\text{Xenic acid}}{H_2XeO_4}$$

2. In alkaline solutions it undergoes disproportionation.

$$4\,XeO_3 + 12\,OH^- \longrightarrow Xe + 3\,\underset{\text{Perxenate ion}}{XeO_6^{4-}} + 6\,H_2O$$

$$4\,XeO_3 + 12\,NaOH \longrightarrow Xe + 3\,\underset{\text{Sodium perxenate}}{Na_4XeO_6} + 6\,H_2O$$

3. It is a powerful oxidising agent, oxidises Mn(II) to Mn(VII) in strongly acidic solution.

2.8.2 Xenon tetraoxide, XeO_4

Preparation:

It is prepared from barium perxenate or sodium perxenate by reaction with anhydrous sulphuric acid.

$$Ba_2XeO_6 + 2\,H_2SO_4 \longrightarrow XeO_4 + 2\,BaSO_4 + 2\,H_2O$$

It is an unstable gas at room temperature. It explodes at a very low temperature of 233 K.

Table 2.4 : Structures of Some Xenon compounds

Compound	*Structure*
XeF_2	Linear
XeF_4	Square planar
XeF_6	Distorted octahedron
XeO_3	Pyramidal
XeO_4	Tetrahedral

2.9 BONDING IN XENON FLUORIDES AND OXIDES

The observed structures of the xenon compounds are given in Table 2.4.

XeF_2: XeF_2 is a linear molecule with Xe–F distance equal to 0.198 nm. On the basis of VB Theory, the simple explanation will be the promotion of an electron in xenon tom from 5p to 5d level. The unpaired electrons bond with two fluorine atoms. A total of 5 electrons pairs are present around the central xenon atom. A trigonal bipyramidal geometry with the three lone pairs occupying position is predicted. The two bond pairs occupy apical positions and the molecule thus is linear.

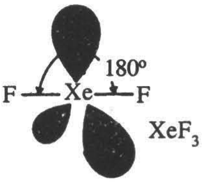
	5s	5p	5d
Ground state Configuration of Xe	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐
Excited state	↑↓	↑↓ ↑↓ ↑	↑ ☐ ☐ ☐

sp^3d hybridization and trigonal bipyramidal geometry

Serious objections were raised on two accounts —

(i) The energy required to promote 5p electron to 5d orbital is very large of the order of 1000 kJ.

(ii) The 5d orbital is too far away from the nucleus of the atom for effective overlap.



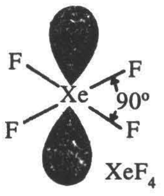
Linear molecule with three nonbonding electron pairs at the points of an equilateral triangle.

XeF_4: The molecule has a square planar structure with a Xe–F bond length of 0.195 nm. According to VB approach sp^3d^2 hybridization following promotion of two of the 5p electrons to 5d orbitals is predicted

Exicted electron configuration of xenon atom

5s	5p	5d
↑↓	↑↓ ↑ ↑	↑ ↑ ☐ ☐

Two lone pairs of electrons occupy the two opposite corners of an octahedron and a square (octahedral) structure is thus explained.



Square planar molecule with two nonbounding electron pairs, one above and one below the plane of the molecule

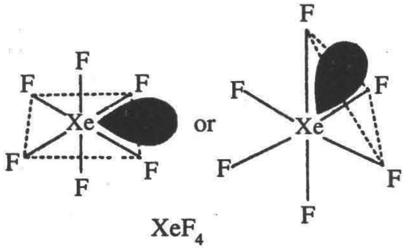
The same objections as in the case of XeF_2 is raised in this case.

XeF_6: XeF_6 has a distorted octahedron structure. The bonding in this compound has been controversial which has not been understood completely. The VB approach predicts sp^3d^3 hybridization.

Exicted electron configuration of xenon atom

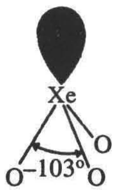
5s	5p	5d
↑↓	↑ ↑ ↑	↑ ↑ ↑ ☐

The six unpaired electrons bonding with six fluorine atoms give an octahedral structure with the lone pair of electrons forming a cap on the octahedron. A distorted octahedron is the shape of the molecule which is in good agreement with the observed structure.



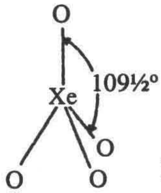
XeF_4

Distorted octahedron with a nonbonding electron pair either at the centre of a face or the midpoint of an edge.



XeO_3

Trigonal pyramidal molecule with a nonbonding electron pair protruding from the apex of the pyramid



XeO_4

Perfect tetrahedron

XeO_3: The structure of the molecule is trigonal pyramid with Xe–O bond length being 0.176 nm. This is in accordance with VB theory which predicts a tetrahedron with one of the corners being occupied by a lone pair. O–Xe–O bond angle is observed to be 103°.

XeO_4: A regular tetrahedron as predicted by the VB theory is the structure of the molecule.

IMPORTANT POINTS

- Helium, neon, argon, krypton, xenon and radon comprise the noble gases and belong to group 18 of the periodic table
- Noble gases enter into very few chemical reactions. Their chemical inertness is related to their highly stable octet configuration.
- The noble gases except radon occur as minor constituents in the atmosphere.
- Radon is radioactive and is a disintegration product of radium.
- Argon was the first noble gas to be discovered in 1894 by Lord Rayleigh.

- Helium was discovered in the sun's chromosphere in 1868 by Normal Lockyer. Helium is also present occluded in radioactive minerals like clevite, monazite, pitchblende, etc.,
- Atmospheric air is the only source for the gases Ne, Ar, Kr and Xe.
- Nitrogen fraction of liquid air contains the more volatile He and Ne. Oxygen fraction of liquid air contains Ar, Kr and Xe.
- The various gases are separated by fractional distillation
- Helium is present in the natural gas to the extent of 7%. After the removal of CO_2, the gas is liquefied to remove hydrocarbons. The residual gas is compressed and cooled when all gases except He liquefies. It is further purified by passing over activated charcoal.
- Neon has a characteristic red glow and used in neon lamps; used for filling voltage stabilisers, in photoelectric cells etc.,
- Argon is used to provide inert atmosphere for metallurgical operations, for filling voltage stabilisers, in photoelectric cells etc.
- Krypton is used in colour display lamps and in high efficiency filament lamps.
- Xenon is used in high intensity photographic flash tubes.
- Radon is used in radiotherapy for the treatment of cancer.
- Xenon forms XeF_2, XeF_4 and XeF_6.
- XeF_2 can be obtained either by direct fluorination or by reaction with dioxygen difluoride.
- XeF_2 is the least volatile fluorides of xenon and can be stored indefinitely in silica, nickel or monel containers.
- XeF_2 is soluble in liquid HF. It undergoes slow hydrolysis in water.
- XeF_2 is a strong oxidising and fluorinating agent.
- XeF_2 is a linear molecule with Xe–F bond distance equal to 0.198 nm. Xe is sp^3d^2 hybridised with a trigonal bipyramidal geometry.
- XeF_4 is obtained by direct fluorination of Xe or by reaction with dioxygen diflouride at low temperature.
- XeF_4 is soluble in liquid HF. It reacts violently with water and the final product of hydrolysis is XeO_3.
- XeF_4 is a fairly strong fluorinating and oxidising agent.
- XeF_4 has a square planar structure with a Xe–F bond length 0.195 nm Xe is sp^3d^2 hybridized with octahedral geometry. Two lone pairs occupy two opposite corners of octahedron.
- XeF_6 is obtained by heating a mixture of Xe and F_2 in the ratio 1 : 20 at a high pressure or by reaction with dioxygen difluoride at a very low temperature.
- XeF_6 is the most volatile of xenon fluorides. It cannot be stored in glass container as it reacts with silica.
- The solution of XeF_6 in liquid HF is conducting as it forms ions in solution.
- XeF_6 is a powerful oxidising agent and the most powerful fluorinating agent.

- XeF_6 reacts violently with water forming XeO_3.
- XeF_6 can act at a Lewis acid and forms stable octafluoroxenates with heavier alkali fluorides.
- XeF_6 has a distorted octahedral structure. Xe is in sp^3d^3 hybridisation.
- XeO_3 is obtained by the hydrolysis of XeF_4 or XeF_6.
- XeO_3 is a nonvolatile highly explosive solid.
- XeO_3 dissolves in water to form a weak acid, xenic acid.
- XeO_3 disproportionates in alkaline solution.
- XeO_3 is a powerful oxidising agent.
- XeO_3 has trigonal pyramid structure with Xe–O bond length being 0.176 nm. Xe is sp^3 hybridised. O–Xe–O bond angle is 103°.
- XeO_4 is an unstable gas, exploding even at a low temperature. It is prepared by reaction of anhydrous H_2SO_4 with barium perxenate or sodium perxenate.
- XeO_4 has a regular tetrahedron structure.

EXERCISE

Short Answer Type Questions:

1. Periodic table was incomplete before the discovery of noble gases. Comment.
2. What are noble gases? Why is the earlier name – 'inert gases' not appropriate?
3. (a) Which noble gas is obtained from radioactive disintegration?
   (b) Which noble gas is relatively more abundant in the atmosphere?
4. How was argon discovered?
5. How is helium isolated from natural gas?
6. How are the noble gases distributed in the two fractions of liquid air?
7. Give the important uses of helium
8. Helium–oxygen mixture is used in diving apparatus? Why?
9. Name the inert gases used in the following —
   (a) in nuclear reactors.
   (b) to provide inert atmosphere in metallurgical welding.
   (c) in radiotherapy.
10. All noble gases are monoatomic molecules and chemically inert. Give reasons.
11. While fluorides of xenon and krypton are known, similar compounds of helium and argon are not known, why?
12. How is XeF_2 prepared? How is it separated from XeF_4?
13. How does XeF_4 react with KI?
14. Write a note on the fluorinating reactions of XeF_2
15. How is pure XeF_4 prepared? How does it react with water?
16. How is XeF_6 prepared and separated from XeF_4?
17. Both XeF_4 and XeF_6 dissolve in liquid HF. While the solution of XeF_6 in HF in conducting the other is not — explain.

18. Why is the reaction of XeF_6 with water dangerous?
19. How are oxides of Xe prepared?
20. Discuss the structure of XeF_2.
21. Discuss the bonding in XeF_2, XeF_4 and XeF_6 in the light of VB theory.

Essay Type Questions:

1. Write a note on the chemical inertness of noble gases in the light of electron configuration, ionization energy and electron affinity.
2. Write a brief note on the discovery of Ar, He and Ne.
3. How are noble gases isolated from the fractions of liquid air?
4. How is argon isolated from liquid air?
5. How is neon isolated from liquid air?
6. Give the important uses (a) He, (b) Ne and (c) Ar.
7. Name the different fluorides of xenon known so far. Briefly discuss their behaviour as oxidising and fluorinating agents.
8. How does XeO_3 react with (i) water (ii) alkali?
9. Explain the structures of XeF_2 and XeF_4 on the basis of VB theory. What were the objections raised?
10. Explain the structure of XeF_6 on the basis of VB.

❖ ❖ ❖

Chapter 3

Compounds of Non-Metals

SYLLABUS

3.1 COMPOUNDS OF BORON

Boron is the first member of Group 13 elements. It is a non–metal and forms only covalent compounds. It exhibits an oxidation state +3 in all its compounds. The electron configuration of boron is ns^2np^1 and boron is said to form three covalent bonds using sp^2 hybrid orbitals. The compounds of boron are electron deficient and accept a pair of electrons (Lewis acids). The bonding in certain boron compounds is of considerable theoretical interest.

3.2 BORON TRIFLUORIDE BF_3

Boron forms trihalides with all the four halogens. Boron trifluoride is the most important halide of boron.

3.2.1 Preparation

1. It is prepared by heating a mixture of boron trioxide, calcium fluoride and concentrated sulphuric acid (Borax can be used in place of boron trioxide)

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \xrightarrow{\text{heat}} 3CaSO_4 + 3H_2O + 2BF_3\uparrow$$

$$Na_2B_4O_7 + 3CaF_2 + 8H_2SO_4 \xrightarrow{\text{heat}} 6CaSO_4 + 7H_2O + 2NaHSO_4 + 4BF_3\uparrow$$

BF_3 passes out as a colourless gas and is collected over mercury. (It is highly soluble in water).

2. It is prepared by heating together boron trioxide and ammonium fluoborate

$$B_2O_3 + 6NH_4BF_4 \xrightarrow{\text{heat}} 8BF_3 + 6NH_3 + 3H_2O$$

3.2.2 Properties

It is a colourless gas with pungent smell

It boils at –101°C.

It fumes strongly in moist air. It is highly soluble in water and forms two hydrates BF_3H_2O and BF_32H_2O.

The solution hydrolyses forming boric acid and hydrofluoric acid.

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

If excess boron trifluoride be passed it dissolves in hydrofluoric acid formed; hydrofluoboric acid is obtained.

$$BF_3 + HF \longrightarrow \underset{\text{Hydrofluoboric acid}}{H(BF_4)}$$

Boron is tetracovalent in this acid.

Since boron in boron trifluoride has only six electrons in its outer shell, it is an electron deficient compound. It can accept a pair of electrons i.e., behaves as a Lewis acid. For example,

with ammonia $F_3B + :NH_3 \longrightarrow F_3B \leftarrow NH_3$

with hydrogen sulphide $F_3B + :SH_2 \longrightarrow F_3B \leftarrow SH_2$

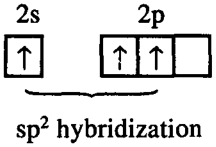
with fluoride ion $F_3B + :F^- \longrightarrow [F_3B \leftarrow F]^-$ or $[BF_4]^-$

This tendency of BF_3 to accept a pair of electrons makes it a good catalyst in a number of organic reactions like alkylation, ester formation etc. The complex with ethers is used for this purpose. $(C_2H_5)_2O \rightarrow BF_3$, a viscous liquid and $(CH_3)_2O \rightarrow BF_3$, a colourless liquid boiling at 126°C are commercially available.

3.2.3 Structure

The shape of boron trifluoride molecule is planar triangle with bond angles 120°. VSEPR theory predicts sp^2 hybridization of boron atom and a planar triangle shape.

Electronic configuration of boron atom
(excited state)

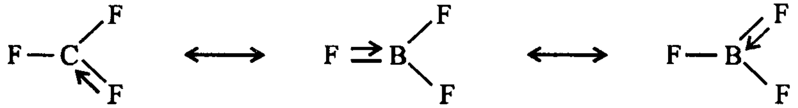


The three sp^2 hybrid orbitals overlap with 2p orbitals of three fluorine atoms to form BF_3.

The B–F bond length is 0.130 nm and the bond energy is 646 $kJmol^{-1}$.

The bond length is shorter than expected from the covalent radii of boron and fluorine atoms; also, the bond energy is unexpectedly higher for a single bond. Besides the strength as a Lewis acid is the least in BF_3 which again is not the order expected according to the relative electronegativity of the halogen atoms.

These observations can be explained in terms of $p\pi - p\pi$ interaction. The empty p_z orbital of B not involved in hybridization is perpendicular to the plane of the molecule. This can accept a pair of electrons from a complete p orbital on any one of the fluorine atoms and a lateral overlap is possible. A dative π bond is formed resulting in an octet of electrons around boron atom. An additional $p\pi - p\pi$ bond is formed between boron and fluorine atoms giving rise to a double bond character. Since the three B – F bond lengths are identical, a resonance exists as shown.



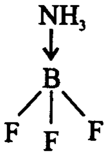
The molecule is a resonance hybrid of the above three structures. This type of bond formation is known as *back–bonding.*

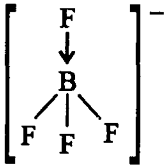
The modern explanation is that the double bond is delocalised. The unhybridized p_z orbital of boron atom and three p_z orbitals from the three fluorine atoms form a four centre π molecular orbital covering all the four atoms containing two bonding electrons.

The electron deficiency of boron is compensated and hence the Lewis acid character of BF_3 is decreased.

This tendency to form $p\pi - p\pi$ bond is much less in BCl_3 and still less in BBr_3. This is probably due to the poor overlap of $2p_z$ orbital of boron with $3p_z$ (or $4p_z$) orbitals of chlorine (or bromine) due to appreciable difference in their energy levels.

In presence of electron donor molecules like ether, ammonia, fluoride ion etc., the $2p_z$ orbital of boron atom in BF_3 gets filled and a tetrahedral molecule or ion is formed. For example,





Once such a tetrahedral complex is formed the possibility of π bonding no longer exists. The B–F bond distance in such complexes is 0.139 nm, longer than 0.130 nm in BF_3.

3.3 BORAZOLE OR BORAZINE $B_3N_3H_6$

Borazole or borazine is sometimes called 'inorganic benzene because of its superficial resemblance to benzene.

3.3.1 Preparation

It is prepared by heating boron trichloride and ammonium chloride and then reducing the B-trichloroborazine with sodium borohydride.

$$3BCl_3 + 3NH_4Cl \xrightarrow{150^0C} B_3N_3H_3Cl_3 \xrightarrow[\text{NaBH}_4 \text{ in ether}]{\text{reduction}} B_3N_3H_6$$

3.3.2 Properties

Borazine is a colourless liquid, boiling at 55° C. It decomposes slowly on standing. It has an aromatic odour.

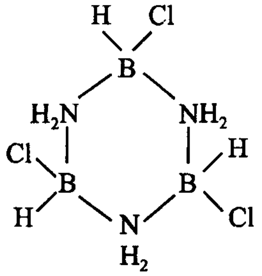
Borazine is much more reactive than benzene. Unlike in benzene (C–C) the B–N bond is polar and is hence more reactive.

It readily adds on 3 molecules of hydrogen chloride.

$$B_3N_3H_6 + 3HCl \longrightarrow B_3N_3Cl_3H_9$$

The negative chlorine group is attached to boron.

Similar addition reactions are possible with water, methanol, etc., but the products being unstable the ring breaks up completely.

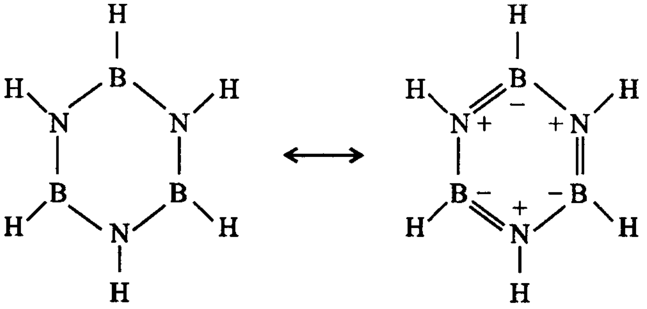


It undergoes hydrolysis with water at high temperature.

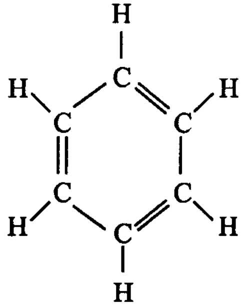
$$B_3N_3H_6 + 9H_2O \longrightarrow \underset{[H_3BO_3]}{3B(OH)_3} + 3NH_3 + 3H_2$$

3.3.3 Structure

A boron atom has 3 valence electrons and a nitrogen atom has 5 valence electrons which add up to 8 valence electrons just as in two adjacent carbon atoms in graphite. The structure of borazine is very similar to that of benzene with a planar hexagon Each B–N bond length is 0.144 nm.



Borazine Borazine



Benzene

According to the valence bond theory, borazine is a resonance hybrid of the two structures shown below. In terms of orbital theory, delocalisation of lone pairs of electrons on the nitrogen atom takes place. The compound has aromatic character.

3.4 BORON HYDRIDES

Though boron and the other elements of group III do not directly react with hydrogen, a number of interesting hydrides of boron are known. By analogy with the alkanes they are sometimes referred to as *boranes*. As many as 20 boranes have been reported and about 11 of them are well characterized. The boranes are classified into two series of boranes namely *nidoboranes* and *arachnoboranes*.

Nidoboranes have the general formula B_nH_{n+4}. Diborane B_2H_6, Pentaborane– 9 B_5H_9, hexaborane–10 B_6H_{10} belong to this series.

The *arachnoboranes* are relatively less stable and have the general formula B_nH_{n+6}. Tetraborane B_4H_{10}, Pentaborane–11 B_5H_{11}, hexaborane–12 B_6H_{12} belong in this series.

Diborane is the simplest and extensively studied borane.

3.5 DIBORANE B_2H_6

Boranes were first prepared by Alfred Stock by heating magnesium with boron to obtain magnesium boride. Magnesium boride by reaction with orthophosphoric acid gave a mixture of boranes. This method has now been replaced by other methods as a lot of difficulties are encountered in the separation of the mixture.

3.5.1 Preparation

A number of methods are available for the preparation of diborane.

1. By reducing the etherate complexes of the boron halides by $Li[AlH_4]$.

$$4(Et_2O.BF_3) + 3Li[AlH_4] \xrightarrow{\text{ether}} 2B_2H_6 + 3Li[AlF_4] + 4Et_2O$$

[**Note:** Et_2O is diethyl ether $C_2H_5OC_2H_5$]

2. By reacting sodium borohydride $Na[BH_4]$ and iodine in the solvent diglyme.

$$2Na[BH_4] + I_2 \xrightarrow{\text{diglyme}} B_2H_6 + H_2 + 2NaI$$

[**Note:** Diglyme is a polyether $CH_3OC_2H_4OC_2H_4OCH_3$]

3. By careful addition of sodium borohydride to concentrated sulphuric or phosphoric acid.

$$2Na[BH_4] + H_2SO_4 \longrightarrow B_2H_6 + 2Na_2SO_4 + 2H_2$$

Reactions 1, 2, 3 are convenient laboratory preparations.

4. By reduction of BCl_3 with $Li[AlH_4]$

$$4BCl_3 + 3Li[AlH_4] \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

5. By the action of BF_3 on lithium hydride in ether medium.

$$8BF_3 + 6LiH \longrightarrow 6LiBF_4 + B_2H_6$$

This is a useful large scale method of preparation.

6. Another industrial method of preparation consists in the reduction of boron trioxide with Al and H_2 at high pressure. Anhydrous $AlCl_3$ is used as a catalyst.

$$B_2O_3 + 2Al + 3H_2 \longrightarrow B_2H_6 + Al_2O_3$$

7. A particularly useful method of preparing diborane *in situ*, is by reduction of BF_3 with $Na[BH_4]$ in diglyme.

$$4[Et_2O.BF_3] + 3[NaBH_4] \xrightarrow{\text{diglyme}} 2B_2H_6 + 3Na[BF_4] + 4Et_2O$$

3.5.2 Properties

It is a colourless gas with a boiling point −93° C.

It is stable at low temperatures when dry.

1. It catches fire spontaneously in air and explodes with oxygen. The reaction is highly exothermic.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \qquad \Delta H = -2165\text{ kJ}$$

It needs to be handled very carefully. It reacts with stopcock grease and hence special taps need to be used.

2. It is rapidly hydrolysed by water or alkali at 0°C.

$$B_2H_6 + 6H_2O \longrightarrow \underset{\text{Boric acid}}{2H_3BO_3} + 3H_2$$

$$B_2H_6 + 2KOH + 6H_2O \longrightarrow \underset{\text{Potassium metaborate}}{2KBO_2} + 6H_2$$

3. It readily reacts with ammonia and the product formed depends on reaction conditions.

$$B_2H_6 + 2NH_3 \xrightarrow{\text{low temp}} B_2H_62NH_3 \text{ or } [H_2B(NH_3)_2][BH_4]$$

diammoniate of diborane

$$3B_2H_6 + 6NH_3 \xrightarrow{\text{high temp}} \underset{\text{borazole}}{2B_3N_3H_6} + 12H_2$$

4. It forms sodium borohydride by reaction with sodium amalgum or sodium hydride in ether.

$$B_2H_6 + 2NaH \longrightarrow 2Na[BH_4]$$

5. It reacts with chlorine at room temperature to give BCl_3.

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

6. It reacts with hydrogen halides in presence of corresponding aluminium halides to give halodiborane.

$$B_2H_6 + HCl \longrightarrow \underset{\text{chlorodiborane}}{B_2H_5Cl} + H_2$$

7. It reacts with CO to form borane carbonyl

$$B_2H_6 + 2CO \xrightarrow{20\text{ atm, }200^\circ\text{C}} 2H_3BCO$$

8. Heating of diborane results in the formation of higher boranes. Depending on the conditions, the boranes formed is different.

$$B_2H_6 \xrightarrow[200\ \text{atm}]{80\text{–}90^\circ\text{C}} B_4H_{10}$$

$$B_2H_6 \xrightarrow[200\text{–}250^\circ\text{C}]{\text{rapid}} B_5H_9$$

$$B_2H_6 \xrightarrow[\text{tube at } 150^\circ\text{ C}]{\text{slow pyrolysis in a}} B_{10}H_{14}$$

A number of reactions of borane are of importance in organic synthesis.

3.5.3 Structure

The bonding and structures of boranes are of great interest as they are different from all other hydrides. As there are not enough valency electrons to form conventional two electron bonds between all of the adjacent pairs of atoms, these compounds are *electron deficient compounds*.

The structure of diborane is found to be as shown (Fig. 3.1) by electron diffraction studies.

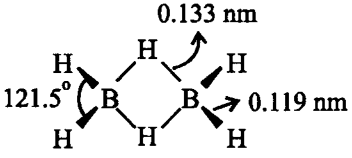


Fig. 3.1: Structure of diborane

The four hydrogen atoms two each on the left and the right are called *terminal hydrogen* atoms; the other two hydrogen atoms are the *bridging atoms*.

1. The four terminal and the two boron atoms lie in the same plane. The two bridging H atoms are in a plane perpendicular to the rest of the molecule. The rotation between the two B atoms is thus prevented.
2. The B–H bond length of the terminal H atoms correspond to the expected normal value. These four bonds are thus assumed to be normal covalent bonds with a pair of electrons being shared between two atoms.
3. Four of the H atoms in diborane are different from the other two which is confirmed by Raman spectra. Also diborane cannot be methylated beyond $(CH_3)_4B_2H_2$ without breaking the molecule.

The above evidences go to show that the electron deficiency is associated with the bridge groups. A simple orbital description is as follows:

Two BH_2 units are formed by the overlap between 1s orbital of a hydrogen atom with roughly sp^3 hybridised orbitals of boron. Two sp^3 hybrid orbitals of B are used for the two terminal B–H bonds. The two BH_2 units are brought closer such that all the six atoms lie in the same plane. A hydrogen atom placed in between the two BH_2 units and above the plane will result in an overlap of two sp^3 hybrid orbitals of boron atoms (one from each boron atom) and the 1s orbital of hydrogen atom. A delocalized molecular orbital covering all three nuclei (BHB) containing one pair of electrons is formed. This is a three–centre two–electron (3c–2e) bond and makes up one of the bridges. A similar three centre bond is formed with the other atom.

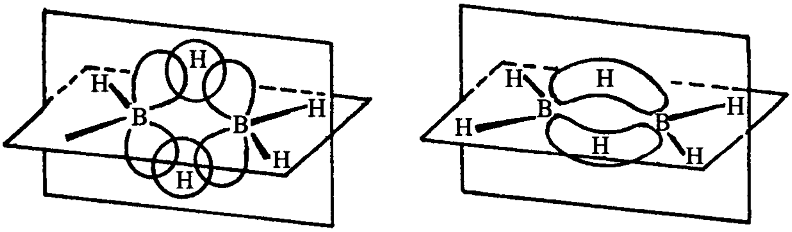


Fig. 3.2: Overlap of sp^3 hybrid orbitals from B with an s orbital from H to give a banana shaped three centre two-electron bond

The *three-centre-two-electron* bond is not as strong as the conventional covalent bond. The shape of the bond is that of a "banana" and hence called a *banana bond.* In diborane two such bonds exists.

3.6 COMPOUNDS OF NITROGEN

Nitrogen is the first member of group 15 elements. The elements in this group have an outer electronic configuration ns^2np^3. The maximum oxidation state of +5 is shown towards oxygen in forming bonds. Nitrogen is a nonmetal and chemically inert. The inertness is attributed to the extreme stability of the molecule. A triple bond exists between the two nitrogen atoms and the bond energy is 940 $kJmol^{-1}$. Nitrogen, unlike the other elements of this groups exhibits a wide range of oxidation states –3 to +5.

3.6.1 Halides of Nitrogen

Nitrogen forms several hydrides of which ammonia is very important. The other hydrides are – hydrazine N_2H_4, hydroxylamine NH_2OH, hydrogen azide HN_3 (or hydrazoic acid)

3.7 HYDRAZINE N_2H_4 (NH_2NH_2)

3.7.1 Preparation

Hydrazine is manufactured by the Raschig process (1907). Hydrazine is obtained by the careful oxidation of ammonia by sodium hypochlorite in aqueous solution. The reaction takes place in two stages.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$

$$2NH_3 + NH_2Cl \longrightarrow NH_2NH_2 + NH_4Cl$$

A side reaction between chloramine and hydrazine needs to be avoided which is catalysed by heavy metal ions.

$$2NH_2Cl + NH_2NH_2 \longrightarrow N_2 + 2NH_4Cl$$

This is achieved using distilled water and adding about 1% glue or gelatin which inhibits the action of heavy metal ions present in solution.

The reactants are mixed at a low temperature along with glue and then heated rapidly. It is kept boiling for sometime. A dilute solution of hydrazine is obtained which can be concentrated by distillation. Alternately, the solution is reacted with dilute sulphuric acid, when hydrazine sulphate $N_2H_4.H_2SO_4$ precipitates out. The crystals of hydrazine sulphate are distilled with an alkali under reduced pressure when hydrate distills over.

$$NH_2NH_2 + H_2SO_4 \longrightarrow \downarrow N_2H_4.H_2SO_4$$

hydrazine sulphate

$$N_2H_4H_2SO_4 + NaOH \longrightarrow NaHSO_4 + N_2H_4.H_2O$$

The liquid is distilled over barium oxide or solid NaOH to obtain anhydrous hydrazine.

$$N_2H_4 \cdot H_2O + BaO \longrightarrow N_2H_4 + Ba(OH)_2$$

3.7.2 Properties

It is a colourless liquid fuming in moist air.

It boils at 114°C and freezes at 2°C.

It has a pungent odour similar to ammonia.

It is soluble in water, alcohol.

1. It burns in air readily with evolution of a large amount of heat.

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O \qquad \Delta H = -621 \text{ kJ}$$

Hydrazine as well as its methyl derivatives have been used as a rocket fuel in the space shuttle, in guided missiles etc.,

2. It decomposes explosively on heating

$$3N_2H_4 \longrightarrow N_2 + 4NH_3$$

3. It is a weak base and can form two series of salts with acids. With halogen hydrides, for example

$$N_2H_4 + HX \longrightarrow N_2H_5^+ + X^-$$

$$N_2H_4 + 2HX \longrightarrow N_2H_6^{2+} + 2X^-$$

They act as Lewis bases which is related to the presence of lone pair of electrons on each nitrogen atom.

4. Hydrazine and its salts are powerful reducing agents. Hydrazine is oxidised to nitrogen.

(a) It reacts with halogens violently reducing them to corresponding halogen acids

$$NH_2NH_2 + 2X_2 \longrightarrow N_2 + 4HX$$

The reaction with iodine is used for the estimation of hydrazine.

(b) Salts of gold, silver and platinum are reduced to the respective metals.

$$N_2H_4 + PtCl_4 \longrightarrow N_2 + Pt\downarrow + 4HCl$$

$$3N_2H_4 + 4Au^{3+} \longrightarrow 4Au\downarrow + 3N_2 + 12H^+$$

$$N_2H_4 + 4Ag^+ + 4OH^- \longrightarrow N_2 + 4Ag\downarrow + 4H_2O$$

The reaction is used to obtain silver mirror.

(c) It reduces cupric salts to cuprous salts, ferric salts to ferrous salts etc.,

$$3N_2H_4 + 4Cu^{2+} \longrightarrow 4Cu^+ + 4H^+ + N_2$$

$$N_2H_4 + 4CuO \longrightarrow \underset{\text{red}}{2Cu_2O} + N_2 + 2H_2O$$

(d) Acidified permanganate solutions are decolourised.

$$5N_2H_4 + 4KMnO_4 + 6H_2SO_4 \longrightarrow 4MnSO_4 + 2K_2SO_4 + 5N_2 + 16H_2O$$

5. It undergoes condensation reaction with carbonyl compounds forming hydrazones.

$$NH_2N\boxed{H_2 + O}HC.C_6H_5 \longrightarrow NH_2N = HC.C_6H_5 + H_2O$$

6. It reacts with sodium in an inert atmosphere to form sodium hydrazide

$$2NH_2NH_2 + 2Na \longrightarrow \underset{\text{sodium hydrazide}}{2NH_2.NHNa} + H_2$$

7. In acidic solutions it may be reduced by more powerful reducing agents to ammonia.

$$N_2H_4 + Zn + 2HCl \longrightarrow 2NH_3 + ZnCl_2$$

3.7.3 Structure

The molecule has an unsymmetrical structure with a dipole moment 1.85D, the N–N bond length of 0.145 nm and the N–H bond length is 0.102 nm. Each nitrogen is tetrahedrally surrounded by one N atom, two H atoms and a lone pair of electrons. The two halves of the molecule is rotated 95° about the N–N bond and a gauche (semi–eclipsed) confirmation is adopted. There is no free rotation of the $-NH_2$ groups.

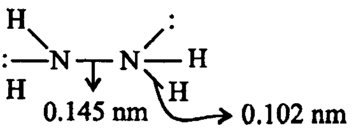


Fig. 3.3: Structure of hydrazine

3.8 HYDROXYLAMINE NH_2OH

Hydroxylamine is prepared in large quantities to make cyclohexanone oxime which is converted to caprolactam which is polymerised to give nylon–6. It was first prepared by Lossen in 1895.

3.8.1 Preparation

There are several methods available for the preparation of hydroxylamine.

1. By reduction of nitric oxide with nascent hydrogen

$$NO + 3[H] \longrightarrow NH_2OH$$

Nitric oxide is passed through a mixture of tin and concentrated hydrochloric acid. Hydroxylamine hydrochloride is present in solution. The excess tin is removed as sulphide by passing hydrogen sulphide. The solution is evaporated to dryness. The solid is distilled with sodium methoxide in methanol to obtain free hydroxylamine.

$$NH_2OH\ HCl + NaOCH_3 \longrightarrow NH_2OH + NaCl + CH_3OH$$

Sodium chloride is filtered off and methanol separated by distillation under reduced pressure.

2. By the reduction of nitrous acid – Through a concentrated solution of sodium nitrite and sodium carbonate, sulphur dioxide gas is passed till just acidic.

$$HONO + 2H_2SO_3 \longrightarrow HO.N(SO_3H)_2 + H_2O$$

Sodium salt of hydroxylamine disulphonic acid is produced. On warming the above solution with dilute sulphuric acid to 80°C, hydroxylammonium bisulphate is formed following hydrolysis.

$$HON(SO_3Na)_2 + 2H_2O \longrightarrow H_3N(OH)HSO_4 + Na_2SO_4$$

Baryta water is added to obtain free hydroxylamine. $BaSO_4$ is precipitated which is filtered off.

$$H_3N(OH)HSO_4 + Ba(OH)_2 \longrightarrow NH_2OH + BaSO_4\downarrow + 2H_2O$$

3. By electrolytic reduction of nitric acid

A well cooled mixture of 50% HNO_3 and 50% H_2SO_4 is electrolysed using amalgamated lead electrodes. The electrolyte is continuously kept cooled in ice.

$$HNO_3 + 2H \longrightarrow HNO_2 + H_2O$$
$$HNO_2 + 4H \longrightarrow NH_2OH + H_2O$$

Hydroxylamine sulphate formed is treated with baryta solution to obtain free hydroxylamine.

$$(NH_2OH)_2\ H_2SO_4 + Ba(OH)_2 \longrightarrow 2NH_2OH + BaSO_4\downarrow + 2H_2O$$

4. By the reduction of dinitrogen tetroxide in hydrochloric acid solution by hydrogen in presence of a platinised charcoal catalyst.

$$N_2O_4 + 5H_2 \xrightarrow{\text{in HCl}} 2NH_2OH + 2H_2O$$

5. By the action of concentrated sulphuric acid on nitromethane at 120° C.

$$CH_3NO_2 + H_2SO_4 \xrightarrow{\text{reflux}} [NH_3OH]^+\ HSO_4^- + CO$$

Hydroxylamine sulphate is converted to chloride by reaction with concentrated hydrochloric acid. The anhydrous hydroxylamine is then obtained as discussed in method 1.

6. By reduction of ethylnitrate with nascent hydrogen.

$$C_2H_5NO_3 + 6H \xrightarrow{\text{Sn/HCl}} NH_2OH + C_2H_5OH + H_2O$$

3.8.2 Properties

Hydroxylamine is a white crystalline solid. It melts at 33° C. It deliquesces in air.

1. It is thermally unstable and decomposes into NH_3, N_2, N_2O and HNO_2 easily. It explodes if heated strongly.

$$3NH_2OH \xrightarrow[\Delta]{} N_2 + NH_3 + 3H_2O$$

[It is generally stored at very low temperature]

2. It is soluble in water, alcohol and ether.

The aqueous solution is weakly basic, weaker than ammonia or hydrazine.

$$NH_2OH + H_2O \rightleftharpoons \underset{\text{hydroxyl ammonium ion}}{[NH_3OH]^+ + OH^-}$$

It disproportionates slowly in acidic solutions.

$$4[NH_2OHH]^+ \rightleftharpoons N_2O + 2NH_4^+ + 2H^+ + 3H_2O$$

and rapidly in alkalis

$$3NH_2OH \longrightarrow N_2 + NH_3 + 3H_2O$$

3. With acids it forms salts which are more stable than hydroxylamine itself.

$$NH_2OH + HCl \longrightarrow [NH_3OH]^+ Cl^-$$

$$NH_2OH + H_2SO_4 \longrightarrow [NH_3OH]^+ HSO_4^-$$

4. In solution it is a powerful reducing agent. It is oxidised to nitrous oxide.

(a) Fehling's solution is reduced to a red precipitate of cuprous oxide

$$2NH_2OH + 4CuO \longrightarrow N_2O + 2Cu_2O + 3H_2O$$

(b) Ferric chloride is reduced to ferrous chloride

$$2NH_2OH + 4FeCl_3 \longrightarrow N_2O + 4FeCl_2 + 4HCl + H_2O$$

(c) Halogens are reduced to corresponding hydracids explosively

$$2NH_2OH + 2Cl_2 \longrightarrow N_2O + H_2O + 4HCl$$

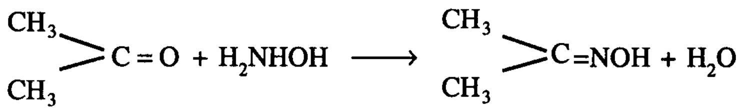
(d) Bromates and iodates are reduced to bromides and iodides respectively.

$$12NH_2OH + 4NaBrO_3 \longrightarrow 4NaBr + 3O_2 + 6N_2 + 18H_2O$$

5. In alkaline medium, it acts as an oxidising agent, for example, ferrous salts are oxidised to ferric salts.

$$NH_2OH + 2Fe(OH)_2 + H_2O \longrightarrow 2Fe(OH)_3 + NH_3$$

6. With carbonyl compounds, it undergoes condensation reaction to form oximes.



$$(CH_3)_2C{=}O + H_2NHOH \longrightarrow (CH_3)_2C{=}NOH + H_2O$$

acetoxime

The oximes are important compounds.

7. It acts as a Lewis base like ammonia and hydrazine. It forms coordinate bonds with metals.

3.8.3 Structure

From X ray and IR studies, the following data are available

N – O bond length is 0.147 nm.

O – H bond length is 0.096 nm.

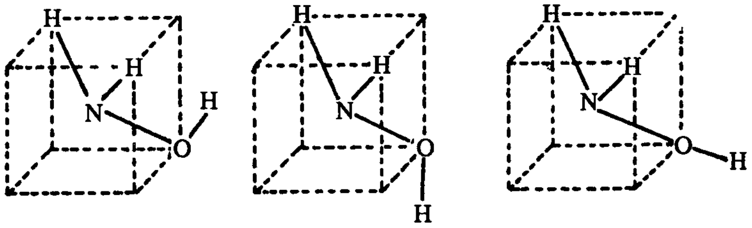
N – H bond length is 0.101 nm.

.HON bond angle is 103°.

HNH bond angle is 107°.

HNO bond angle is 150°.

Hydroxylamine exists in cis–, trans– and various gauche– transformations.



cis trans gauche

Fig. 3.4: Structure of hydroxylamine

The different conformations arise due to varying degrees of rotation of OH group and the N–O bond.

3.9 HYDROGEN AZIDE HN_3

This was earlier known as hydrazoic acid. Unlike ammonia and hydroxylamine, it is acidic in nature.

3.9.1 Preparation

1. The most important method of preparation of hydrogen azide is by passing nitrous oxide gas into fused sodamide at 190° C under anhydrous conditions.

$$N_2O + 2NaNH_2 \xrightarrow[\text{dry}]{190^\circ\text{C}} NaN_3 + NH_3 + NaOH$$

The sodium azide is treated with sulphuric acid followed by careful distillation.

[Sodamide for the above reaction is obtained by reaction of dry ammonia over heated sodium]

2. It is also prepared by the careful oxidation of hydroxylamine with hydrogen peroxide or nitric acid.

$$3N_2H_4 + 5(O) \xrightarrow[\text{or } HNO_3]{H_2O_2} 2HN_3 + 5H_2O$$

3. Anhydrous hydrogen azide is obtained by dropping 2 : 1 sulphuric acid on dry potassium azide.

$$2KN_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HN_3$$

3.9.2 Properties

It is a colourless volatile liquid with a highly irritating odour.

It boils at 37°C.

It is poisonous in nature.

1. Both in liquid and gaseous phase it explodes on heating or when subjected to a shock.

$$2HN_3 \longrightarrow 3N_2 + H_2$$

2. It is highly soluble in water and the solution is a little more stable than the compound itself.

It undergoes ionization in water and the solution is weakly acidic.

$$HN_3 \rightleftharpoons H^+ + N_3^-$$

The solution has pK_a 4.75 which is comparable to that of acetic acid.

3. It reacts with electropositive metals like Zn, Mg etc., forming salts called azides.

$$2HN_3 + Mg \longrightarrow Mg(N_3)_2 + H_2$$
$$3HN_3 + Zn \longrightarrow Zn(N_3)_2 + NH_3 + N_2$$
$$3HN_3 + 2Li \longrightarrow 2LiN_3 + NH_3 + N_2$$
$$3HN_3 + Cu \longrightarrow Cu(N_3)_2 + NH_3 + N_2$$

Unlike other acids + metal reactions, no hydrogen is evolved (Mg is an exception).

The azides of heavy metals like Pb, Ag, Hg are explosives and are used as detonator to set off a high explosive charge.

The azides of alkali metals, on the other hand, do not explode but decompose quietly on heating.

$$3LiN_3 \xrightarrow{heat} Li_3N + 4N_2$$
$$2NaN_3 \xrightarrow{heat} 2Na + 3N_2$$

4. It reacts with bases like ammonia and hydrazine to form colourless crystals.

$$HN_3 + NH_3 \longrightarrow NH_4N_3$$
$$HN_3 + N_2H_4 \longrightarrow N_2H_5N_3$$

5. It is reduced to ammonia or hydrazine in presence of sodium amalgum or Pt by hydrogen.

$$HN_3 + 4H_2 \xrightarrow{Na-Hg} 3NH_3$$
$$2HN_3 + 5H_2 \xrightarrow{Pt} 3NH_2NH_2$$

6. Oxidising agents like acidified $KMnO_4$, oxidise it to nitrogen.

$$2HN_3 + (O) \xrightarrow[KMnO_4]{acidified} 3N_2 + H_2O$$

3.9.3 Structure

The N_3^- ion is found to be linear and is isoelectronic with carbon dioxide. It is also symmetrical and on the basis of molecular orbital picture, there are two σ and two π bonds. The N–N bond length is the same and is 0.116 nm.

The addition of the proton in hydrogen azide necessarily destroys the symmetry of the ion and it has a bent structure. The N–N bond lengths are different.

The HNN bond angle is 112°.

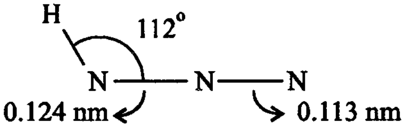


Fig. 3.5: Structure of hydrogen azide

3.10 COMPOUNDS OF SULPHUR

Sulphur is the second element of group 16 of the periodic table. These elements have the outer electronic configuration ns^2np^4 and an oxidation state as high as +6 is expected. This of course is common in the element sulphur. Sulphur also exhibits oxidation state –2, +2 and +4. Various compounds of sulphur such as H_2SO_4, Na_2SO_3 are industrially very important.

Sulphur forms a number of halides and oxohalides. A few of them are discussed here.

3.11 THIONYL CHLORIDE $SOCl_2$

Thionyl chloride is also known as *sulphinyl chloride*. It is also considered as the acid chloride of sulphurous acid.

3.11.1 Preparation

1. It is prepared by passing dry sulphur dioxide over phosphorus pentachloride.

$$PCl_5 + SO_2 \xrightarrow{\text{dry}} SOCl_3 + POCl_2$$

[Sodium sulphite can also be used in place of sulphur dioxide]. The liquid is fractionally distilled to separate the products.

2. Thionyl chloride is also obtained by passing chlorine monoxide over sulphur at –15°C.

$$Cl_2O + S \longrightarrow SOCl_2$$

3. On a commercial scale it is obtained by the action of sulphur trioxide on sulphur monochloride at 80° C.

$$SO_3 + S_2Cl_2 \xrightarrow{80^\circ C} SOCl_2 + SO_2 + S$$

3.11.2 Properties

It is a colourless pungent smelling liquid with a boiling point 78°C.

It fumes in moist air.

It reacts vigorously with water and is hydrolysed to sulphur dioxide and hydrochloric acid.

$$SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl$$
$$SOCl_2 + 2H_2O \longrightarrow H_2SO_3 + 2HCl$$

This reaction is made use of to remove water of hydration from hydrated chlorides. For example,

$$CrCl_36H_2O + 6SOCl_2 \longrightarrow CrCl_3 + 6SO_2 + 12HCl$$

Thionyl chloride undergoes ionisation in solution as

$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^-$$

3.11.3 Structure

The molecule is pyramidal in shape with one unshared pair of electrons on sulphur atom. The hybridization on sulphur atom is sp^3.

S–Cl bond length of 0.207 nm.

S–O bond length of 0.145 nm.

ClSCl bond angle 114°.

ClSO bond angle 100°.

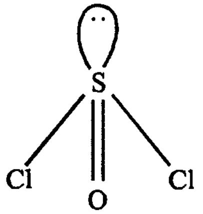


Fig. 3.6: Structure of thionyl chloride

3.12 SULPHURYL CHLORIDE SO_2Cl_2

It is also known as sulphonyl chloride and is considered the dichloro derivative of sulphuric acid. Like thionyl chloride it is also an important chlorinating agent in organic chemistry.

3.12.1 Preparation

It is prepared by direct reaction between dry sulphur dioxide and dry chlorine in presence of camphor as catalyst.

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

3.12.2 Properties

It is a colourless fuming liquid with a boiling point 69° C.

It has a pungent smell.

It is slowly hydrolysed by water to sulphuric acid and hydrochloric acid.

$$SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

It reacts with ammonia in presence of an inert, dry solvent such as dry benzene to form sulphamide.

$$SO_2Cl_2 + 4NH_3 \longrightarrow SO_2(NH_2)_2 + 2NH_4Cl$$

It is a good solvent for many substances such as iodine, ferric chloride etc.

3.12.3 Structure

It has a distorted tetrahedral structure. It is considered as derivative of sulphuric acid where the two hydroxyl groups are replaced by chlorine atoms.

S–O bond length is 0.143 nm.

S–Cl bond length is 0.199 nm.

ClSO bond angle is 106.5°.

OSO bond angle is 120°.

ClSCl bond angle is 111.2°.

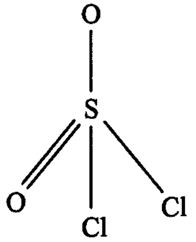


Fig. 3.7: Structure of sulphuryl chloride

3.13 SULPHUR HEXAFLUORIDE SF_6

Sulphur exhibits its highest oxidation state +6 in sulphur hexafluoride. Though a number of halides of sulphur are known (SF_4, SCl_4, SCl_2 etc.) only hexafluoride is the stable compound among hexahalides. Hexachloride, hexabromide and hexaiodide are not known. This may be attributed to the small size of the fluorine atom.

3.13.1 Preparation

It is obtained by burning sulphur in an atmosphere of fluorine.

$$S + 3F_2 \longrightarrow SF_6$$

The other fluorides are also present in the gas obtained. SF_6 is separated by liquefaction at 193 K and then further purified by fractional distillation.

3.13.2 Properties

It is a colourless, odourless gas.

It is highly stable and chemically inert.

It is not affected by water, acids or alkalis. Because of its inertness it finds use a high voltage insulation material (nuclear physics, x-ray and electrical work).

On passing through boiling sodium, it is decomposed.

It is readily hydrolysed by water

$$SF_6 + 8Na \longrightarrow 6NaF + Na_2S$$

3.13.3 Structure

SF_6 is a covalent saturated compound. It has a regular octahedral structure; sp^3d^2 hybridisation is shown by sulphur. The structure is discussed in detail in *Chapter – Chemical bonding.*

3.14 COMPOUNDS OF HALOGENS

Halogens are highly electronegative elements belonging to group 17 of the periodic table. Some of the compounds of halogens are discussed here.

3.15 BLEACHING POWDER $CaOCl_2$

Bleaching powder is considered as a mixture of calcium salts of hydrochloric and hypochlorous acids

It is manufactured by the action of dry Cl_2 on slaked lime.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow \underset{\text{bleaching powder}}{CaCl_2 + Ca(OCl)_2} + H_2O$$

Bleaching powder is prepared in Bachmann's plant where a current of chlorine and hot air is sent from just slightly above the base of a vertical tower. The tower is fitted with horizontal shelves at regular intervals. Each shelf is provided with rotating rakes. Dry slaked lime is allowed to move down the chlorinating tower by a suitable arrangement. As it moves down it meets the upcoming chlorine gas and is converted to bleaching powder. This is collected in the receiver placed at the bottom of the tower. Unreacted chlorine gas is driven away by a current of hot air.

3.15.1 Properties

It is a white powder with a strong smell of chlorine.

It is sparingly soluble in water, a small portion of it remaining insoluble

From X ray analysis it is seen that bleaching powder is a complex mixture of basic calcium hypochlorite and calcium chloride $Ca(OCl)_2Ca(OH)_2CaCl_22H_2O$.

In water, the hypochlorite portion is soluble.

Its solution in cold water gives the reactions of chloride and hypochlorite ions.

$$CaOCl_2 \rightleftharpoons Ca^{2+} + OCl^- + Cl^-$$

On heating the above solution, presence of chloride and chlorate ions are indicated.

$$CaOCl_2 \rightleftharpoons 3Ca^{2+} + ClO_3^- + 5Cl^-$$

Reaction with acids:

With small amounts of dilute acids it acts both as an oxidizing and bleaching agent on account of the nascent oxygen liberated.

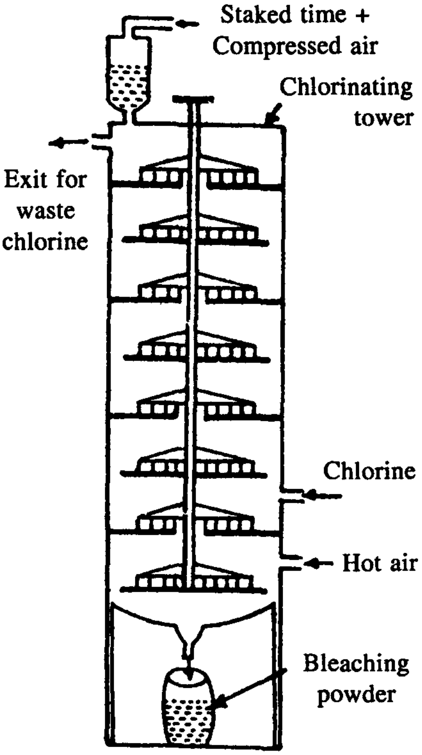


Fig. 3.8: Bachmann's plant for manufacture of bleaching powder

$$2CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HClO$$
$$HClO \longrightarrow HCl + (O)$$

With acid in excess, chlorine is liberated.

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

The chlorine that is liberated is called *the available chlorine*. The commercial sample of bleaching powder is priced according to the amount of available chlorine. The amount of available chlorine in bleaching powder is about 41% according to calculations. The best sample of bleaching powder has about 35-38% available chlorine.

Oxidising action:

It oxidises KI to I_2 in presence of acetic acid.

$$CaOCl_2 + 2CH_3COOH + 2KI \longrightarrow CaCl_2 + I_2 + 2CH_3COOK + H_2O$$

The above reaction forms the basis for the estimation of available chlorine in bleaching powder.

Decomposition:

On long standing, it undergoes slow auto–oxidation and is converted to a mixture of calcium chlorate and calcium chloride.

$$6CaOCl_2 \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$$

This results in a decrease in the percentage of available chlorine in the sample.

3.15.2 Estimation of Percentage of Available Chlorine

Available chlorine in a sample of bleaching powder is estimated volumetrically. A known mass of bleaching powder as a suspension in water is treated with excess of potassium iodide solution. The solution is then acidified with a strong solution of acetic acid. Iodine is liberated which is titrated against standard sodium thiosulphate solution.

Calculation

Mass of bleaching powder = Wg

Volume of sodium thiosulphate = V cm^3

Normality of sodium thiosulphate = N_1

1000 cm^3 of 1N $Na_2S_2O_3$ = 35.5 g of available chlorine.

$$V\ cm^3 \text{ of } N_1\ Na_2S_2O_3 = \frac{V\ cm^3}{1000\ cm^3} \times \frac{N_1}{1\ N} \times 35.5$$

$$= x \text{ g of available chlorine}$$

Wg of a sample of bleaching powder contains x g of available chlorine

∴ 100 g of bleaching powder contains

$$\frac{x\ g}{w\ g} \times 100 = y,$$

Percentage of available chlorine = y.

Bleaching powder is important in textile industry and in paper and pulp bleaching. In textile industry, the fabric to be bleached is first treated with caustic soda solution to remove grease. It is then dipped in a suspension of bleaching powder and left exposed to air. The fabric is then treated with dilute hydrochloric acid to remove any excess of bleaching solution. Lastly it is treated with an antichlor such as sodium thiosulphate to remove excess chlorine and finally washed with water.

In paper and pulp industries, a solution of bleaching powder and $CaCl_2$ is used under the name bleach liquor. Automatic dishwasher detergents use chlorinated trisodium phosphate with 4% available chlorine. Bleaching powder is used as a sterilising agent in the purification of water for drinking purpose and for swimming pool sanitation.

3.15.3 Structure

Bleaching powder is not a simple compound and on the basis of its properties various structures have been proposed. The recent proposal which accounts for its various properties is by Bunn, Clark and Clifford (1935).

On passing Cl_2 over slaked lime basic hypochlorate $Ca(ClO_2)\ 2Ca(OH)_2$ and basic calcium chloride $CaCl_2.Ca(OH)_2\,H_2O$ which is non–deliquescent are first formed.

Further chlorination converts basic hypochlorite to hypochlorite $Ca(ClO)_2 4H_2O$. *Bleaching Powder* is thus considered *a mixture of calcium hypochlorite and basic calcium chloride i.e.,* $Ca(ClO)_2 4H_2O$ *and* $CaCl_2$ $Ca(OH)_2 H_2O$. This is in good agreement with microscopic and X–ray analysis of the substance. This has been further confirmed by phase rule study.

3.16 INTERHALOGEN COMPOUNDS

The halogens react with each other to form interhalogen compounds. These are prepared by direct reaction between the halogens or by the action of a halogen on a lower interhalogen. The product formed depends on the conditions such as temperature and the relative proportions of the reactants used. Only two different halogen atoms are present in any molecule.

These can be divided into four types.

XX', XX'_3, XX'_5 and XX'_7 where X is the less electronegative and heavier halogen atom.

Table 3.1 gives a list of interhalogen compounds and their physical state at 25° C.

Table 3.1: Interhalogen Compounds

XX'	XX'_3	XX'_5	XX'_7
$ClF(g)$ Colourless b.p. –100°C	$ClF_3(g)$ Colourless b.p. 12°C	$ClF_5(g)$ Colourless b.p. –14°C	
$BrF(g)$ Pale brown b.p. ≈ 20°C	BrF_3 Yellow b.p. 126°C	BrF_5 Colourless b.p. 41°C	
$BrCl(g)$ Red brown			
$ICl(s)$ Ruby red m.p. 27°C	$ICl_3(s)$ Bright yellow sublimes at 64°C		
$IBr(s)$ Black m.p. 40°C			
IF Unstable	$IF_3(s)$ *(unstable)* Yellow m.p. –28°C	$IF_5(l)$ Colourless b.p. 100°C	$IF_7(g)$ Colourless

The bonds in interhalogen compounds are essentially covalent because of the comparable electronegativities of the two halogens involved. The compounds XX' and XX'_3 are possible between halogens of very close electronegativity like F and Cl or Br and Cl. The compounds XX'_5 and XX'_7 are shown only by large atoms like Br and I with smaller atoms like F. This is because 5 or 7 atoms can be packed around a large atom only when they are small.

The X – X′ bond in interhalogens are weaker than X – X bond in halogens so that the interhalogens are generally more reactive. On hydrolysis, they give rise to halide (X^-) and the oxohalide ion.

3.17 CHLORINE TRIFLUORIDE ClF_3

3.17.1 Preparation

It is prepared by the direct action of halogens at 300° C.

$$Cl_2 + \underset{\text{excess}}{3F_2} \xrightarrow{300^\circ C} 2ClF_3$$

Reaction of fluorine with chlorine fluoride also gives ClF_3. The reaction is carried out in a vessel of copper–nickel or monel metal.

3.17.2 Properties

It is a colourless gas, can be liquefied and solidified. Commercially it is available as a liquid in steel containers.

It is very reactive. It catches fire spontaneously with wood, asbestos; reacts vigorously with stopcock grease and many other organic compounds including cotton and paper.

It reacts explosively with water.

$$ClF_3 + 2H_2O \longrightarrow 3HF + \underset{\text{Chlorous acid}}{HClO_2}$$

Elements like S, P, As, Mo, W etc., burn in ClF_3.

It is a powerful fluorinating agent for inorganic compounds. It is used to fluorinate organic compounds after dilution with nitrogen, so as to moderate the reaction.

$$4ClF_3 + 6MgO \longrightarrow 6MgF_2 + 2Cl_2 + 3O_2$$

$$4ClF_3 + 2Al_2O_3 \longrightarrow 4AlF_3 + 2Cl_2 + 3O_2$$

$$2ClF_3 + 2NH_3 \longrightarrow 6HF + Cl_2 + N_2$$

$$ClF_3 + BF_3 \longrightarrow (ClF_2)^+ (BF_4)^-$$

It undergoes auto ionisation as

$$2ClF_3 \rightleftharpoons (ClF_2)^+ (ClF_4)^-$$

It forms volatile fluoride UF_6 with uranium.

$$2ClF_3 + U \longrightarrow UF_6 + Cl_2$$

The reaction is useful for separating the fission products from spent fuel rods. Plutonium forms a fluoride PuF_4 which is non–volatile.

It is used in nuclear industry to make gaseous UF_6, useful in enriching U–235 isotope.

Mixed with hydrazine it is used as a rocket fuel in short range rockets.

3.17.3 Structure

The molecule is T–shaped planar, with bond angles 87.5°. The structure is trigonal bipyramid with two of the equatorial positions being occupied by two lone pair of electrons. The equatorial Cl–F bond length is 0.171 nm while the apical Cl–F bond length is 0.162 nm.

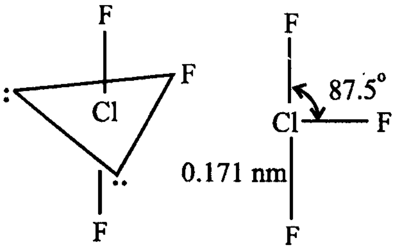


Fig. 3.9: Structure of chlorine trifluoride

3.18 BROMINE PENTAFLUORIDE BrF_5

3.18.1 Preparation

Bromine Pentafluoride is prepared by heating bromine (diluted with nitrogen) with excess fluorine at 150°C.

$$Br_2 + 5F_2 \xrightarrow[150°C]{heat} 2BrF_5$$

3.18.2 Properties

It is a colourless liquid boiling at 61°C.

It is very reactive. (less than ClF_3)

It reacts explosively with water.

$$BrF_5 + 3H_2O \longrightarrow 5HF + HBrO_3$$

It attacks silica forming silicon tetrafluoride.

$$2BrF_5 + SiO_2 \longrightarrow SiF_4 + 2BrF_3 + O_2$$

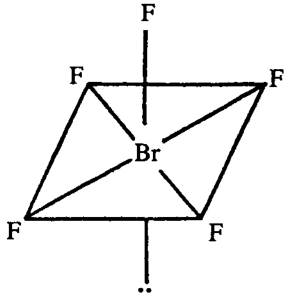


Fig. 3.10: Structure of BrF_5

3.18.3 Structure

BrF_5 has a square pyramidal structure i.e., octahedral with a corner being occupied by unshared pair of electrons. The central atom is slightly below the plane.

The FBrF bond angle is 85°. The Br–F apical bond length is 0.169 nm while the Br–F bond length in the base is 0.177 nm.

3.19 IODINE HEPTAFLUORIDE IF_7

IF_7 is the only interhalogen of the type XX'_7

3.19.1 Preparation

It is obtained by the direct combination of iodine and fluorine at 250–300°C.

$$I_2 + 7F_2 \xrightarrow{250 - 300^{o}\,C} 2IF_7$$

It is also obtained by reaction between iodine pentafluoride IF_5 and fluorine or iodide with fluorine.

$$IF_5 + F_2 \xrightarrow{250^{o}\,C} 2IF_7$$

$$KI + 4F_2 \longrightarrow IF_7 + KF$$

3.19.2 Properties

It is a colourless reactive gas..

It readily undergoes hydrolysis with water

$$IF_7 + H_2O \longrightarrow 2HF + IOF_5$$

It reacts with silica, caesium fluoride.

$$2IF_7 + SiO_2 \longrightarrow 2IOF_5 + SiF_4$$

With caesium fluoride a complex is formed.

$$IF_7 + CsF \longrightarrow Cs^+ [IF_8]^-$$

It is a violent fluorinating agent.

3.19.3 Structure

The structure of IF_7 is rather unusual – a pentagonal bipyramidal (sp^3d^3 hybridization is involved).

The equatorial I – F bond length is 0.186 nm and the apical I – F bond length is 0.179 nm.

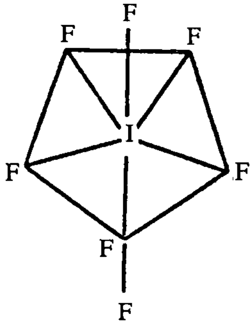


Fig. 3.11: Structure IF_7

IMPORTANT POINTS

- Boron trifluoride BF_3 is the most important halide of boron. It is prepared starting from boron trioxide or borax by heating with a mixture of calcium fluoride and concentrated sulphuric acid.
- BF_3 is a colourless fuming gas with a pungent smell. The aqueous solution forms hydrofluoric acid and boric acid.
- BF_3 is an electron deficient compound with only six electrons around boron. It acts as a Lewis acid. It is hence a good catalyst in organic reactions like alkylation, acylation etc.
- BF_3 is a planar triangular molecule with a bond angle 120°.
- The empty p_z orbital on B atom accepts a pair of electrons from a complete p orbital of one of the fluorine atom and a lateral overlap becomes possible. This is known as back–bonding. In BF_3 the B–F bond is shorter than the normal covalent B–F bond and is stronger.
- Borazole $B_3N_3H_6$ or borazine (also called inorganic benzene) is prepared by heating together BCl_3 and NH_4Cl and then reducing the product with sodium borohydride.
- Borazine is a colourless unstable liquid with an aromatic odour. It adds on 3 molecules of HCl like benzene but is more reactive than benzene. On hydrolysis with water at high temperature, boric acid, ammonia and hydrogen are formed.
- The structure of borazine is very similar to that of benzene, a planar hexagon with a B–N bond length 0.144 nm.
- Boron hydrides, sometimes referred to as boranes have general formula B_nH_{n+4} or B_nH_{n+6}.
- Diborane B_2H_6 is the simplest borane and can be prepared by a number of methods starting from boron trichloride, boron trifluoride or boron trioxide. Lithium aluminium hydride is one of the reducing agents used. Sodium borohydride is another reducing agent which reduces BF_3 *in situ* in diglyme medium.

- Diborane is a colourless gas and explodes with oxygen. It catches fire spontaneously in air and forms boron trioxide.
- Diborane is very reactive and reacts with NH_3, Cl_2, CO, hydrogen halides etc. It can be reduced to sodium borohydride by Na–Hg or NaH in ether.
- Higher boranes such as B_4H_{10}, B_5H_9 are formed by heating diborane to different temperatures.
- Boranes are electron deficient compounds and the bonding in these compounds are of great interest
- In diborane there are four terminal H atoms and two bridging H atoms.
- The terminal H atoms and B atoms are in the same plane. The two bridging H atoms are in a perpendicular plane.
- A three–centre two–electron bond is formed between the two boron atoms and a bridging H atom. Electron deficiency is associated with this bond which is also known as a banana bond. A similar bond is formed with the other bridging H atom and two B atoms. In diborane there are two such banana bonds.
- Other than NH_3, nitrogen forms hydrides such as hydrazine N_2H_4, hydroxylamine NH_2OH and hydrogen azide HN_3.
- Hydrazine is manufactured by careful oxidation of ammonia by sodium hypochlorite in aqueous solution.
- Hydrazine is a colourless fuming liquid with a pungent odour. It is soluble in alcohol and water.
- Hydrazine burns in air, evolving a large amount of heat. It decomposes explosively on heating.
- Hydrazine acts as a Lewis base due to the presence of a lone pair of electrons on nitrogen atom. It is a weak base forming two series of salts with acids.
- Hydrazine is a powerful reducing agent – reduces metallic salts, acidified $KMn0_4$, halogens etc. It is oxidised to nitrogen.
- Hydrazine may be reduced by more powerful reducing agents to ammonia.
- Hydrazine undergoes condensation reactions with carbonyl compounds.
- Hydrazine forms sodium hydrazide with sodium in an inert atmosphere.
- Hydrazine has an unsymmetrical structure in which each N atom is surrounded tetrahedrally by one N atom, two H atoms and a lone pair of electrons. A gauche conformation is adopted and there is no free rotation of $-NH_2$ groups.
- Hydrazine and its methyl derivatives are used as rocket fuel.
- Hydroxylamine may be prepared by the reduction of nitric oxide, nitrous acid, ethyl nitrate etc., using nascent hydrogen, SO_2 etc. It is also obtained by the electrolytic reduction of HNO_3.
- Hydroxylamine is a white crystalline explosive solid and thermally unstable.
- The solution of hydroxylamine is a very weak base, it disproportionates slowly in acidic solutions and rapidly in alkalis.
- Hydroxylamine is a powerful reducing agent – reduces Fehling's solution, halogens, bromates, iodates etc. It is oxidised to nitrous oxide.

- In alkaline solution, NH_2OH is an oxidising agent. It forms oximes with carbonyl compounds.
- Hydroxylamine can exist in cis–, trans– or gauche conformations.
- Hydrogen azide or hydrazoic acid is acidic in nature. It is prepared starting from fused sodamide, hydrazine or potassium azide.
- Hydrogen azide is a colourless, volatile poisonous and explosive liquid.
- The aqueous solution of hydrogen azide is weakly acidic. It reacts with metals like Zn, Li, Cu etc., forming metal azides and liberating N_2. Heavy metals azides are explosive.
- Hydrogen azide is reduced to NH_3 by H_2. It may be oxidised to N_2 by acidified $KMnO_4$.
- Hydrogen azide has a bent structure with a HNN bond angle 112° and different N – N bond lengths.
- Thionyl chloride $SOCl_2$, is considered the acid chloride of sulphurous acid
- $SOCl_2$ is prepared from PCl_5 and dry SO_2 or from Cl_2O and S at low temperature
- $SOCl_2$ is a colourless pungent fuming liquid. It is readily acted upon by water to form SO_2 and HCl. It is used to remove water of hydration from hydrated salts.
- $SOCl_2$ is pyramidal in shape with an unshared pair of electrons on S.
- Sulphuryl chloride SO_2Cl_2 is considered as a dichloro derivative of sulphuric acid. It is an important chlorinating agent in organic chemistry.
- SO_2Cl_2 is prepared by reaction between SO_2 and dry Cl_2.
- SO_2Cl_2 is a colourless fuming liquid, undergoing slow hydrolysis to form H_2SO_4 and HCl.
- SO_2Cl_2 has a distorted tetrahedral structure.
- SF_6 is the only stable hexahalide of sulphur.
- SF_6 is obtained by burning S in an atmosphere of fluorine and separating it by liquefaction.
- SF_6 is highly stable and chemically inert (not affected by water, acids, alkalis). It finds use as high voltage insulating material.
- SF_6 has a regular oxctahedral structure.
- Bleaching powder $CaOCl_2$ is considered a mixture of calcium salts of hydrochloric and hypochlorous acids. It is manufactured by the action of dry chlorine on slaked lime.
- Bleaching powder is white and sparingly soluble in water.
- With small amounts of acids it acts both as an oxidising and bleaching agent due to liberation of nascent oxygen.
- Chlorine is liberated when bleaching powder is heated with excess acid. This is called available chlorine. A very good sample of bleaching powder has about 35 – 38% available chlorine.
- The percentage of available chlorine in a given sample of bleaching powder decreases on long standing.
- Bleaching powder is useful in textile, paper and pulp industries.

- Interhalogen compounds are formed when halogens combine with each other. Compounds of the type XX′, XX'_3, XX'_5, XX'_7 are possible where X is the less electronegative and heavier halogen atom.
- The X–X′ bond is a weaker covalent bond than X–X bonds, Interhalogens are more reactive than halogens.
- Chlorine trifluoride ClF_3 is obtained by direct action of halogens.
- ClF_3 is a colourless gas, very reactive, highly inflammable and attacks stop cock, grease, cotton, paper and a number of organic compounds.
- ClF_3 is a powerful fluorinating agent for inorganic compounds. It forms volatile UF_6 with uranium which helps in separating the spent fuel and fission products in nuclear reactors.
- A mixture of hyrazine and chlorine trifluoride is used as a rocket fuel.
- ClF_3 is a T–shaped planar molecule with bond angle 87.5°.
- Bromine pentafluoride BrF_5 is prepared by heating bromine (diluted with nitrogen) and excess fluorine.
- BrF_5 is a colourless liquid, very reactive; it attacks silica
- The structure of BrF_5 is square pyramidal with FBrF bond angle 85°.
- Iodine pentafluoride IF_7 is the only interhalogen compound of the type XX'_7. It is obtained by the action of fluorine on I2, IF_5 or KI.
- IF_7 is a colourless reactive gas, undergoes hydrolysis with water and is a violent fluorinating agent.
- IF_7 has a pentagonal bipyramidal structure.

EXERCISE

Short Answer Type Questions:

1. How is boron trifluoride prepared?
2. What is the kind of hybridization shown by B in its compounds?
3. Give the Lewis acid character of BF_3.
4. Give an account of electron acceptor property of BF_3
5. On what property of BF_3 is its catalytic action based.
6. Discuss the structure of BF_3 on the basis of VSEPR theory.
7. Which compound is called inorganic benzene? Why?
8. How does BF_3 react with water? Explain with equations.
9. Give one reaction of BF_3.
10. How is borazine prepared?
11. How does borazine react with water?
12. Write the structure of borazole.
13. Discuss the structure of borazine.
14. What are boranes? How are they classified?
15. How many sodium borohydride be converted to diborane? Write equations
16. Give a method of preparation of diborane.

17. How may diborane be prepared starting from boron trifluoride?
18. How does diborane react with (a) water (b) ammonia. Write equations.
19. Explain what happens when diborane is heated?
20. Why is diborane called an electron deficient compound?
21. Draw the structure of diborane and give the bond lengths. What is unusual about the bonding in this compound?
22. Are all the six H atoms in diborane identical in all aspects? If not, bring out the difference between them with suitable illustrations.
23. Arrange BF_3, BCl_3, BBr_3 in the order of Lewis acid strength.
24. Explain why BF_3 is a weaker Lewis acid then BCl_3.
25. How is hydrazine prepared?
26. Write equations for the preparation of hydrazine by Rasechig process?
27. Name the different hydrides of nitrogen and give their formulae. Which of these is (a) basic (b) acidic in nature?
28. Give two reactions of hydrazine
29. Mention a reaction each of hydrazine on which the following uses are based.
    (a) As a space rocket fuel (b) To obtain a silver mirror
30. Write two reactions to indicate the reducing nature of hydrazine.
31. How does hydrazine react with (a) organic carbonyl compounds say benzaldehyde (b) sodium, (c) halogens, (d) acidified $KMnO_4$. Write equations.
32. Discuss the structure of hydrazine.
33. What is the major use of hydroxylamine? How is hydroxylamine prepared?
34. How is hydroxylamine prepared starting from (a) NO (b) CH_3NO_2?
35. How may nitric acid be converted to hydroxylamine?
36. Give two reactions of hydroxylamine.
37. How does hydroxylamine react with (a) halogens (b) sodium bromate (c) acetone?
38. Discuss the structure of hydroxylamine.
39. How is hydrogen azide prepared from sodamide?
40. How is anhydrous hydrogen azide prepared?
41. What is the nature of hydrogen azide in aqueous solution?
42. Give a reaction of hydrogen azide with a metal to show its acidic character. How is this reaction different from that of other acids with metals?
43. Discuss the structure of hydrogen azide.
44. Give two methods of preparation of thionyl chloride.
45. How does thionyl chloride react with water? Why is this reaction important?
46. Discuss the structure of thionyl chloride.
47. Give a method of preparation of thionyl chloride.
48. Discuss the structure of sulphuryl chloride.
49. Give two uses each for (i) thionyl chloride (ii) hydrazine.
50. How does sulphuryl chloride react with ammonia?

51. Give one reaction of sulphuryl chloride
52. How is sulphur hexafluoride prepared?
53 SF_6 is a well known stable compound. However, SCl_6, SBr_6 are not known to exist. Explain.
54. What is meant by 'available chlorine' in bleaching powder?
55. Give the composition of bleaching powder?
56. What are interhalogen compounds? How many different types of interhalogens are present?
57. To what kind of halogens X and X′ correspond to XX′ ? Can XX'_7 be possible between Cl_2 an Br_2? If not why?
58. How is ClF_3 prepared?
59. Write a note on the fluorinating action of ClF_3.
60. Discuss the structure of ClF_3 giving its angle and bond lengths.
61. Discuss the structure of BrF_5.
62. How does IF_7 react with (a) silica (b) water?
63. Write the shapes and hybridisation involved in IF_7.
64. Discuss the structure of IF_7.
65. Write a note on metal azides.

Essay Type Questions:

1. Discuss the structure of diborane and explain the special feature of bonding in it.
2. How is hydrazine manufactured?
3. How is bleaching powder manufactured?
4. Write the structure of bleaching powder.
5. Discuss the structure of bleaching powder.
6. Describe how the percentage of available chlorine in a given sample of bleaching powder is estimated.
7. Write a note on interhalogen compounds.

◆ ◆ ◆

Chapter 4

Silicates

SYLLABUS

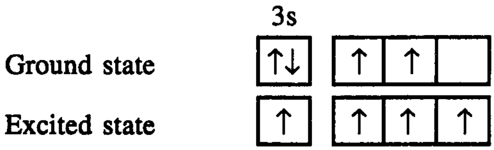
4.1 INTRODUCTION
4.2 CLASSIFICATION OF SILICATES
4.3 FELDSPARS AND ZEOLITES

4.1 INTRODUCTION

Silicates are considered as the salts of silicic acid H_2SiO_4. They are found abundantly in earth's crust as silicate minerals and aluminosilicate clays. They are crystalline in nature. All silicates have a silicate unit $(SiO_4)^{4-}$ which has a tetrahedral structure.

The silicon atom has an outer valence electron configuration $3s^2 3p_x^1 3p_y^1$ (similar to carbon).

Outer electronic configuration of silicon



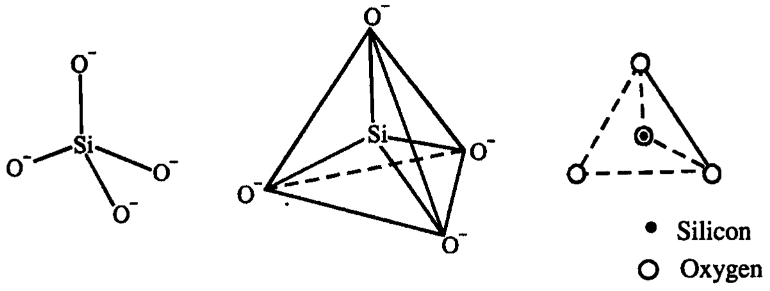


Fig. 4.1: Tetrahedral structure of $(SiO_4)^{4-}$ ion

Following sp^3 hybridisation of these atomic orbitals four hybrid orbitals result. They form four bonds with four oxygen atoms and a tetrahedral $[SiO_4]^{4-}$ unit results. Each oxygen atom on this unit has a negative charge which is satisfied by bonding with metal ions, or by linking with silicate units. The Si – O bond is not purely covalent and has an appreciable degree of ionic character. This is because the electronegativity difference between Si (1.8) and O (3.5) is fairly large. The bond is very strong. This accounts for the insolubility of most of the silicates in water and their stability.

4.2 CLASSIFICATION OF SILICATES

The silicate units get linked to one another in different ways and that forms the basis of their classification.

4.2.1 Orthosilicates

In orthosilicates discrete silicate units $(SiO_4)^{4-}$ exist. In the crystalline lattice, the oxygens of each silicate unit are coordinated round the metal ions thus forming a neutral structure. Common examples of this type are –

Zircon $ZnSiO_4$, *willemite* Zn_2SiO_4, *phenacite* Be_2SiO_4. The metal cation is surrounded by oxygen atoms of silicate units either tetrahedrally or octahedrally.

Garnets also come under this category. The general formula of garnets is $M_3^{II}\ M_2^{III}\ (SiO_4)_3$ where M^{II} can be Mg^{2+}, Ca^{2+} or Fe^{2+} and M^{III} can be Al^{3+}, Fe^{3+} or Cr^{3+}. The silicate units are arranged such that M^{II} ions show a coordination number 8 and M^{III} ions show a coordination number 6.

4.2.2 Pyrosilicates

The pyrosilicates contain units of disilicate ions $(Si_2O_7)^{6-}$ which is formed by the condensation of two silicate units through an oxygen atom. The anion has 6 units of negative changes corresponding to the 6 oxygen atoms; the oxygen atom forming a bridge has no charge on it.

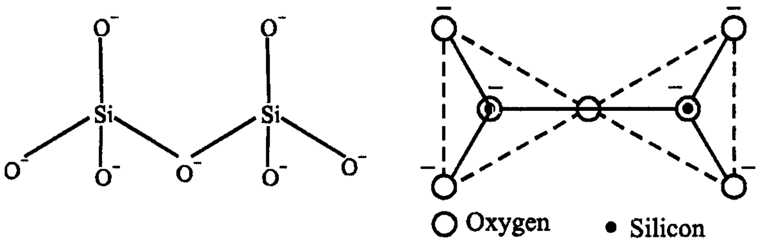


Fig. 4.2: Structure of $(Si_2\ O_7)^{6-}$ *ion in pyrosilicates*

This kind of structure is seen in the mineral *thortveitite* $Sc_2Si_2O_7$. The Sc^{3+} ions are octahedrally coordinated. Another example is *hemimorphite* $Zn_4(OH)_2Si_2O_7$.

4.2.3 Cyclic Silicates

When two oxygen atoms per silicate anion i.e., $(SiO_4)^{2-}$ tetrahedron is shared, a cyclic structure is obtained. Of these, $(Si_6O_{18})^{6-}$ unit is important.

Examples include – *beryl* $Be_3Al_2Si_6O_{18}$, *benitoite*, $BaTiSi_3O_9$, *wollastonite* $Ca_3Si_3O_9$.

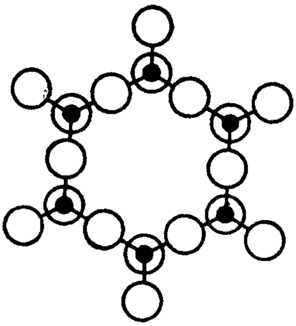


Fig. 4.3: The $(Si_6 O_{18})^{12-}$ group structure found in beryl

In the mineral beryl, the $(Si_6O_{18})^{12-}$ groups are so arranged that the metal cations are coordinated with the oxygen atoms as per requirement and at the same time an open structure with wide channels are formed.

4.2.4 Chain Silicates

A chain structure becomes possible when two oxygen atoms per silicate tetrahedron are shared forming a polymeric anion chain. In the metasilicate anion, the primary unit is $(SiO_3)^{2-}$. The chain extends throughout the crystal and are held together by the metal ions lying between them.

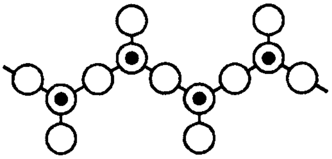


Fig. 4.4: Chain-like metasilicate $(SiO_3)^{2-}$ group

Pyroxene minerals like *diopside* $CaMg(SiO_3)_2$, *enstatite* $MgSiO_3$, *jadeite* $NaAl(SiO_3)_2$ and synthetic silicates like Na_2SiO_3, Li_2SiO_3 are common examples.

Double chain structures are observed in certain minerals. In these cases two simple chains are cross-linked by sharing oxygen atoms. The basic unit is $(Si_4O_{11})^{6-}$. Adjacent double chains are joined by the metal cations. The resulting structure is mechanically very strong in direction of orientation of anions; it is weak in the perpendicular direction. A fibrous nature is thus imparted to the mineral. This type of structure exist in a class of minerals called *amphiboles* like *tremolite* $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$, *amocite*·(Mg, Fe)$_7$ $(Si_8\ O_{22})$ $(OH)_2$.

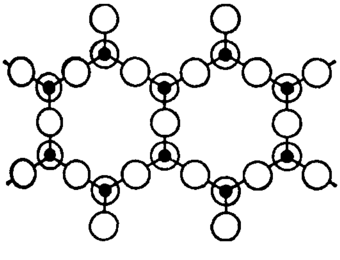


Fig. 4.5: Cross-linked $[(Si_4O_{11})]^{6-}$ groups

4.2.5 Sheet Silicates

The process of cross linking of silicate tetrahedron through oxygen atoms can be extended to three oxygen atoms per silicon atom when two - dimensional sheets are formed.

The basic unit is $(Si_2O_5)^{2-}$. The only oxygen atom of the silicate anion that does not form a bridge with other tetrahedra carries a negative charge which is neutralised by the binding cations lying between the sheets. The parallel sheets are held together by weak electrostatic forces and as a result, these minerals are soft and cleave easily.

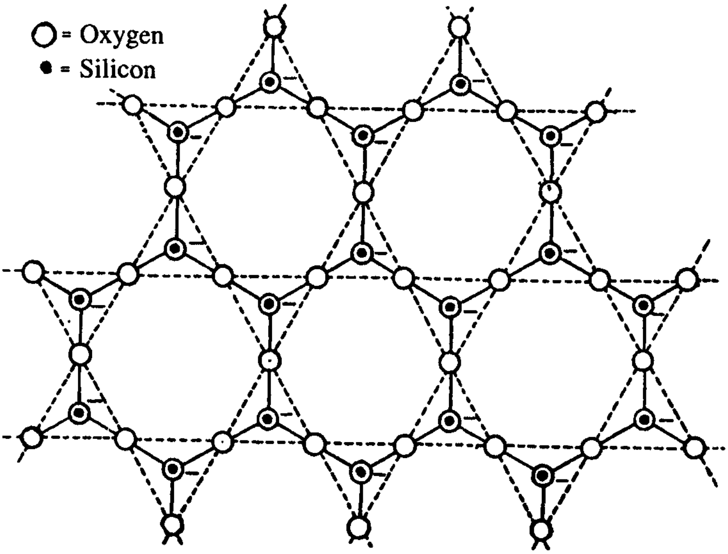


Fig. 4.6: Two-dimensional structure of sheet silicates

Talc $Mg_2(Si_2O_5)_2\ Mg(OH)_2$, *kaolinite* $Al_2(OH)_4Si_2O_5$ are common examples of this class of silicates.

Talc is known for its softness and smoothness. It is used as a dry lubricant.

4.2.6 Three Dimensional Silicates

When there is cross-linking of all the four oxygen atoms in the silicate anion a three-dimensional structure is produced. This is neutral as the charges on all the oxygen atoms get satisfied. The general formula is $(SiO_2)_n$. The common examples are *quartz, cristobalite, tridymite.*

4.3 FELDSPARS AND ZEOLITES

In the three dimensional neutral silicate structure, the silicon ions Si^{4+} may be isomorphically replaced by Al^{3+} ions. In other words, a silicate $(SiO_4)^{4-}$ is replaced by an aluminate $(AlO_4)^{5-}$ ion. In such a case, in order to maintain neutrality, a monovalent cation need to be introduced. Such minerals are called aluminosilicates.

Feldspars, zeolites, mica, clay are examples of aluminosilicates.

Feldspar, $KAlSi_3O_8$, *Zeolite* $NaAlSi_2O_6H_2O$.

4.3.1 Zeolites

Zeolites are aluminosilicates with a general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y]zH_2O$ where M is a cation like K^+, Na^+, Ca^{2+}. *They have a three dimensional network with a honeycomb structure. The presence of open channels and cavities in their structure accounts for their 'base exchange' property and as molecular sieves.*

In zeolites, the cations move freely through the open pore structure and can be exchanged with other cations. This base exchange is reversible and a state of equilibrium is attained. Thus if a sodium zeolite such as *analcite* $NaAlSi_2O_6.H_2O$ is treated with a solution of silver nitrate, the sodium ions get replaced by silver ions and a silver zeolite is obtained.

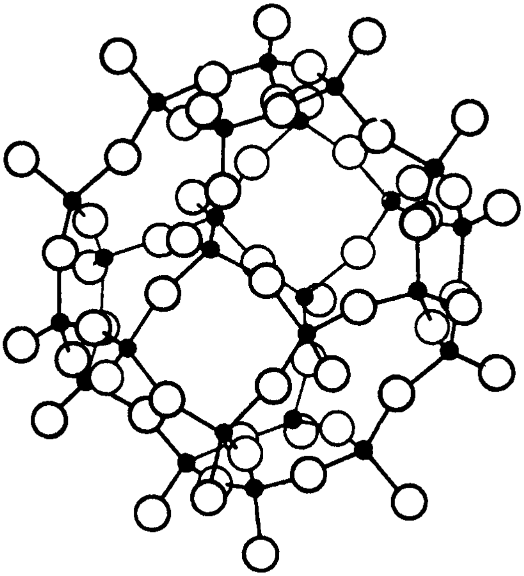


Fig. 4.7: The arrangement of AlO_4 and SiO_4 tetrahedra

This property of zeolites is made use of in softening of hard water. Certain synthetic zeolites are used to exchange calcium ions present in hard water.

$$Na_2OAl_2O_3\ nSiO_2\ mH_2O + \underset{\text{hard water}}{CaSO_4} \rightarrow CaOAl_2O_3nSiO_2 \cdot mH_2O + Na_2SO_4$$

The zeolite can be regenerated by treating it with a solution of NaCl.

Zeolites also act as molecular sieves. The channels have diameters in the range 40 – 70 nm. They have a considerable absorptive power for gases other than water vapour. Depending upon the cross-section of the channel, smaller molecules like oxygen, nitrogen get excluded while the larger complex molecules like branched hydrocarbons, aromatic hydrocarbons are not taken up. This property helps in separation of gaseous mixtures.

The mineral, *mordenite*, for example has a channel diameter 40 – 49 nm and can exclude methane and ethane slowly but no other higher hydrocarbon.

Sodium silicate, Na_2SiO_3 is the only common silicate soluble in water. Most of the other silicates are insoluble due to the presence of the strong Si – O bond in silicates.

IMPORTANT POINTS

- Silicates are considered salts of silica acid – found in earth's crust as silicate minerals and aluminosilicate clays.
- The silicate unit $(SiO_4)^{4-}$ has a tetrahedral structure.
- The Si–O bond is very strong.
- Silicates are classified on the basis of the type of linkage between the silicate units.
- Orthosilicates have discrete silicate units. Examples are zircon, phenacite, willemite and also garnets.
- Pyrosilicates contain two silicate units joined through an oxygen atom. Hemimorphite and thortveitite are examples.
- Cyclic silicates are formed when two oxygen atoms of silicate anions are shared. Beryl, benetoite, wollastonite are examples.
- A polymeric anion formed by sharing two oxygen atoms of the silicate anion results in a chain structure – chain silicates. Pyroxene minerals like diopside, enstatite, jadeite are examples.
- Amphiboles minerals like tremolite, amocite have double chain structures where two simple chains are cross-linked by sharing oxygen atoms.
- Sheet silicates result due to cross-linkage of three oxygen atoms of silicate anion. Two dimensional sheets are formed. Talc and kaolinite are common examples.
- When all the four oxygen atoms of the silicate anion are cross-linked, a three dimensional, neutral structure is obtained. Quartz, tridymite, cristobalite are examples.
- Feldspars and zeolites are aluminosilicates. The silicon-ion Si^{4+} in silicate anion is replaced by Al^{3+}. A monovalent cation is also present to maintain neutrality.
- Zeolites have a honeycomb structure with open channels and cavities. They act as molecular sieves. They also have 'base exchange' property.
- Zeolites are useful to soften hard water. Calcium ions in hard water are exchanged with sodium ions in zeolites.
- Zeolites can exclude small gas molecules and thus help in separation of gaseous mixtures.
- Sodium silicate is only common water soluble silicate.

EXERCISE

Answer the following questions:

1. Discuss the structure of silicate ion.
2. What is the nature of Si-O bond? Justify your answer.
3. What are orthosilicates? Write the structure of the basic unit.

4. How are the silicate units linked in pyrosilicates? Give an example of a mineral having this structure.
5. What is the basic unit in cyclic silicate? Write its structure. Give the name and formula of a mineral having this structure.
6. Write a note on chain silicates.
7. What kind of linkage is found in two dimensional sheet silicates? What is the basic unit?
8. Talc is mineral known for its softness. Account for this property in terms of its structure.
9. Why is a three dimensional silicate neutral?
10. What are aluminosilicates? Structurally how are they related to silicates? Give examples.
11. Write a note on zeolites.
12. Zeolites serve as base exchanger and as a molecular sieve. Explain these properties in the light of their structures.
13. Why are most silicates water insoluble? Name a water soluble silicate.

❖ ❖ ❖

Chapter 5

Nonaqueous Solvents

SYLLABUS

5.1 INTRODUCTION
5.2 LIQUID AMMONIA
5.3 LIQUID SULPHUR DIOXIDE

5.1 INTRODUCTION

Most chemical reactions take place in solution in which the solvent plays an important role. Although water is the best known solvent, there are other solvents such as glacial acetic acid, liquid ammonia, liquid sulphur dioxide, sulphuric acid, benzene, carbon tetrachloride, alcohol etc., in which chemical reactions can take place. While organic solvents such as benzene, carbon tetrachloride are non polar solvents and dissolve non polar organic compounds, others like liquid ammonia, sulphuric acid, etc., are polar solvents.

Water in which most of inorganic chemical reactions take place is perhaps the best solvent for the following reasons –

1. easy availability and cheap
2. has a long liquid range from 273 K – 373 K.
3. has a high dielectric constant (78.5) and dissolves practically all ionic substances
4. a poor conductor of electricity but undergoes auto-ionisation.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

5. the aqueous solutions of ionic salts are good conductors of electricity.
6. certain reactions like precipitation, neutralisation can take place instantaneously in this medium

No other solvent has such a wide range of properties as water and for this reason water is considered an "universal solvent". Some of the other non-aqueous solvents have certain properties similar to water if not to the same extent and have their own usefulness.

Solvents may be classified as: (i) *protonic solvents* and (ii) *aprotic solvents.*

In protonic solvents, a transferable proton is present, H_2O, NH_3, H_2SO_4, CH_3COOH, HF are examples of protonic solvents. These undergo autoionisation as –

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

Protonic solvents may be acidic (e.g., glacial acetic acid, liquid HF, anhydrous sulphuric acid etc.) basic (e.g., liquid NH_3) or amphiprotic (e.g., water).

Aprotic solvents do not ionize and can neither accept nor donate protons. These may be non-polar like CCl_4, C_6H_6 or polar like liquid SO_2, acetonitrile CH_3 C≡N etc.

5.2 LIQUID AMMONIA

Liquid ammonia is the most extensively studied solvent and resembles water to a large extent. In both ammonia and water there is a fairly large degree of association due to hydrogen bonding. However, its low dielectric constant (22 at 240 K) resulting in a decreased solubility of certain ionic substances such as phosphates, sulphates and its restricted liquid range 195 K to 240 K makes it a less important solvent than water. In certain aspects particularly for non polar molecules it is a better solvent than water.

Some of the important reactions in liquid ammonia are discussed here.

5.2.1 Precipitation reactions

These reactions take place in ammonia just as in an aqueous solution. The compound of low solubility product is precipitated. Most chlorides, (except of Na, NH_4^+, Be) sulphides, bromides, iodides are insoluble in liquid ammonia while metal nitrates are soluble in liquid ammonia. In many cases, the direction of the reaction is reversed in liquid ammonia. For example, in aqueous solution

$$KCl + AgNO_3 \longrightarrow \downarrow AgCl + KNO_3$$

is reversed in liquid ammonia.

$$AgCl + KNO_3 \longrightarrow \downarrow KCl + AgNO_3$$

Similarly in liquid ammonia

$$2NH_4I + Zn(NO_3)_2 \longrightarrow \downarrow ZnI_2 + 2NH_4NO_3$$
$$2NH_4Br + Ba(NO_3)_2 \longrightarrow \downarrow BaBr_2 + 2NH_4NO_3$$

Ammonium sulphide in liquid ammonia precipitates metallic sulphides [similar to precipitation by H_2S in aqueous solution]

$$(NH_4)_2S + Ba(NO_3)_2 \longrightarrow \downarrow BaS + 2NH_4NO_3$$
$$(NH_4)_2S + Cu(NO_3)_2 \longrightarrow \downarrow CuS + 2NH_4NO_3$$

Metals may also be precipitated as complex halides.

$$2NaCl + Ca(NO_3)_2 + 8NH_3 \longrightarrow [Ca(NH_3)_8]Cl_2\downarrow + 2NaNO_3$$
$$2AgBr + Ba(NO_3)_2 + 8NH_3 \longrightarrow [Ba(NH_3)_8]Br_2\downarrow + 2AgNO_3$$

5.2.2 Neutralisation reactions

Ammonia undergoes autoionization like water as –

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

Just as in water, substances which produce NH_4^+ ions (H_3O^+ ions in water) are acids and substances which produces NH_2^- ions are bases (OH^- ions in water). Thus all ammonium salts are acids and amides are bases in liquid ammonia. Acid-base neutralization reaction occur as in aqueous media.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NaOH} \longrightarrow \underset{\text{salt}}{NaCl} + \underset{\text{solvent}}{H_2O} \quad \text{[in aqueous medium]}$$

$$\underset{\text{acid}}{NH_4Cl} + \underset{\text{base}}{NaNH_2} \longrightarrow \underset{\text{salt}}{NaCl} + \underset{\text{solvent}}{2NH_3} \quad \text{[in ammonia]}$$

$$NH_4NO_3 + KNH_2 \longrightarrow KNO_3 + 2NH_3$$

$$2NH_4I + PbNH \longrightarrow PbI_2 + 3NH_3$$

Ammonium salts dissolve metal oxides, hydroxides in liquid ammonia (similar to reactions of basic oxides and hydroxides by an acid).

$$2NH_4Cl + CaO \longrightarrow CaCl_2 + 2NH_3 + H_2O$$

$$NH_4NO_3 + KOH \longrightarrow KNO_3 + NH_3 + H_2O$$

The neutralization reactions can be studied using phenolphthalein as an indicator.

5.2.3 Amphoteric behaviour

Amphoteric behaviour is observed in liquid ammonia just as in water. For example, $Zn(OH)_2$ is amphoteric in water, and similarly zinc amide $Zn(NH_2)_2$ is amphoteric in ammonia. In both the cases, complex formation is observed.

$$Zn^{2+} + NaOH \xrightarrow[\text{aqueous}]{} \underset{\text{insoluble}}{\downarrow Zn(OH)_2}$$

$$Zn(OH) + \underset{\text{excess}}{NaOH} \longrightarrow \underset{\text{soluble}}{Na_2[Zn(OH)_4]}$$

$$Zn^{2+} + KNH_2 \xrightarrow[\text{ammonia}]{} \underset{\text{insoluble}}{\downarrow Zn(NH)_2}$$

$$Zn(NH)_2 + \underset{\text{excess}}{KNH_2} \longrightarrow \underset{\text{soluble}}{K_2[Zn(NH_2)_4]}$$

5.2.4 Solvolysis reaction

In solvolysis reactions, the solvent breaks up into two parts and one or both the parts get attached to the solute molecule or ion. In water, these reactions are called hydrolysis reactions. On the same lines, the reactions in liquid ammonia are called *ammonolysis*. For example,

$$\left.\begin{array}{rcl} Cl_2 + 2H_2O & \longrightarrow & HOCl + H_3O^+ + Cl^- \\ POCl_3 + 6H_2O & \longrightarrow & PO(OH)_3 + 3H_3O^+ + 3Cl^- \end{array}\right\} \text{in water}$$

$$\left.\begin{array}{rcl} Cl_2 + 2NH_3 & \longrightarrow & NH_2Cl + NH_4^+ + Cl^- \\ POCl_3 + 6NH_3 & \longrightarrow & PO(NH_2)_3 + 3NH_4^+ + 3Cl^- \end{array}\right\} \text{in ammonia}$$

Other examples of ammonolysis are

$$\begin{aligned} SiCl_4 + 8NH_3 &\longrightarrow Si(NH_2)_4 + 4NH_4Cl \\ PCl_3 + 6NH_3 &\longrightarrow P(NH_2)_3 + 3NH_4^+ + 3Cl^- \\ HgCl_2 + NH_3 &\longrightarrow HgNH_2Cl + 3NH_4^+ + Cl^- \\ NaH + NH_3 &\longrightarrow NaNH_2 + H_2 \end{aligned}$$

Following solvolysis, there is an increase in concentration of either the cation (NH_4^+) or the anion (NH_2^-) of the solvent.

5.2.5 Solvation

Solvation is a phenomenon where solvent molecules get attached to solute molecules or ions. Similar to hydration, ammonia molecules may get attached to solute species which is called *ammonation.*

$$\begin{aligned} CaCl_2 + 8NH_3 &\longrightarrow CaCl_2 8NH_3 \\ BF_3 + NH_3 &\longrightarrow BF_3NH_3 \\ SO_3 + 2NH_3 &\longrightarrow SO_3 2NH_3 \end{aligned}$$

5.2.6 Levelling effect of liquid NH_3

The strong acids in water react completely with liquid ammonia and ammonium ions are formed.

$$\begin{aligned} HCl + NH_3 &\longrightarrow NH_4^+ + Cl^- \\ HClO_4 + NH_3 &\longrightarrow NH_4^+ + ClO_4^- \end{aligned}$$

In fact, even weak acids in water like CH_3COOH, oxalic acid, react completely with ammonia.

$$\begin{aligned} CH_3COOH + NH_3 &\longrightarrow NH_4^+ + CH_3COO^- \\ (COOH)_2 + 2NH_3 &\longrightarrow 2NH_4^+ + (COO)_2^{2-} \end{aligned}$$

Thus all the acids appear very strong in liquid ammonia. The acid strengths are levelled by ammonia. *Ammonia is thus called a levelling solvent.* Further, even molecules which show no acidic behaviour in water behave like weak acids in ammonia. Urea for example, behaves as a weak acid.

$$\underset{\text{urea}}{NH_2CONH_2} + NH_3 \rightleftharpoons NH_4^+ + NH_2CONH^-$$

On the other hand, most species that are considered bases in water are either insoluble or behave as weak bases in ammonia.

5.2.7 Solubility of alkali and some alkaline earth metals in ammonia

Liquid ammonia is a very good solvent for alkali metals and the heavier alkaline earth metals like Ca, Sr and Ba. The dilute solutions are blue in colour (irrespective of the metal involved) and as the concentration of the dissolved metal increases, the solution changes to bronze with metallic lustre. The solutions have a conductivity quite comparable to that of pure metals. The solution exhibits paramagnetism indicating the presence of free electrons.

Since the visible region of spectra of all the metals remain same, the presence of a common species is expected, which is the solvated electron. Thus, alkali metals in liquid ammonia dissociate to form a metal cation and a solvated electron.

$$M \xrightarrow[\text{dilute}]{\text{liquid ammonia}} [M(NH_3)_n]^+ + [e(NH_3)_x]^-$$

This accounts for electrical conductivity and paramagnetism.

The solution decomposes slowly liberating H_2, which is catalysed by ultraviolet light, iron or platinum.

$$M + NH_3 \longrightarrow MNH_2 + \frac{1}{2}H_2$$

On evaporating solutions of alkali metals the metals are recovered. In the case of alkaline earth metals, however, a solid ammoniate $M[NH_3]_x$ is obtained on evaporation.

5.2.8 Redox reactions of metal solutions

The solutions of metals in liquid ammonia are very good reducing agents, because of the presence of free electrons.

$$2Na + 2NH_4Br \longrightarrow 2NaBr + 2NH_3 + H_2$$

$$2Na + S \longrightarrow Na_2S$$

The strong oxidising agents in water are very weak oxidising agents in liquid ammonia. HNO_3 for example, is not an oxidizing agent in ammonia. $KMnO_4$ is a weak oxidizing agent and can be reduced to manganate and oxides of manganese quite readily by potassium in liquid ammonia.

$$2KMnO_4 + 4K + 4NH_3 \rightleftharpoons 2K_2MnO_4 + MnO_2 + 4KNH_2 + 2H_2$$

In conclusion, it may be said that the behaviour of liquid ammonia solutions is quite similar to that of aqueous solutions with a few exceptions.

5.3 LIQUID SULPHUR DIOXIDE

Liquid sulphur dioxide is an example of an aprotic solvent and has a wide liquid range from 200 K to 265 K. It is a gas at room temperature but can be easily liquefied. Its dielectric constant is quite low (17.4 at 225 K) and the ionic compounds have a low solubility in liquid SO_2. However, covalent compounds like Br_2, I_2, BCl_3, CS_2 etc., dissolve in liquid SO_2. It also dissolves a number of organic compounds.

Some of the reactions in liquid sulphur dioxide are discussed here:

5.3.1 Precipitation reactions

The solubility of inorganic salts in liquid SO_2 varies widely and cannot be generalised. Some precipitation reactions are —

$$BaI_2 + Zn(SCN)_2 \longrightarrow Ba(SCN)_2\downarrow + ZnI_2$$

$$AlCl_3 + 3NaI \longrightarrow 3NaCl\downarrow + AlI_3$$

$$PbF_2 + L1_2SO_4 \longrightarrow 2LiF + PbSO_4\downarrow$$

$$2CH_3COOAg + SOCl_2 \longrightarrow 2AgCl\downarrow + (CH_3COO)_2SO$$

A variety of thionyl derivatives can be prepared as shown below —

$$2KBr + SOCl_2 \longrightarrow 2KCl\downarrow + SOBr_2 \text{ (thionyl bromide)}$$

$$2NH_4CN + SOCl_2 \longrightarrow 2NH_4Cl\downarrow + SO(SCN)_2$$

5.3.2 Solvolysis reactions

Solvolysis reactions in liquid sulphur dioxide are less common.

$$PCl_5 + SO_2 \longrightarrow POCl_3\downarrow + SOCl_2$$

The more soluble salts from addition compounds with the solvent such as $AlCl_3SO_2$, $LiI.2SO_2$, $KCNS.SO_2$.

5.3.3 Organic reactions

Many organic reactions are carried out in liquid sulphur dioxide.

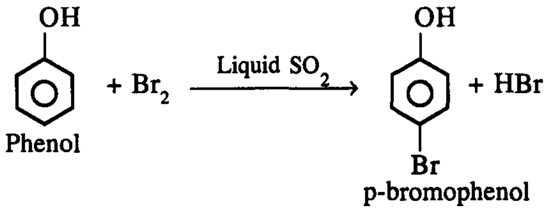
(a) Sulphonation: Aromatic hydrocarbons undergo sulphonation with chlorosulphonic acid.

$$C_6H_6 + Cl.SO_3H \xrightarrow[SO_2]{\text{Liquid}} C_6H_5SO_3H + HCl$$

(b) Friedel-Crafts reactions: Since anhydrous aluminium chloride is soluble in liquid SO_2, Friedel-Crafts reactions are carried out in this medium.

$$C_6H_6 + CH_3COCl \xrightarrow[\text{in liquid } SO_2]{\text{anh. } AlCl_3} C_6H_5COCH_3 + HCl$$

(c) Bromination: Bromine dissolved in liquid SO_2 reacts with organic compounds when bromination takes place.



$$RCH = CH_2 + Br_2 \xrightarrow{\text{Liquid } SO_2} RCHBrCH_2Br$$

5.3.4 Acid-base reactions

The following reactions are considered as acid-base reactions. Salt and the solvent are the products.

$$SOCl_2 + K_2SO_3 \longrightarrow 2KCl + 2SO_2$$

$$SOBr_2 + CsSO_3 \longrightarrow 2CsBr + 2SO_2$$

$$SO(SCN)_2 + Na_2SO_3 \longrightarrow 2NaSCN + 2SO_2$$

In the above reactions SO^{2+} ion is regarded analogous to H_3O^+ ion and SO_3^{2-} is regarded as analogous to OH^- ion in aqueous medium. Thus, thionyl compounds are considered acids and sulphites as bases.

SO_2 was assumed to undergo auto-ionization as

$$SO_2 + SO_2 \rightleftharpoons SO_3^{2-} + SO_2^{2+}$$

As there is no evidence for the formation of these ions, this ionization is not accepted any more.

IMPORTANT POINTS

- Other than water, solvents such as glacial acetic acid, liquid ammonia, liquid sulphur dioxide, carbon tetrachloride, alcohol etc., can serve as solvents in which chemical reactions can take place.
- Non-aqueous solvents may be polar or nonpolar. Solvents may be classified as protonic and aprotic solvents.
- In protonic solvents, a transferable proton is present –H_2O, NH_3 etc, and undergo auto-ionization.
- Aprotic solvents neither accept nor donate protons –CCl_4, C_6H_6 etc. and do not ionize.
- Liquid ammonia is an important nonaqueous solvent and resembles water to a large extent.
- The liquid range of liquid ammonia is only between 195K to 240K and has a low dielectric constant. While the solubility of ionic substances is decreased in ammonia, it is a better solvent than water for certain nonpolar molecules.
- Precipitation reactions take place in ammonia just as in water. Most chlorides, bromides, iodides and sulphides are insoluble in ammonia. Metal nitrates are soluble in ammonia.
- Metallic sulphides are precipitated in liquid ammonia by ammonium sulphide.
- Neutralization reactions take place between ammonium salts (acids) and amides (bases) in liquid ammonia.
- Similar to dissolution of basic oxides and hydroxides in acids, ammonium salts dissolve metal oxides and hydroxides in liquid ammonia.
- Certain substances such as $Zn(NH_2)_2$ show amphoteric behaviour in liquid ammonia.
- Ammonolysis reactions take place in liquid ammonia forming amides and ammonium ions.
- Ammonation is a phenomenon similar to hydration –$CaCl_2$ $8NH_3$, BF_3NH_3 etc.
- All acids weak (CH_3COOH) as well as strong (HCl) react completely with liquid ammonia and appear to be equally strong. This is called levelling effect. Many bases in aqueous solution may behave like very weak bases in liquid ammonia.
- Alkali metals and Ca, Si and Ba dissolve in liquid ammonia. The solutions are blue in colour irrespective of the dissolved metal. Bronze metallic lustre is observed in concentrated solutions. Such solutions are paramagnetic and conduct electricity. Solvated electrons and metal cations are present in these solutions.
- Metal solutions decompose to liberate H_2.
- Alkali metal solutions on evaporation leave behind the metals while alkaline earth metal solutions give solid ammoniate on evaporation.

- Solutions of metals in liquid ammonia are very good reducing agents. Strong oxidising agents such as HNO_3, $KMnO_4$ are either not an oxidising agent (HNO_3) or are weak oxidising agents ($KMnO_4$) in liquid ammonia.
- Liquid sulphur dioxide is an aprotic solvent and has a liquid range from 200 K to 265 K with a low dielectric constant. A number of organic compounds, halogens dissolve in liquid SO_2.
- Certain inorganic salts alike NaCl, $PbSO_4$, AgCl, KCl etc., precipitate in liquid SO_2. Solvolysis reactions are less common in sulphur dioxide.
- Many organic reactions such as bromination, sulphonation, Friedel-Crafts reactions are carried out in liquid sulphur dioxide.
- Thionyl compounds ($SOCl_2$) are considered as acids and sulphites ($NaSO_3$) are considered as bases in liquid SO_2 medium. Reactions between thionyl compounds and sulphites are regarded as acid-base reactions.

EXERCISE

Short answer type questions:

1. Name two nonaqueous solvents. Write two reactions that can occur in each one of them.
2. What are non aqueous solvents? How are they classified? Explain with an example.
3. Compare liquid ammonia as a solvent with water.
4. Explain neutralization reactions in liquid ammonia as a solvent.
5. Which compounds are considered (a) acids and (b) bases in liquid ammonia and why?
6. Explain the levelling effect of ammonia.
7. Write a note on the solubility of alkali metals in liquid ammonia.
8. Write a note on metal ammonia solution.
9. How do you account for the blue colour exhibited by all the metals in liquid ammonia?
10. Write a note on liquid ammonia as a nonaqueous solvent.
11. Discuss the use of liquid ammonia as a solvent.
12. What kind of compounds are soluble in liquid SO_2?
13. Write a note on the precipitation reactions in liquid SO_2.
14. Why is it considered convenient to carry out certain reactions in liquid SO_2 medium?
15. Write a note on liquid sulphur dioxide as a nonaqueous solvent.

Chapter 6

Aromatic Hydrocarbons

SYLLABUS

6.1 INTRODUCTION
6.2 BENZENE: (PHENE) C_6H_6
6.3 STRUCTURE OF BENZENE
6.4 HUCKEL'S AROMATICITY RULE OR (4n + 2) RULE
6.5 NOMENCLATURE OF BENZENE DERIVATIVES
6.6 MECHANISM OF AROMATIC SUBSTITUTION
6.7 ORIENTATION EFFECT OR ORIENTING INFLUENCE OF THE SUBSTITUENTS
6.8 HYDROGENATION OF AROMATIC COMPOUNDS
6.9 SIDE - CHAIN OXIDATION
6.10 OXIDATION OF NAPHTHALENE
6.11 OXIDATION OF ANTHRACENE
6.12 OXIDATION OF PHENANTHRENE

6.1 INTRODUCTION

Early in the development of organic chemistry, organic compounds were arbitrarily classified as aliphatic or aromatic. Aliphatic compounds have open-chain structure. In addition to aliphatic compounds, there was a large number of compounds which were obtained from natural sources e.g., resins, balsams, aromatic oils etc., all of which had a pleasant odour. These compounds had higher percentage of carbon content than the corresponding aliphatic hydrocarbons and most of the simple compounds contained atleast six carbon atoms. These compounds were known as aromatic compounds. Further more, when these aromatic compounds were subjected to various methods of treatment, they often produced benzene or derivatives of benzene.

Thus, aromatic compounds are benzenoid compounds; these are cyclic, but their properties are different from those of alicyclic compounds.

6.2 BENZENE: (PHENE) C_6H_6

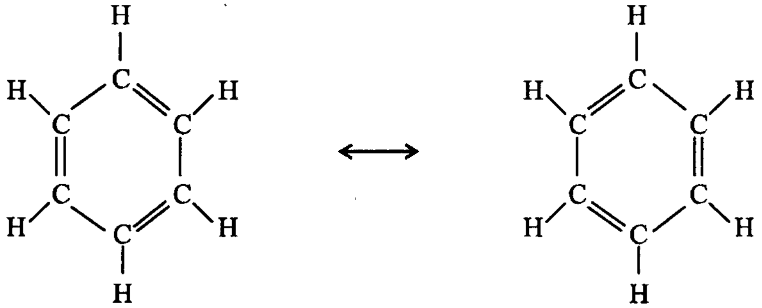
Benzene was first isolated by Faraday (1825) from cylinders of compressed illuminating gas obtained from the pyrolysis of whale oil. In 1845, benzene was found in coal-tar by Hofmann.

6.3 STRUCTURE OF BENZENE

Benzene is the corner-stone of all aromatic compounds and its properties may be regarded as typical of aromatic compounds. As the properties of a compound depend upon its structure, it is quite appropriate first to study the structure of benzene.

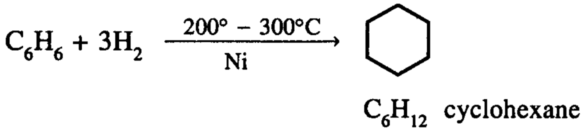
6.3.1 Kekule Structure of Benzene

Kekule in 1865 proposed a closed chain structure. According to him, six carbon atoms are linked together in the form of a hexagonal ring. Each carbon atom is attached to one hydrogen atom. The benzene molecule is flat, planar in which all the six carbon and six hydrogen atoms are lying in one plane. In order to account for the tetravalency of carbon atoms, alternate double and single bonds between carbon atoms were proposed.



Kekule's structure of benzene explained satisfactorily the following points.

1. That benzene contains three double bonds.
2. That all six hydrogen atoms in benzene are equivalent, and benzene gives only one monosubstituted product, C_6H_5X.
3. That there are three possible disubstituted products of benzene (ortho, meta, para).
4. Hydrogenation of benzene at 200 – 300°C yields cyclohexane which is a ring compound. This proves that benzene contains six carbon atoms and a cyclic structure.



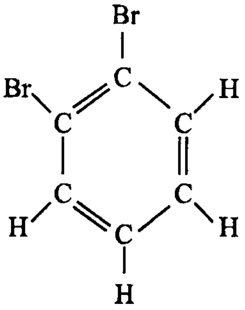
6.3.2 Objections to Kekule's Structure

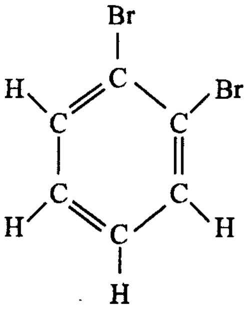
The structure of benzene postulated by Kekule could not explain the following facts:

(i) From the Kekule's structure, one should expect that benzene due to the presence of three double bonds should show chemical properties similar to the alkenes but it does not do so. Benzene does not decolourise the purple colour of alkaline $KMnO_4$ or orange red colour of bromine water.

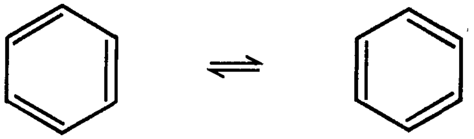
(ii) In Kekule's structure, there are double and single bonds between carbon atoms. Therefore, there should be two types of bond lengths (i.e., C – C, 0.154 nm and C = C, 0.134 nm). Actually, all the bonds of benzene are of equal length 0.139 nm and the bond angles, C – C – C are 120°. The length of the carbon-carbon bonds is in between that of single and double bonds. This has been confirmed by X-ray and electron diffraction studies. This also shows that the six carbon atoms of benzene are in one plane and are arranged as a regular hexagon. This could not be explained by Kekule's structure.

(iii) On the basis of Kekule's structure, two orthodibromobenzenes are possible. The two carbon atoms to which the Br atoms attached are linked by a single bond in one structure and by a double bond in another. In reality, only one ortho dibromobenzene is known.





In order to explain this, Kekule postulated that benzene may be considered as a mixture of two rapidly interconverting forms in which the single and the double bonds rapidly interconvert.

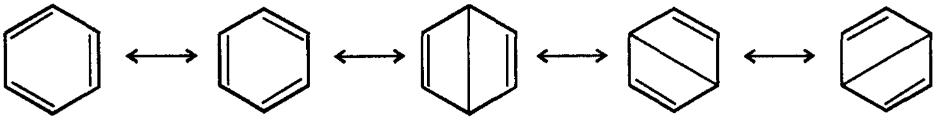


(iv) The suggestion that benzene molecule is having three alternate double bonds is not correct.

6.3.3 Resonance Theory (Valence Bond Theory)

Resonance theory is based on X-ray and electron diffraction studies of benzene which have clearly demonstrated that the six carbon atoms of benzene are in one plane and are arranged as a regular hexagon. The six carbon-carbon bonds are equivalent in length (0.139 nm). They are shorter than a normal carbon-carbon single bond (0.154 nm) but longer than a normal carbon-carbon double bond (0.134 nm).

According to this theory, if a single structure written for a compound fails to account for all its properties, then such a molecule may be considered as a hybrid of two or more electronic structures. All these structures together are able to account for all the properties of the compound, but no single structure will be able to account for all of them. However, if we write different structures for a compound, a necessary condition is that the positions of the nuclei in all structures must be the same; only the positions of bonding electrons can be changed. Thus, *benzene is represented as a resonance hybrid of the following structures which are known as resonance forms, or canonical forms or contributing forms.*

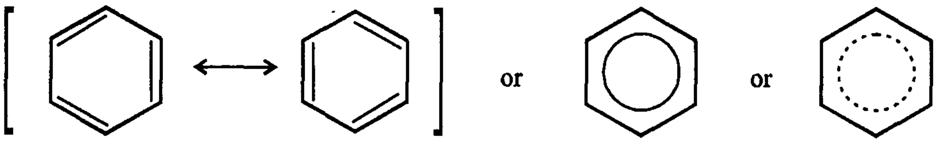


(I) (II) (III) (IV) (V)

Kekule formulae Dewar formulae

The structures I and II are given by Kekule while the structures III, IV and V are given by Dewar. A double headed arrow (↔) which is put in between the two contributing structures indicates resonance. The true structure of benzene is represented neither by I, nor by II, III, IV, or V but is actually *a resonance hybrid* which cannot be represented by a conventional structure. The various contributing structures I, II, III, IV and V shown above may be considered as the nearest representation of the actual molecule. Although all the canonical structures are contributing their characteristics to the resonance hybrid, their contributions may not be the same. For example, in benzene, two Kekule's structures I and II are of lowest energy (highest stability) and contribute nearly 80 per cent to the character of the hybrid. The net effect of the resonance in the case of benzene is that all the bonds are equivalent i.e. neither double bonds nor single bonds but intermediate between a single and a double bond in character. Also, *the resonance hybrid is more stable than any of the contributing forms and this increase in stability is known as resonance energy. Greater the number of canonical forms, the higher the resonance energy and the greater the stabilisation. The difference is energy between the hybrid (actual molecule) and the most stable (lowest energy) canonical form is called resonance energy.*

Resonance between imaginary structures having localised bond (valence bond theory) or delocalization of π orbitals (molecular orbital theory) have both been found to explain the bonding state of benzene. The benzene molecule may be represented either as a hybrid of Kekule structures (valence bond theory) or as a regular carbon hexagon having an inscribed circle or dotted circle that symbolizes the three delocalized π orbitals.

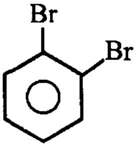


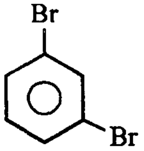
Valence bond theory Molecular orbital theory

On the whole, resonance delocalises the π bonds, thus the C – C bonds in benzene is neither purely single nor purely double at any time. This was supported by X-ray diffraction and spectroscopic studies which revealed that benzene molecule is planar and consists of six carbon atoms arranged in a regular hexagonal ring; the bond distance between two adjacent carbon atoms is 0.139 nm, each C – H bond has a length of 0.109 nm, and all bond angles are of 120°.

The resonance hybrid structure of benzene explains all the properties of benzene.

(i) *Isomer number:* Since all the carbon-carbon bonds in benzene are equivalent, there can be no distinction between any two ortho disubstituted products. Hence in all, only three disubstituted products (one *o*–, one *m*– and one *p*-) are possible.


1,2 – dibromo benzene


1,3 – dibromo benzene


1,4 – dibromo benzene

(ii) *Bond lengths:* According to resonance hybrid structure, benzene contains no true carbon-carbon double or single bonds. In other words, all the carbon-carbon bonds in benzene are equivalent and are intermediate between single and double bonds which agrees with the observed carbon-carbon bond length (0.139 nm) in benzene.

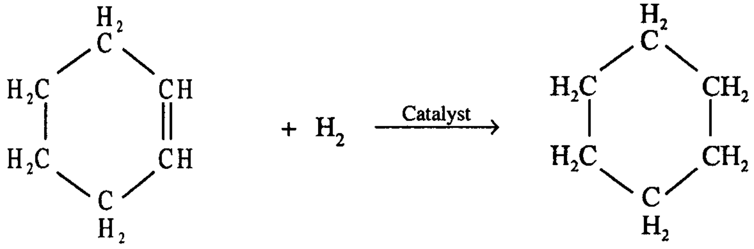
(iii) *Unusual stability:* The unusual stability and peculiar behaviour of benzene is due to high resonance energy (151.2 kJ mol^{-1}) of benzene. In general, a resonance hybrid is always more stable than any of the contributing structures.

Substitution reactions in benzene rather than addition reactions are due to the fact that in the former reactions resonance-stabilised benzene ring system is retained while the addition reactions lead to the destruction of benzene system. For example, addition of one molecule of hydrogen to benzene would destroy benzene ring and form cyclohexadiene which is less stable than benzene.

6.3.4 Calculation of Resonance Energy

The resonance hybrid has less energy and is said to be more stable than any one of the resonating structures. *The difference in energy between the hybrid and the most stable canonical structure is known as the resonance energy of the molecule.* For example, the total energy of the benzene hybrid is lower than the energy of classical Kekule structure by about 151.2 kJ mol^{-1}. *Benzene is said to be stabilised by a resonance energy of 151.2 kJ* mol^{-1}. It is observed that larger the number of the possible canonical structures, greater will be the resonance energy and hence stability of the compound.

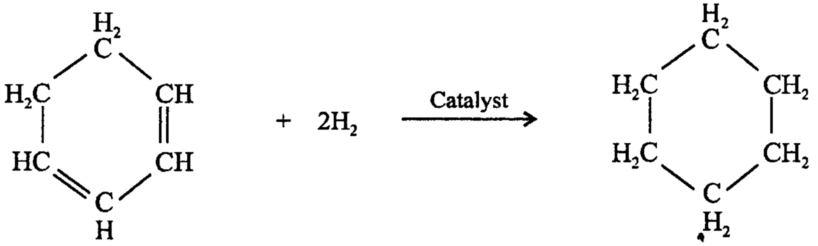
Resonance energy of benzene can be calculated by finding the difference between the experimental enthalpy of hydrogenation of benzene and the calculated enthalpy of hydrogenation of a hypothetical cyclic triolefin of six carbon atoms in which no resonance is possible.



Cyclohexene Cyclohexane

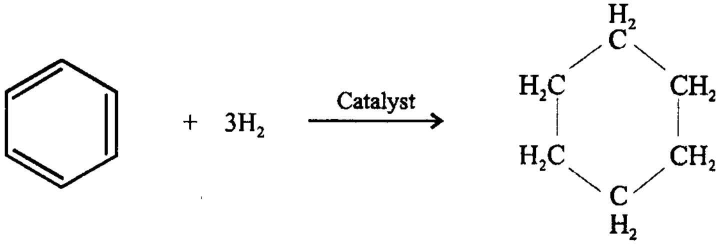
When cyclohexene, having one double bond, is hydrogenated, it yields cyclohexane and liberates 119.66 kJ of heat per mole.

When 1,3–cyclohexadiene, having two double bonds, is hydrogenated, it liberates 231.18 kJ of heat per mole. This quantity of heat liberated is almost twice the quantity of heat liberated in the first case ($2 \times 119.66 = 239.32$ kJ mol^{-1}).



1,3 Cyclohexadiene Cyclohexane

As benzene is having three double bonds, it should, on hydrogenation, liberate $-3 \times 119.66 = -358.98$ kJ of heat per mole. But actually benzene on hydrogenation liberates only 208.36 kJ/mol. Thus, benzene on hydrogenation liberates 150.62 kJ/mol ($358.98 - 208.36 = 150.62$ kJ mol^{-1}) less energy than the quantity predicted for a cyclic compound with three double bonds. In other words, benzene is more stable than a compound having 3 double bonds by 150.62 kJ. This implies that the resonance energy of benzene is 150.62 kJ mol^{-1}.



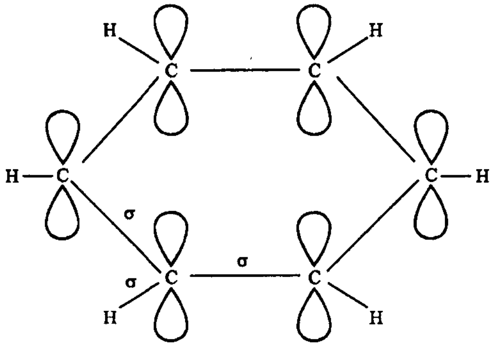
Benzene Cyclohexane

It is possible to reach the same conclusion from the enthalpy of combustion of benzene.

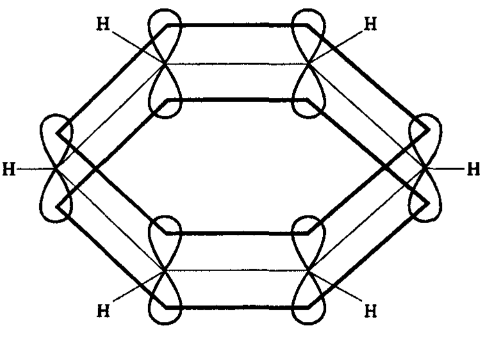
6.3.5 Molecular Orbital Theory

A more detailed picture of about the structure of benzene molecule is obtained from a consideration of the bond orbitals in the molecule.

1. In benzene, each carbon atom is sp^2 hybridized and bonded to two neighbouring carbon atoms and one hydrogen atom by sigma (σ) bond. These are directed towards the corners of an equilateral triangle.
2. It is a flat, symmetrical molecule with all carbon and hydrogen atoms lying in the same plane. The six carbon atoms lie at the angle of a regular hexagon; every bond angle is 120°.
3. In addition to the three atomic orbitals used for sp^2 hybridization, each carbon atom has a fourth orbital - a p orbital (unhybridized) perpendicular to the plane of the regular hexagon. Each of these unhybridized p orbital consists of two lobes one below and one above the plane of the ring. All these (six) p orbitals are parallel to each other, but perpendicular to the plane of the ring.
4. The p orbital of one carbon atom overlap with the p orbital of the adjacent carbon atom, resulting in the formation of π bond. But the overlap is not limited to a pair of p orbitals as in ethylene. The p orbital overlap is extended to all six carbon atoms, resulting in the formation of a delocalized π bond which is much stronger than a localized π bond (ethene). This delocalization of electrons of six p orbitals form two continuous doughnut shaped electron clouds, one lying above and the other below the plane of the hexagonal ring.



Hexagon of benzene with 6 p orbitals perpendicular to the molecular plane.



Structure of benzene indicating delocalized π bonds lying above and below the plane of the molecule.

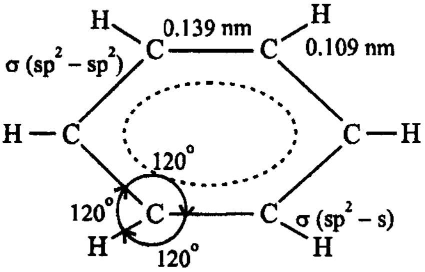
The extra stabilization (decrease in energy) attained by the molecule due to delocalization of 6 p electrons is known as *delocalization energy* and corresponds to resonance energy (VB theory).

6.3.6 Evidence in Favour of Molecular Orbital Structure

The molecular orbital structure of benzene explains all the known characteristics of benzene.

(i) *Flat ring structure:* Since each of the carbon atoms of benzene constituting the ring is in sp^2 hybridised state, each C – C – H bond angle is of 120° and the resulting molecule is flat.

(ii) *Bond length:* In the benzene molecule each C – C bond length is 0.139 nm, each C – H bond length is 0.109nm.



Bond angles and bond lengths in benzene

(iii) *Isomer number:* According to molecular orbital theory, since all the six carbon atoms of benzene are completely equivalent, hydrogen atoms attached to these are also equivalent. Hence benzene forms only one mono - substituted and three disubstituted products.

(iv) *Unusual stability:* This is due to delocalisation of electrons. The term resonance energy is sometimes replaced by delocalisation energy.

(v) *Electrophilic substitution:* Since benzene ring is surrounded by the p – electrons cloud above and below the plane of atoms, it is readily attacked by electron – seeking reagents (electrophiles). Remember that despite delocalisation, π electrons are more loosely held than the σ electrons and are thus readily available to an electrophile. Further since substitution reactions lead to resonance – stabilised substituted benzene derivatives substitutions are the main reactions of benzene.

6.4 HUCKEL'S AROMATICITY RULE OR (4n + 2) RULE

Huckel (1937) carried out M.O. calculations on monocyclic systems – C_nH_n containing n π – electrons and each carbon atom providing one π – electron, and as a result, connected aromatic stability (delocalization energy) with the presence of (4n + 2) π electrons in a closed shell, where n is an integer.

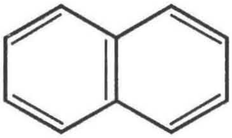
Thus, to be aromatic, a molecule must have 2 (n = 0), 6 (n = 1), 10 (n = 2)..... π – electrons. The essential requirement for aromaticity is a planar ring containing (4n + 2) π electrons (n = 0, 1, 2, 3.....). Those molecules that possess (4n + 2) π – electrons are associated with extra stability, due to the delocalization of π – electrons.

Huckel's rule states that among monocyclic, planar, fully conjugated molecules, only those possessing (4n + 2) π electrons (n = 0, 1, 2, 3....) have special aromatic stability.

In benzene ring (n = 1) there are (4 + 2) = 6 π electrons. This is referred to as *aromatic sextet of electrons. The aromatic sextet leads to extra stability,* as all the 6 electrons are filled in the bonding molecular orbitals, leaving the antibonding molecular orbitals of high energy completely empty. Examples – benzene, pyridine, thiophene etc.

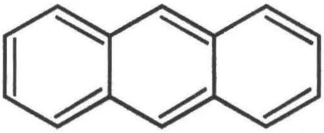
6.4.1 Polycyclic Systems

Huckel's (4n + 2) π electron rule can be extended to polycyclic conjugated systems. For example, naphthalene (n = 2) has [(4 × 2) + 2] π electrons i.e., 10 π electrons and obeys Huckel's rule which justifies the extra stability and aromatic character of naphthalene molecule.

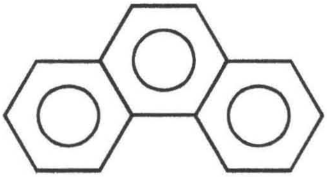


naphthalene

In anthracene (n = 3) there are [(4 × 3) + 2) i.e., 14 π electrons



Similarly in phenanthrene (n = 3) there are [(4 × 3) + 2] π electrons i.e., 14 π electrons. Both these compounds are found to be aromatic and possess extra stability as stated by Huckel's rule.



Phenanthrene

6.5 NOMENCLATURE OF BENZENE DERIVATIVES

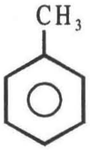
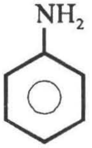
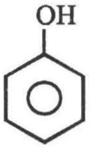
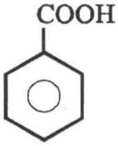
Many derivatives of benzene are named by simply prefixing the name of the substituent group to the word – benzene. For example

chlorobenzene

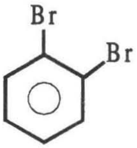
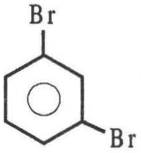
nitrobenzene

iodobenzene

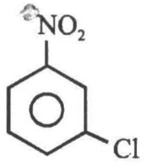
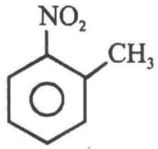
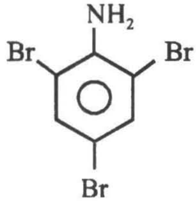
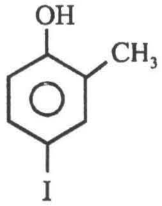
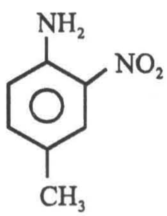
Other derivatives have special names which may sometimes show no resemblance to the name of the attached substituent

Formula	*Common name*	*IUPAC name*
	toluene	methylbenzene
	aniline	aminobenzene or benzenamine
	phenol	hydroxybenzene
	benzoic acid	benzoic acid

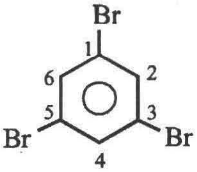
If the same substituent is present more than once in the benzene ring, their positions must be indicated by the use of names ortho, meta and para abbreviated as o – m – and p – respectively. For example,

Formula	*Common name*	*IUPAC name*
	o – dibromobenzene	1,2 – dibromobenzene
	m – dibromobenzene	1,3 – dibromobenzene
	p – dibromobenzene	1,4 – dibromoenzene

When two or more functional groups are present, number 1 (one) is given to principal functional group. If one of the two groups is the kind, that gives a special name to the molecule, then the compound is named as a derivative of that special compound.

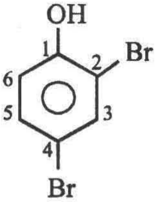
Formula	*Common name*	*IUPAC name*
	p – bromo iodobenzene	4 – bromo iodobenzene
	m – chloro nitrobenzene	3 – chloro nitrobenzene
	o – nitrotoluene	2 – nitrotoluene
	p – bromo phenol	4 – bromophenol
	2, 4, 6 – tribromo aniline	2, 4, 6 – tribromo aminobenzene
	——	4–iodo–2–methyl phenol
	2–nitro–p–toluidine	4–amino–3–nitrotoluene

If all the groups are the same, each is given a number, the sequence being the one that gives the lowest combination of numbers



1, 3, 5 – tribromo benzene

If the groups are different, the last named group is understood to be in position one and the other groups are numbered according to lowest sum rule.



2, 4 – dibromophenol

6.6 MECHANISM OF AROMATIC SUBSTITUTION

There are three possible mechanisms for aromatic substitution

1. Electrophilic aromatic substitution
2. Nucleophilic aromatic substitution
3. Free radical aromatic substitution

Of these the common substitution reactions are those which involve electrophilic reagents, as the delocalized π bond in benzene serves as a source of electrons for electrophilic reagents.

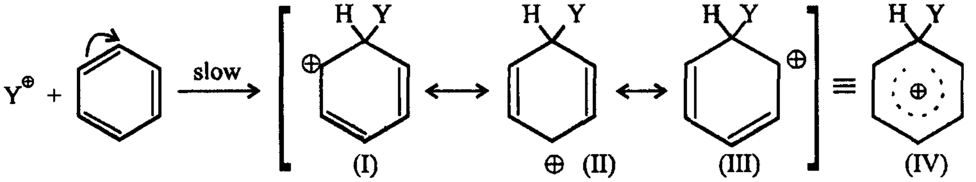
6.6.1 Electrophilic substitution

Nitration, halogenation, sulphonation, alkylation and acylation are examples of aromatic electrophilic substitution. These reactions are initiated either by electrophiles or substances which produce electrophilic species.

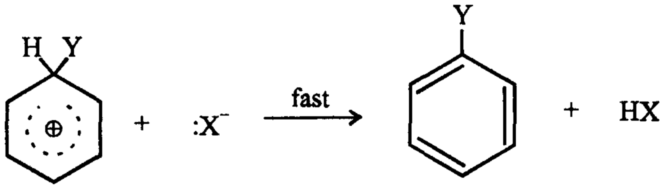
Mechanism

The reaction is bimolecular and takes place via the formation of an intermediate. The electrophile attacks the benzene ring and forms an intermediate carbonium ion (also known as benzonium ion). The carbonium ion is a resonance hybrid of structures I, II and III. The hybrid structure of the intermediate is represented by structure IV. *Formation of the intermediate is a slow step and is the rate determining step.* The intermediate is relatively stable, due to delocalization of the positive charge on five carbon atoms.

In many reactions intermediate carbonium ions have been detected spectroscopically and in some cases the salts of carbonium ions have been isolated.



The reaction is completed by the abstraction of a proton from the carbonium ion by an anionic species present in the reaction mixture.



Thus, the electrophilic aromatic substitution reactions are bimolecular.

6.6.2 Mechanism of Nitration of Benzene

Treatment of benzene with a mixture of concentrated nitric acid and concentrated sulphuric acid brings about nitration giving nitrobenzene as the product. The species which brings about nitration is the electrophilic nitronium ion (NO_2^+) which is generated *in situ*. The function of sulphuric acid is to protonate the nitric acid to give H_3O^+ and NO_2^+ ions.

(i) Generation of electrophile

$$\begin{aligned} H_2SO_4 + HNO_3 &\rightleftharpoons HSO_4^- + H_2\overset{+}{O}NO_2 \\ H_2\overset{+}{O}NO_2 &\rightleftharpoons H_2O + N\overset{+}{O}_2 \\ H_2SO_4 + H_2O &\rightleftharpoons HSO_4^- + H_3\overset{+}{O} \\ \hline 2H_2SO_4 + HNO_3 &\rightleftharpoons H_3\overset{+}{O} + N\overset{+}{O}_2 + 2HSO_4^- \end{aligned}$$

Very strong acids such as perchloric acid can also be used in place of sulphuric acid to release $N\overset{+}{O}_2$ ion from HNO_3. Furthermore, HF and BF_3 also catalyse nitration by assisting the release of nitronium ion

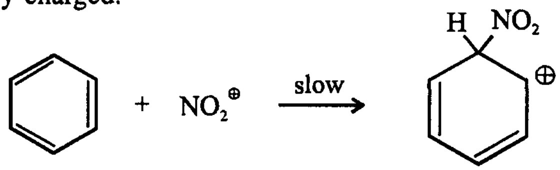
$$BF_3 + HNO_3 \longrightarrow N\overset{+}{O}_2 + HO - BF_3^-$$

$$2HF + HNO_3 \longrightarrow N\overset{+}{O}_2 + H_3\overset{+}{O} + 2F^-$$

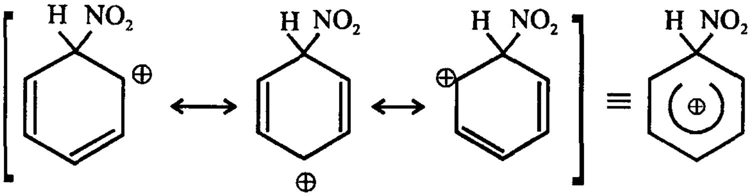
The nitration of benzene using nitric acid alone is very slow because nitric acid by itself is not sufficiently strong to give an appreciable concentration of $N\overset{+}{O}_2$ ions.

(ii) Attack of the electrophile : The nitronium ion acts as an electrophile. It attacks the π electrons of the benzene to form a σ bond with any one carbon

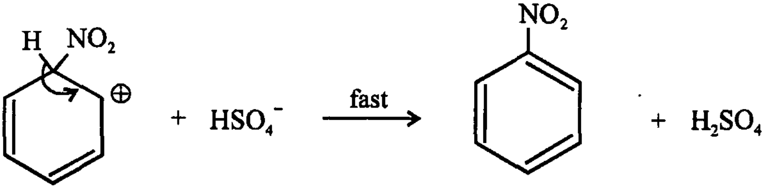
atom. The carbon atom which has lost its share of the π electrons becomes positively charged.



It is a slow step and the rate of this step decides the rate of formation of nitrated product. Also, the carbocation is stabilised by resonance.



(iii) *Loss of proton from the carbocation :* Although the carbocation is relatively stabler, it is quite reactive as one of the carbon atoms has only six electrons Also, it is not aromatic and tries to stabilise itself by regaining its aromatic structure. This can be achieved by losing a proton to the basic ion, HSO_4^-. Although HSO_4^- is an extremely weak base, the tendency of the phenonium ion to lose a H^+ is so high that even this slight basicity is quite sufficient for capture of a proton.



Thus, nitration and other electrophilic substitutions of aromatic compounds involve the following essential steps:

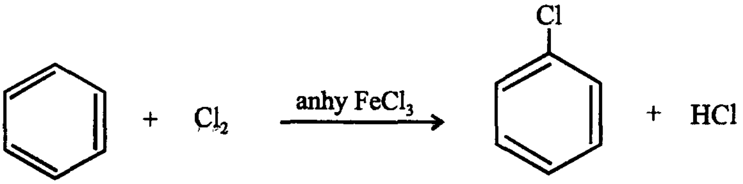
(i) Formation of an electrophile.

(ii) Slow attack of the electrophile on the aromatic compound to form a carbocation.

(iii) Rapid loss of a proton from the carbocation.

6.6.3 Mechanism of Halogenation

When aromatic compounds are treated with halogen, in the presence of halogen carrier (e.g., $FeCl_3$) and in the absence of light, halo derivatives are formed.

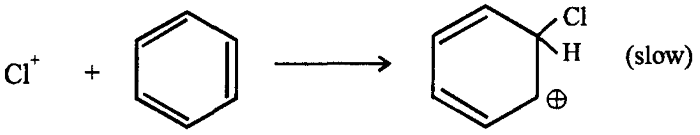


Halogenation takes place in three steps.

(i) Generation of electrophile

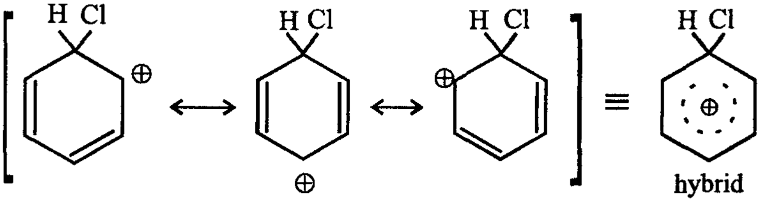
$$Cl_2 + FeCl_3 \rightleftharpoons Cl^+ + FeCl_4^-$$

(ii) Attack of electrophile on the aromatic compound

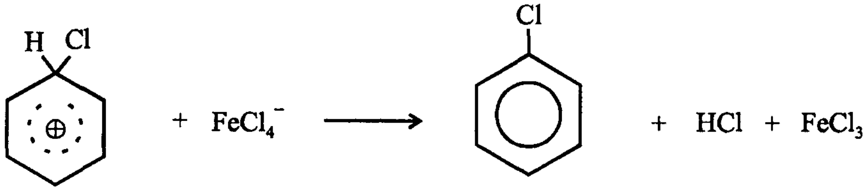


Intermediate carbonium ion

The positively charged chlorine, attacks electron rich benzene ring and forms the carbonium ion, which is stabilized by resonance. The canonical structures and the resonance hybrid are represented as



(iii) Loss of proton by carbonium ion : The carbonium ion loses a proton rapidly to $FeCl_4^-$, in order to regain its aromaticity, and results in the formation of chlorobenzene.



Chlorobenzene

$FeCl_3$ acts as Lewis acid and abstracts Cl^- from Cl_2 and thus helps in the formation of Cl^+ (electrophile)

6.6.4 Mechanism of Sulphonation

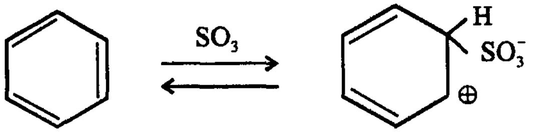
Sulphonation of aromatic compounds takes place using oleum or sulphuric acid containing excess of sulphur trioxide. Mechanism of sulphonation involves the following steps.

(i) Generation of electrophile

Sulphuric acid generates the electrophile sulphur trioxide (SO_3). SO_3 acts as Lewis acid (electrophile) as sulphur atom in SO_3 has only six electrons in its valence shell.

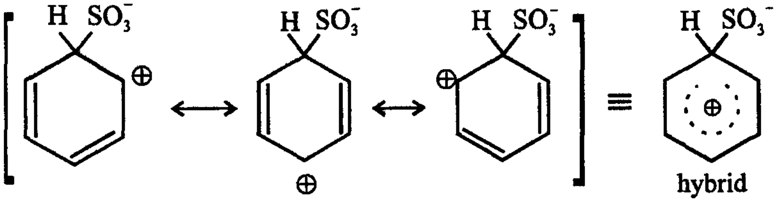
$$2\,H_2SO_4 \rightleftharpoons H_3\overset{+}{O} + HSO_4^- + \underset{\text{electrophile}}{SO_3}$$

(ii) Attack of electrophile on aromatic ring



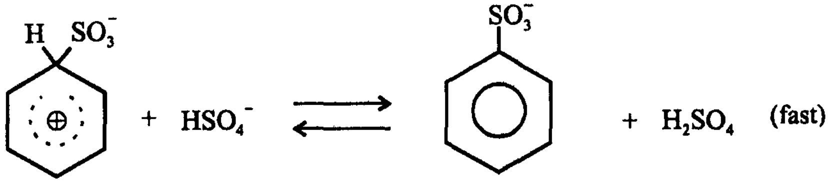
(slow)

carbocation
(resonance stabilized)



The neutral electrophile attacks the electron rich benzene ring and forms a carbocation intermediate which is stabilized by resonance.

(iii) Loss of proton



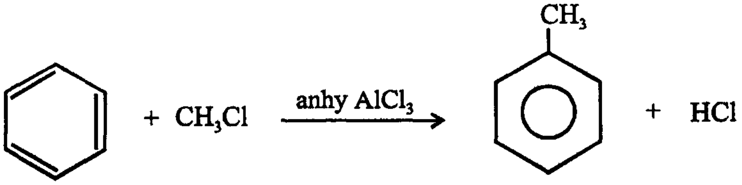
The intermediate loses a proton and forms the onion of benzene sulphuric acid.

(iv) $C_6H_5SO_3^- + H_3O^+ \rightleftharpoons C_6H_5SO_3H + H_2O$

The equilibrium is shifted to the left preferably, as the anion of benzene sulphonic acid is more stable (benzene sulphonic acid is a strong acid and is highly dissociated).

6.6.5 Mechanism of Friedel – Crafts Reaction

Friedel – Crafts alkylation is an electrophilic aromatic substitution reaction, in which an alkyl group is introduced in benzene ring, in the presence of anhydrous aluminium chloride



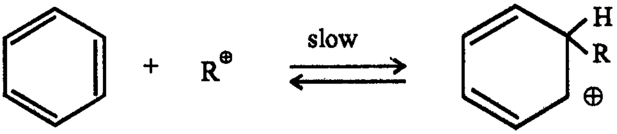
The various steps involved in the mechanism of Friedel-Crafts alkylation are

(i) Generation of electrophile

An alkyl halide reacts with Lewis acid (anhy $AlCl_3$) and forms an alkyl carbocation by acid – base equilibrium reaction

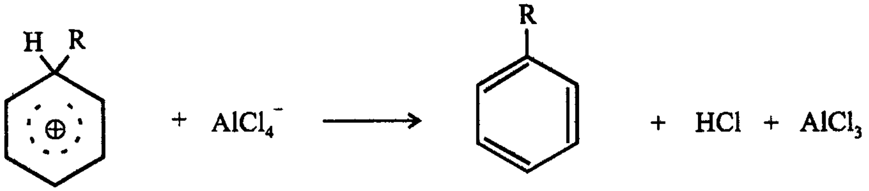
$$\mathrm{RCl + AlCl_3} \rightleftharpoons \underset{\text{carbocation}}{\mathrm{R^{\oplus}}} + \mathrm{AlCl_4^-}$$

(ii) Attack of electrophile on aromatic ring



Alkyl carbocation attacks the benzene ring and forms an intermediate carbocation which is stabilized by resonance.

(iii) Loss of proton



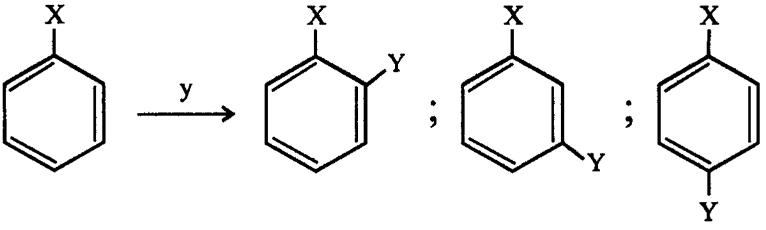
(if R = CH_3, the final product is toluene)

Lewis acid $AlCl_3$ helps to generate the electrophile R^+ by abstracting Cl^- and forming $AlCl_4^-$.

6.7 ORIENTATION EFFECT OR ORIENTING INFLUENCE OF THE SUBSTITUENTS

All the six hydrogen atoms of benzene nucleus are identical; hence if one group (say X) is introduced into the benzene nucleus only one product is obtained. On the other hand, if a second substituent (say Y) is introduced in a monosubstituted derivative, three isomeric disubstituted products are possible.

However, experiments have revealed that all the three products are never formed in equal quantities and the main product is either a mixture of *ortho–* and *para –* isomers (*m–* isomer being negligible in amount) or only the *meta – isomer* (*o–* and *p–* isomer being negligible in amounts).



Monosubstituted derivative — *ortho–* *meta–* *para–*

Disubstituted derivatives

Further experiments have revealed that it is the nature of the group already present (X in above case) on the benzene nucleus that directs the incoming group

(Y in above case) either to ortho and para positions (both) or only to meta position. *This effect of the group already present on the nucleus is known as directive influence of the group or orientation effect.* On the basis of this effect all the known groups in organic chemistry have been classified into two types.

1. ***o,p* – directing groups:** *These groups tend to direct the incoming group mainly to the ortho and para positions. Further, the presence of these groups, except halogens, enhances further electrophilic substitution in the benzene nucleus (i.e., they activate the nucleus) and hence they are known as activating groups. Such groups are:*

$-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OR$, $-CH_3$, $-CH_2-R$, $-Cl$, $-Br$, $-I$, $-C_6H_5$.

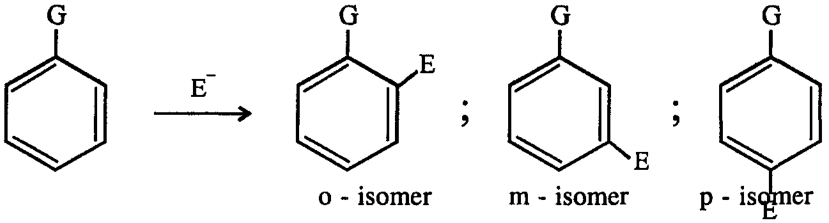
2. ***m* – directing groups:** *These groups tend to direct the new entering group mainly in the meta position. Further the presence of these groups hinders further electrophilic substitution (i.e., they deactivate the benzene ring) and hence they are known as deactivating groups.* Such groups are:

$-NO_2$, $-CN$, $-SO_2Cl$, $-CHO$, $-COR$, $-COOH$, $-COCl$, $-COOR$

6.7.1 Electronic Interpretation of Orienting Influence of the Substituents

The process of finding the relative positions of various groups attached to the nucleus in an unknown derivative is termed *orientation.*

If a monosubstituted benzene, C_6H_5G, undergoes further electrophilic substitution, the new group can enter any one of the three positions, viz., ortho, meta or para with respect to the group already present in the ring.



(G is the group already present in monosubstituted benzene)

Generally a mixture of all the three isomers is formed. The relative proportions of each isomer present in the mixture, for the monosubstituted benzene having a particular functional group is given in the following table.

Group	*Ortho(%)*	*Para(%)*	*Meta(%)*
F	12	88	trace
Cl	30	70	trace
Br	37	62	1
I	38	60	2
OH	50 - 55	45 - 55	trace
CH_3	37	62	1
$NHCOCH_3$	19	79	2
NO_2	6.4	0.3	93.3
COOH	19	1	80
CHO	o + p = 28		72
$N(CH_3)^+$	–	11	89
SO_3H	21	7	72
CN	o + p = 19		81

From the above table, it can be visualised that there are two types of substituent groups. In the presence of one type of group the new substituent enters mainly in the *ortho* and *para* positions with respect to that group. However, in the case of the other type of groups, the new substituent enters mainly the meta position with respect to the group and the meta isomer constitutes the major product of the reaction. It therefore implies that a group already present in a monosubstituted benzene, exerts directing influence on the new incoming substituent. This directing influence is known as *orientation of substitution.*

It can be seen from above that very few groups lead to all *ortho* and *para* - substitution or all *meta* - substitution. A substitutent which gives 40% or more *meta* - isomer is classified as *m* - directing group.

In general, ortho - para directing groups are $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, $-NHCOCH_3$, - halogens, $-C_6H_5$, and the alkyl groups.

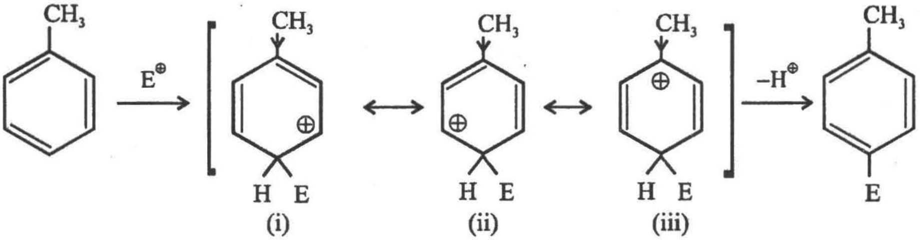
The meta directing groups are $-NO_2$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-SO_3H$, $-CN$ etc.

The substituent G already present in the ring not only decides the *orientation of substitution* but also effects the reactivity of the ring towards further substitution. For example *ortho - para* directing groups, in general, activate the aromatic ring, and hence further substitution occurs more quickly than in benzene. Halogens, however, constitute an exception to the above general rule. They are ortho - para directing and yet, further substitution reaction in their case, becomes slower and somewhat difficult than a similar substitution reaction carried out with benzene itself. Therefore, they are said to be deactivating.

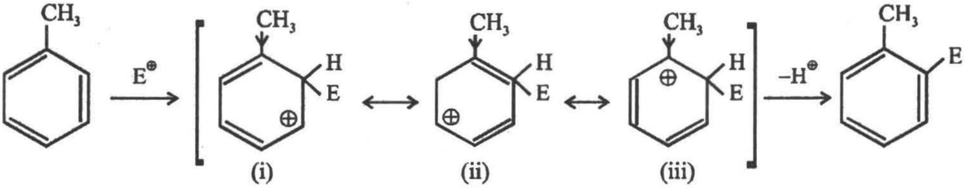
Unlike the ortho - para directing groups, the meta directing groups have always been found to deactivate the ring, i.e., further substitution reactions become more difficult and slower than a similar action with benzene itself.

Toluene

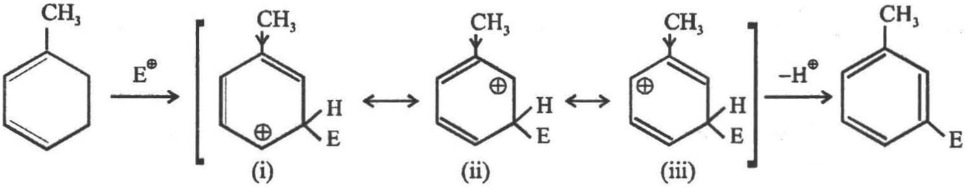
1. *CH_3 group is ortho - para directing and electron releasing group.*
2. When a electrophile (E^+) attacks toluene at the para position the resulting intermediate (transition state) is having the following resonance forms.



The intermediate from ortho attack will be having the following contributing forms.



When the attack occurs at the meta position, resonance forms of the intermediate will be as follows:

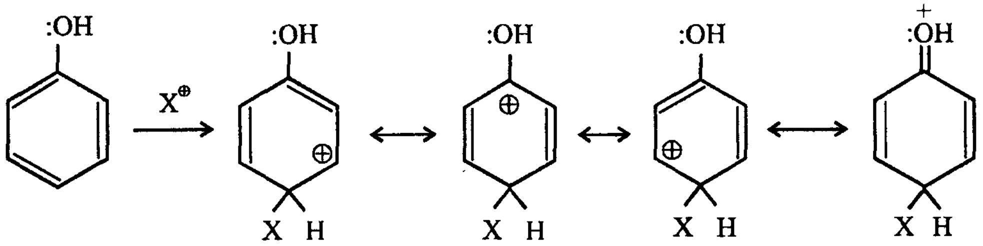


Due to the electron - donating effect of methyl group, one of the resonance forms obtained from ortho or para attack gets stabilised more. This form has positive charge situated on the carbon to which the methyl group is attached. Similar stabilisation of the intermediate does not occur when the attack occurs at the meta position. It means that a more favourable transition state (intermediate) results when the attack occurs at the *o*– and *p*–position of toluene. This explains the ortho- and para - directing influence of the methyl group on the compound.

Phenol

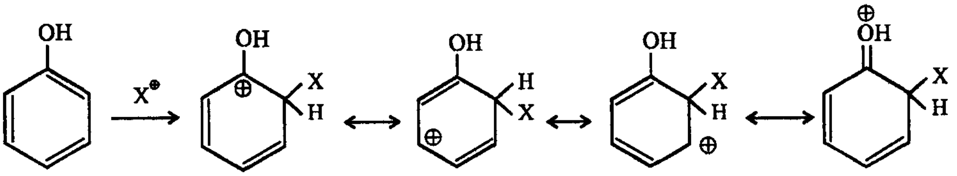
The OH group in phenol is ortho, para directing and activating group.

In phenol, electrophilic attack at the p-position gives rise to an intermediate represented by the following resonance forms:



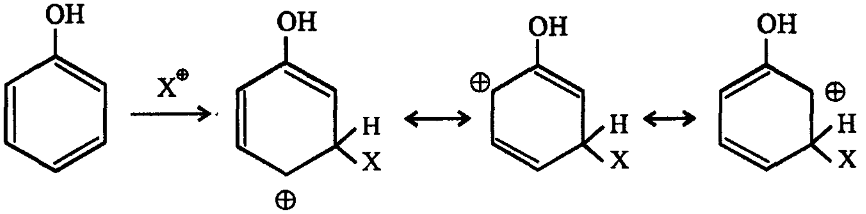
Among these forms the last one is particularly important because its contribution is maximum, as it has an additional bond. A new bond would stabilize a structure approximately by an amount equal to the bond energy.

Electrophilic attack at ortho position.



The same type of stabilization of the intermediate occurs if the attack occurs at the o-position of phenol.

When the attack occurs at the meta position, the resulting intermediate will have resonance forms shown as follows:



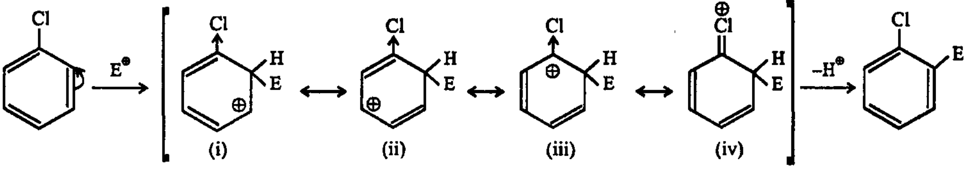
It can be seen that there are only three resonance forms in this case. Further, the stabilization of intermediate by a resonance form with an additional double bond that occurs when the attack is at *o*– or *p*– position is absent if the attack is at the *m*-position. Hence, the –OH group of phenol would act as a powerful *o*–, *p*–directing group.

Oxygen having an electron withdrawing inductive effect (–I) also tends to make the intermediate less stable. But the magnitude of this effect is much smaller than the resonance effect (+R). Therefore, the net effect would be large stabilization of the intermediate.

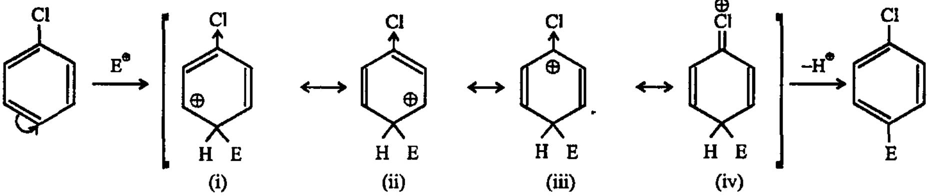
Chlorobenzene

The following resonance forms are obtained for the intermediates formed by the attack at ortho, para and meta positions, in the case of chlorobenzene.

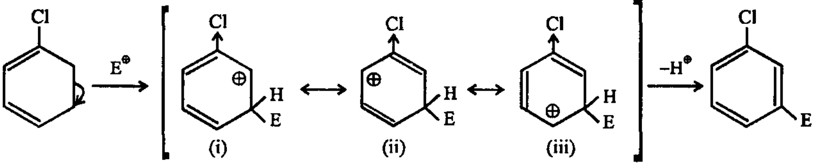
ortho attack



para attack



meta attack



In the case of attack at meta position,

(i) there are only three resonance forms.

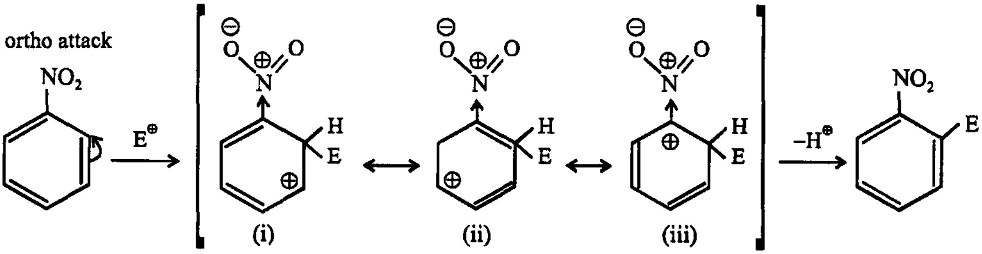
(ii) the stabilization of intermediate by a resonance form with an additional double bond that occurs if the attack occurs at the ortho- or para position is absent. Hence, the –Cl group of chlorobenzene would act as a powerful *o*–, *p*– directing group.

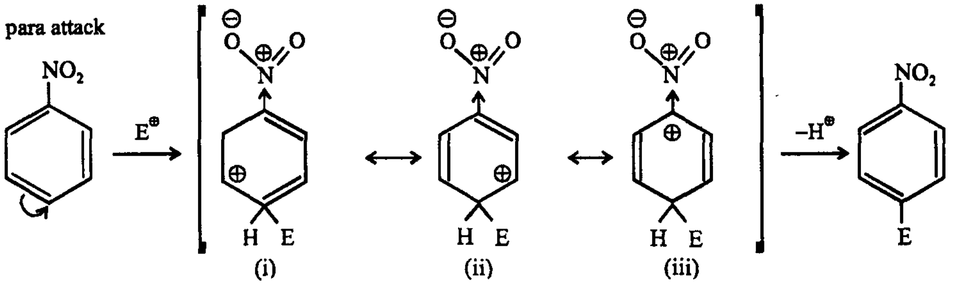
In the case of chlorine, there also exists the electron - withdrawing inductive effect like that of oxygen. But in this case the two effects are almost equal in magnitude. The inductive effect tends to deactivate all positions. The molecule gets activated at the *o*– and *p*– positions due to resonance, but gets deactivated due to the electronegativity of chlorine atom. The net result would be that chlorobenzene undergoes substitution at the ortho or para position at a *slower* rate.

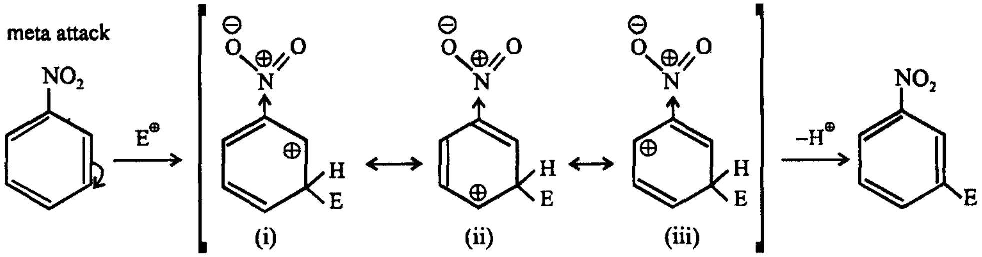
Nitrobenzene

In case of nitrobenzene, the nitro group is meta directing. This can be understood by examining the resonance forms of the intermediate that are obtained by the electrophilic attack on nitrobenzene at *o*–, *p*– and *m*-positions.

ortho attack







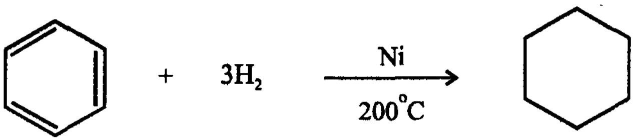
It can be seen that ortho or para attack gives rise to an intermediate with a resonance form in which the positive charge resides on the carbon atom to which the NO_2 group is attached. This particular resonance form contributes little to the stability of the intermediate because the nitrogen of the nitro group also carries a positive charge. Thus, *o*– or *p*–substituted intermediate actually have only two resonance forms contributing to its structure while the meta substituted intermediate has three. Thus the latter would be relatively more stable and its formation gets favoured. In addition to the resonance effect, the inductive effect of the nitro group must also be taken into account. As the nitro group is an electron withdrawing group, it deactivates the benzene ring. Hence, attack of an electrophile on nitrobenzene molecule is difficult. However, if the reaction does take place, it occurs slowly and gives rise to a meta product.

Thus, by the application of resonance theory and by considering the inductive effects, it becomes possible to predict whether a particular substituent in a benzene ring is *o*–, *p*-directing or *m*-directing and whether the reaction occurs at a faster or slower rate.

Meta substituted products are also obtained in the case of benzoic acid, benzaldehyde and benzene sulphonic acid.

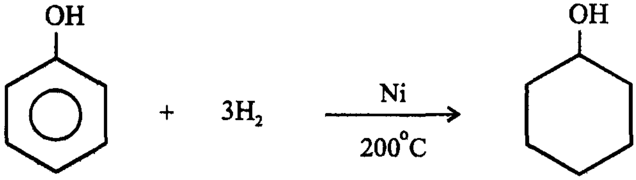
6.8 HYDROGENATION OF AROMATIC COMPOUNDS

Aromatic compounds when subjected to catalytic hydrogenation in the presence of nickel at 200 - 250°C, give cyclohexane or its derivatives. For example, when benzene is subjected to catalytic hydrogenation at 200°C in the presence of nickel, cyclohexane is formed.



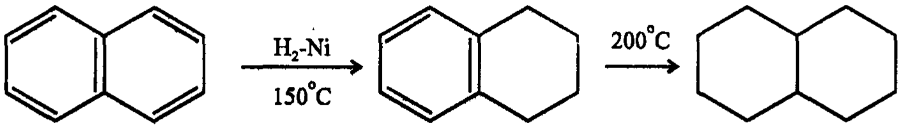
cyclohexane, C_6H_{12}

Similarly, catalytic hydrogenation of phenol, produces cyclohexanol



Cyclohexanol, $C_6H_{11}OH$

When naphthalene is catalytically hydrogenated under pressure using nickel, tetralin and then decahydronaphthalene (decalin) are obtained.

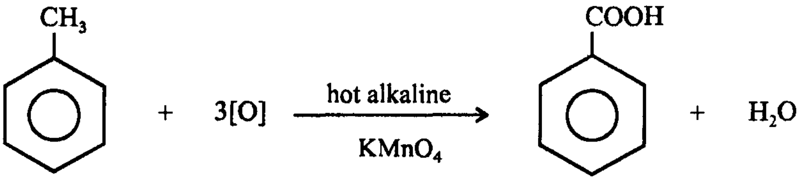


tetralin decalin

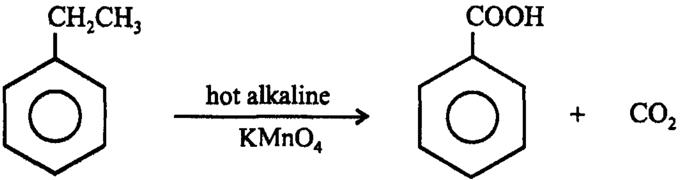
6.9 SIDE - CHAIN OXIDATION

The side chain present in alkyl benzenes is oxidized to –COOH (carboxylic acid) group, when heated with $KMn0_4$. ($K_2Cr_20_7$ or dilute nitric acid can also be used as oxidizing agent) However oxidation of the side chain is difficult when compared to oxidation of alkenes, and requires prolonged treatment with hot $KMn0_4$.

When toluene is oxidized with hot alkaline $KMn0_4$, benzoic acid is formed

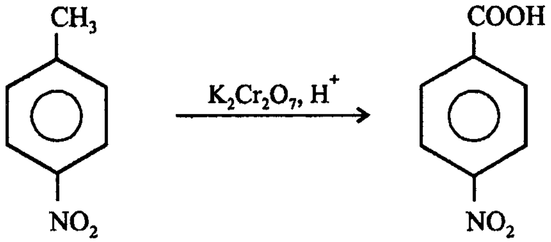


Irrespective of the length of alkyl side chain, alkyl benzenes on oxidation yield benzoic acid

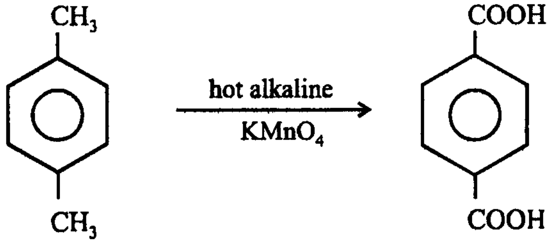


ethylbenzene

p–nitrotoluene on oxidation, gives p–nitrobenzoic acid.



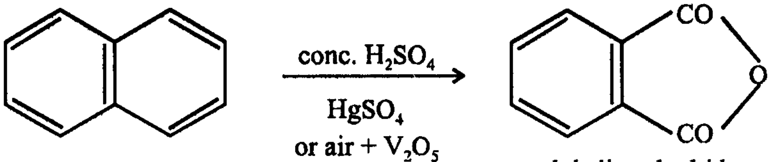
Similarly p–xylene on oxidation gives terephthalic acid



6.10 OXIDATION OF NAPHTHALENE

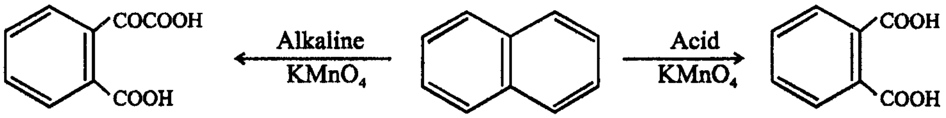
Naphthalene undergoes oxidation to give different products depending on the nature of the oxidising agent. For example,

(i) With concentrated sulphuric acid and mercuric sulphate or air in the presence of vanadium pentoxide, naphthalene is oxidised to phthalic anhydride.



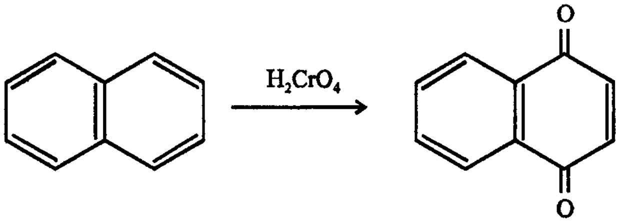
phthalic anhydride

(ii) Potassium permanganate in acid solution oxidises naphthalene to phthalic acid while in alkaline solution it oxidises it to phthalonic acid.



phthalonic acid phthalic acid

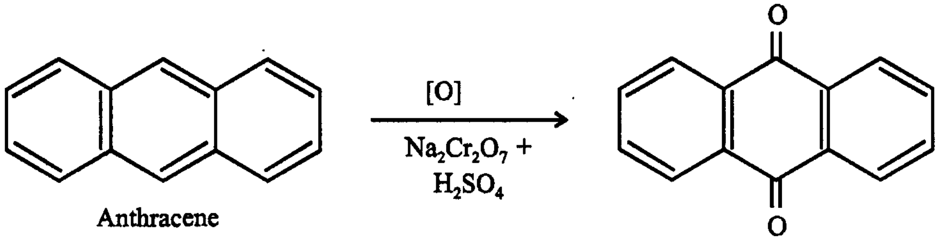
(iii) With chromic acid it is oxidised to 1, 4-naphthaquinone.



1,4 - naphthaquinone

6.11 OXIDATION OF ANTHRACENE

Anthracene on oxidation with concentrated nitric acid or $Na_2Cr_2O_7/H_2SO_4$ yields anthraquinone.



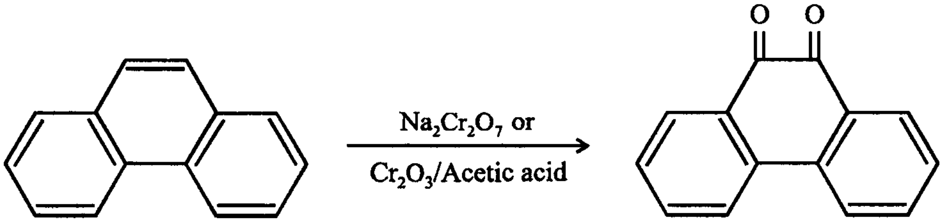
Anthracene

Anthraquinone

Anthraquinone gives pale – yellow odourless, needle - shaped crystals (m.p. 268° C) which sublime on heating.

6.12 OXIDATION OF PHENANTHRENE

When phenanthrene is oxidised by sodium dichromate or chromium trioxide in glacial acetic acid, phenanthraquinone (9, 10 - dihydroxyphenanthrene) is obtained.



Phenanthrene

Phenanthraquinone

IMPORTANT POINTS

- Kekule was the first to propose a satisfactory ring structure of benzene.
- Benzene molecule is made up of 12 σ and 3 π bonds.
- Benzene molecule has a planar structure due to sp^2 hybridisation of all the carbon atoms.
- Benzene ring is stabilized by resonance.
- Resonance energy is the difference in energy between the hybrid form and the most stable canonical (contributing) structure.
- Resonance energy of benzene is 151.2 kJ mol^{-1}. The energy of hybrid form (or) actual structure of benzene is 151.2 kJ less when compared to the Kekule (most stable) form of benzene per mole.
- Molecular orbital theory explains the presence of delocalized (or) extended π bond in benzene (by the overlap of all 6 unhybridized p orbitals) which justifies the extra stability of benzene.

- According to Huckel's rule, monocyclic, planar, conjugated systems containing (4n + 2) π electrons are associated with extra stability and is known as aromatic stability.
- Benzene and its derivatives prefer to undergo aromatic substitution reactions rather than addition reactions as aromaticity is retained in substitution reactions.
- Addition reactions of benzene destruct the aromatic ring (delocalized π bond) and hence the products are less stable.
- Friedel - crafts alkylation of benzene takes place in the presence of Lewis acid, and $AlCl_3$, which generates the electrophile R^+.
- Substituent groups may be divided into two classes:

  (a) Orthopara directors: Examples are $-OH$, $-NH_2$, $-Cl$, $-Br$, $-I$, $-CH_3$, $-C_2H_5$, etc.

  (b) Meta directors: Examples are $-NO_2$, $-COOH$, $-CHO$, $-C \equiv N$, etc.
- Ortho - para directors are electron repelling groups and the meta directors are electron attracting groups. For example, toluene can be more readily nitrated than benzene.
- Halogens deactivate the ring but also cause ortho - para orientation.
- The $-CH_3$ group pushes the electrons towards the benzene ring by inductive mechanism, thus enriching the ortho and para positions more than meta.
- A typical benzene substitution reaction involves preliminary addition of an electrophilic agent to the ring forming a carbonium ion which is followed by loss of a proton to regenerate the conjugated aromatic system.
- In nitration of benzene, the species which brings about nitration giving nitrobenzene is the electrophilic nitronium ion, NO_2^+.
- Sulphonation is carried out by the action of sulphuric acid which proceeds via an electron deficient SO_3H^+ or via an electrophile SO_3 molecule.
- Naphthalene possesses aromatic stability as it contains 10 π electrons (n = 2).
- Anthracene and phenanthrene possess 14 π electrons (n = 3).
- Hydrogenation of benzene and its derivatives result in the formation of cyclohexane and its derivatives.
- Oxidation of alkyl benzenes give benzoic acid, irrespective of the length of the side chain.
- Oxidation of naphthalene with conc. H_2SO_4 and $HgSO_4$ or air and V_2O_5 yields phthalic anhydride.

EXERCISE

Answer the following questions:

1. What are aromatic compounds?
2. State Hùckel's rule
3. What is resonance energy?
4. Draw the Kekule structures of benzene.
5. How would you prove that benzene contains a cyclic structure?
6. Explain any two limitations of Kekule structure.

7. Why benzene readily undergoes electrophilic substitution?
8. Why is $FeCl_3$ used in halogenation of benzene?
9. What is the function of $AlCl_3$ in Friedel Crafts reaction?
10. Draw the structures of (a) anthracene (b) naphthalene.
11. Explain Huckel's rule in naphthalene and anthracene.
12. Arrange the following compounds in the decreasing order of reactivity
    (i) benzene (ii) toluene (iii) nitrobenzene.
13. What is orientation effect?
14. Name a few ortho, para directing groups.
15. Give examples for meta directing groups.
16. Why is toluene nitrated more readily than benzene?
17. Classify the following as ortho - para directing and meta directing groups
    $-CH_3$, $-NO_2$, $-COOH$, $-NH_2$, $-OH$, $-C_6H_5$, $-CHO$, $-Cl$, $-Br$, $-HR$, $-COCH_3$.
18. Halogens are deactivating yet they are ortho - para directing. Explain .
19. What are activating groups? How do they influence the reaction rate? Give example.

0. Convert

benzene ⟶ cyclohexane
naphthalene ⟶ phthalic anhydride
naphthalene ⟶ phthalic acid
anthracene ⟶ anthro quinone.

say Type Questions:

1. Explain the mechanism of aromatic electrophilic substitution in benzene.
2. Explain the mechanism of nitration of benzene.
3. Explain the orientation of substitution in toluene with the help of resonance structures.
4. Discuss the molecular - orbital theory of structure of benzene.
5. Describe the valence bond theory of benzene ring.
6. Write a note on the directive influence of substituents on further substitution in benzene ring.
7. Explain the statement - electron releasing groups are ortho and para directors and electron withdrawing groups are metadirectors.

❖ ❖ ❖

Chapter 7

Organic Halides

SYLLABUS

7.1 INTRODUCTION

The class of organic compounds that are obtained by the replacement of one or more hydrogen atoms in hydrocarbons by a corresponding number of halogen atoms are called *halogen derivatives*. They are further classified as mono, di, tri and tetrahalogen derivatives according to the number of halogen atoms present in the molecule.

7.2 ALKYL HALIDES

Alkyl halides are monohalogen derivatives of alkanes in which one of the hydrogen atom is replaced by a halogen.

$$C_nH_{2n+2} \xrightarrow[+X]{-H} C_nH_{2n+1}X$$

where X = Cl, Br or I. Their general formula is RX where R is an alkyl group and X is a halogen atom. For example:

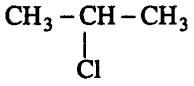
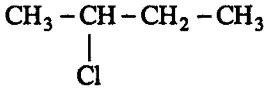
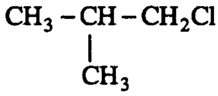
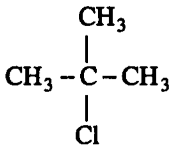
CH_3–Cl	C_2H_5Br	C_2H_5I
methyl chloride	ethyl bromide	ethyl iodide

7.2.1 Nomenclature

In common naming system, these compounds are named as alkyl derivatives of hydrogen halides.

Branched chain alkyl halides may be distinguished as primary, secondary (sec) or tertiary (tert) wherever necessary.

In *IUPAC SYSTEM*, alkyl halides are named as *haloalkanes*. Their systematic name is obtained by prefixing fluoro, chloro, bromo or iodo to the name of the parent hydrocarbon. In complex derivatives, the numeral indicating the position of the halogen atom is prefixed by the conventions of the IUPAC system.

Formula	*Common name*	*IUPAC name*
CH_3-Cl	methyl chloride	chloromethane
CH_3-CH_2-Br	ethyl bromide	bromoethane
$CH_3-CH_2-CH_2Cl$	propyl chloride	chloropropane
 $CH_3-\underset{Cl}{\underset{\mid}{CH}}-CH_3$	isopropyl chloride	2-chloropropane
 $CH_3-\underset{Cl}{\underset{\mid}{CH}}-CH_2-CH_3$	sec-butyl chloride	2-chlorobutane
 $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2Cl$	isobutyl chloride	1-chloro-2-methyl propane
 $CH_3-\overset{CH_3}{\overset{\mid}{\underset{Cl}{\underset{\mid}{C}}}}-CH_3$	tert-butyl chloride	2-chloro-2-methyl propane

7.2.2 Classification of Alkyl Halides

In alkanes there are four types of carbon atoms.

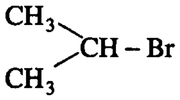
A carbon atom attached to only one (or none) carbon atom is known as *primary carbon atom.*

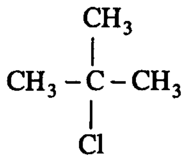
A carbon atom attached to two other carbon atoms is known as *secondary carbon atom.*

A carbon atom attached to three other carbon atoms is known as *tertiary carbon atom.*

A carbon connected to four other carbon atoms is known as *quaternary carbon atom.*

Alkyl halides are classified as primary, secondary and tertiary alkyl halides, depending on the type of carbon to which the halogen atom is attached. For example,

CH_3CH_2Cl	primary alkyl halide	ethyl chloride
$(CH_3)_2-CH-CH_2Cl$	primary alkyl halide	isobutyl chloride
 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH-Br$	secondary alkyl halide	isopropyl bromide



$CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3$

tertiary alkyl halide tert-butyl chloride

7.2.3 Isomerism in Alkyl Halides

Alkyl halides exhibit structural isomerism. It is the phenomenon of existence of two or more compounds with same molecular formula, but different structural arrangement.

Chain Isomerism

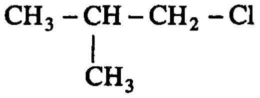
It is a type of structural isomerism exhibited by isomeric alkyl halides, that *differ in the number of carbon atoms forming the parent chain. Alkyl halides that have same molecular formula but differ in the length of the parent chain, are called chain isomers and the phenomenon of their existence is known as chain isomerism.*

For example, n-butyl chloride and isobutyl chloride are chain isomers.

$CH_3-CH_2-CH_2-CH_2-Cl$

n-butyl chloride

1-chlorobutane



$CH_3-\underset{CH_3}{CH}-CH_2-Cl$

isobutyl chloride

1-chloro 2-methyl propane

Positional Isomerism

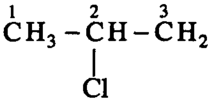
This isomerism arises due to *the difference in the position of the halogen atom in alkyl halides having same molecular formula. The compounds are called positional isomers and the phenomenon is called positional isomerism.*

For example, propyl chloride and isopropyl chloride exhibit positional isomerism.

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-Cl$

propyl chloride

1-chloropropane



$\overset{1}{C}H_3-\underset{Cl}{\overset{2}{C}H}-\overset{3}{C}H_2$

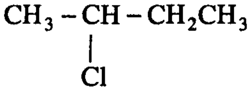
isopropyl chloride

2-chloropropane

n-butyl chloride and secondary butyl chloride exhibits positional isomerism.

$CH_3-CH_2-CH_2-CH_2-Cl$

1-chlorobutane



$CH_3-\underset{Cl}{CH}-CH_2CH_3$

sec.butyl chloride

2-chlorobutane

7.3 METHODS OF PREPARATION OF ALKYL HALIDES

Alkyl halides may be prepared by the following general methods.

(1) **From alcohols:** Action of hydrogen halides (or) phosphorus halides (or) thionyl chloride on alcohols yield alkyl halides. For example,

(a) $CH_3CH_2OH + HCl\uparrow \xrightarrow[ZnCl_2]{\text{anhy}} CH_3CH_2Cl + H_2O$

(b) $CH_3CH_2OH + HBr \xrightarrow[+ H_2SO_4]{NaBr} CH_3CH_2Br + H_2O$

(c) $3\ CH_3CH_2-CH_2OH + PCl_3 \longrightarrow 3\ CH_3CH_2CH_2Cl + H_3PO_3$

(d) $3\ CH_3CH_2CH_2OH + PBr_3 \longrightarrow 3\ CH_3CH_2CH_2Br + H_3PO_3$

(e) $CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$

(f) $CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2\uparrow + HCl\uparrow$

In general, $ROH \xrightarrow[\text{(or) } (P + X_2)]{HX \text{ or } PX_3} RX$

This reaction is a nucleophilic substitution reaction and is an important method for the preparation of primary alkyl halides.

Phosphorous halides and thionyl chloride are preferred to hydrogen halides, as alcohols tend to undergo dehydration in the presence of acids.

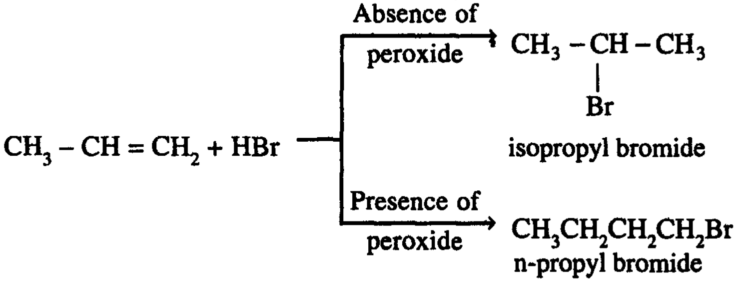
The order of reactivity of various alcohols follows the order.

primary > secondary > tertiary

(2) **From alkenes:** Addition of hydrogen halides to alkenes, yield alkyl halides. For example

$$CH_2=CH_2 + HBr \longrightarrow CH_3-CH_2-Br$$

ethene ethyl bromide



$$CH_3-CH=CH_2 + HBr \xrightarrow[\text{peroxide}]{\text{Absence of}} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

isopropyl bromide

$$CH_3-CH=CH_2 + HBr \xrightarrow[\text{peroxide}]{\text{Presence of}} CH_3CH_2CH_2CH_2Br$$

n-propyl bromide

$$RCH=CH_2 + HCl \longrightarrow RCH_2CH_2Cl$$

7.4 NUCLEOPHILIC SUBSTITUTION REACTIONS

The carbon-halogen bond in alkyl halide is polar. When a stronger nucleophile approaches an alkyl halide, the halogen atom along with its bonding electron pair is replaced by the incoming nucleophile, which forms a new bond with the carbon atom of the alkyl group.

$$\overset{\delta^+}{R}-\overset{\delta^-}{X} \xrightarrow{:OH^-} R-OH + :X^-$$

The substitution reaction in which a weaker nucleophile is substituted (replaced) by a stronger nucleophile (base, electron rich group) is called nucleophilic substitution reaction (S_N). 'S' stands for substitution and 'N' stands for nucleophilic.

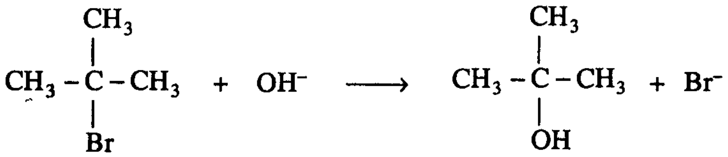
7.4.1 Mechanism of Nucleophilic Substitution Reactions

A nucleophilic substitution reaction involves two changes viz., (i) breaking the bond between carbon atom and leaving group. (ii) forming a new bond between carbon atom and entering group (incoming nucleophile). Based on kinetic studies, two distinct pathways are suggested for these reactions.

(a) Unimolecular nucleophilic substitution (S_N1)

Nucleophilic substitution reactions that follow I order kinetics (depends on the concentration of alkyl halide alone) and takes place in two steps are called S_N1 reactions.

Hydrolysis of tertiary butyl bromide by alkali resulting in the formation of tertiary butyl alcohol is an example for S_N1 reaction.

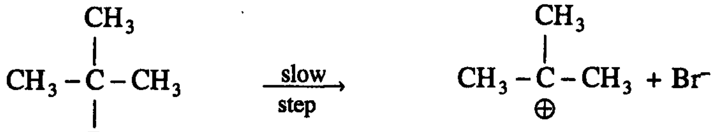


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3 \;+\; OH^- \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3 \;+\; Br^-$$

$$\text{rate} = k\,[(CH_3)_3-C-Br]$$

It is a first order reaction as the rate depends on the concentration of tert butyl bromide alone.

Mechanism: The reaction takes place in two steps. In the first step, the tertiary butyl bromide ionizes to form bromide ion and tertiary butyl carbocation.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3 \xrightarrow[\text{step}]{\text{slow}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\oplus}{C}}-CH_3 + Br^-$$

tert. butyl carbonium ion

The first step, being the slow step is the rate determining step (rds) and hence the rate of the reaction depends only on the concentration of the alkyl halide and is independent on the concentration of alkali. Thus the reaction follows I order.

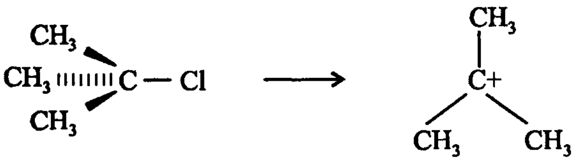
Alkyl groups being electron releasing (+I), push the electrons towards the carbon carrying halogen and facilitates the cleavage of C–Br bond.

In the second step, the hydroxide ion (OH^-) attacks the positively charged carbon atom of the carbocation.

$$(CH_3)_3\,C^+ \quad + OH^- \longrightarrow (CH_3)_3-C-OH$$

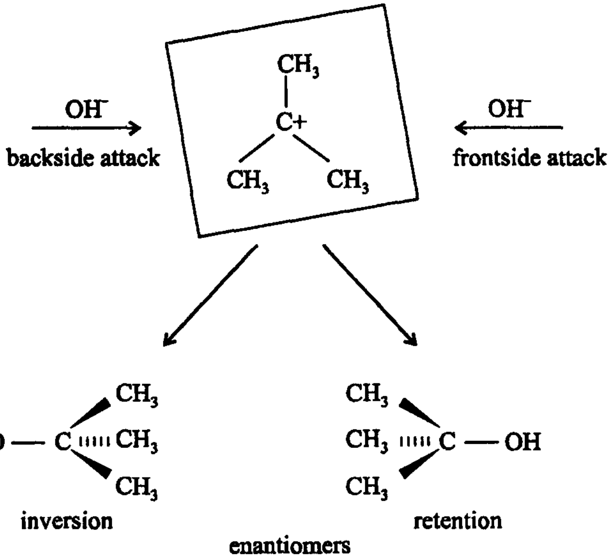
tert. butyl alcohol

Stereochemistry: The carbonium ion formed is planar in shape and the C – C – C bond angle is found to be 120°.


planar carbocation

In the second step, the OH^- ion can attack the carbonium ion either from the front side (same side of the leaving group) (or) from the back side (rear side). This leads to the formation of two enantiomers, in one there is retention in configuration and in another there is inversion in configuration.

The enantiomer with inversion in configuration is a predominant product.



(b) Mechanism of bimolecular nucleophilic substitution (S_N2)

Nucleophilic substitution reactions that follow second order kinetics and takes place in one step are called S_N2 reactions. The rate determining step is the formation of intermediate transition state where both the reactant molecules undergo simultaneous covalency change. i.e., in an S_N2 reaction, breaking of bond between the carbon atom and leaving nucleophile and making of bond between the carbon atom and incoming nucleophile occurs simultaneously.

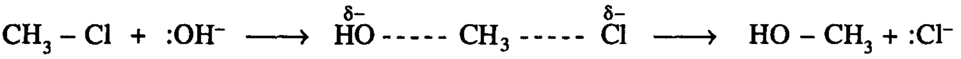
Hydrolysis of primary alkyl halides with aqueous alkali follows S_N2 mechanism. For example, methyl chloride undergoes hydrolysis with sodium hydroxide following second order kinetics.

$$CH_3Cl + NaOH \longrightarrow CH_3OH + NaCl$$

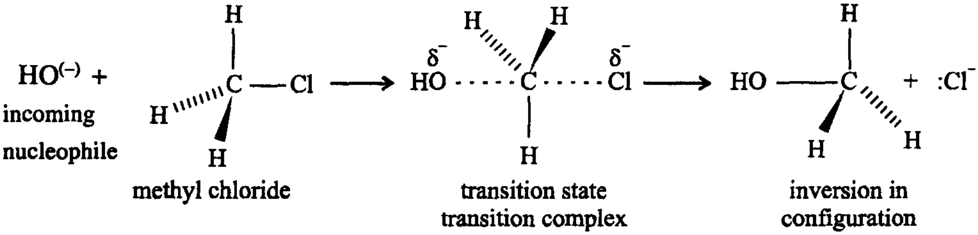
$$\text{rate} = k\,[CH_3Cl]\,[NaOH]$$

This is a second order reaction as the rate depends on concentration of both the substrate and the reagent.

The mechanism of the reaction is depicted as under.



$$CH_3-Cl + :OH^- \longrightarrow \overset{\delta-}{HO}\text{-----}CH_3\text{-----}\overset{\delta-}{Cl} \longrightarrow HO-CH_3 + :Cl^-$$



In methyl chloride, due to the polar nature of C–Cl bond, C acquires a partial positive charge and Cl acquires a partial negative change.

The incoming nucleophile (OH^-) attacks the positively charged carbon atom from the back (or) rear side (at the face farthest from Cl) in order to avoid repulsion between the negatively charged leaving nucleophile and incoming nucleophile.

In the transition state, the carbon atom is partially bonded to both –OH and –Cl groups and both the groups carry a partial negative charge. (The C–Cl bond is not completely cleaved and the C–OH bond is not completely formed). The carbon atom and the three hydrogen atoms are in the same plane (sp^2 hybridization), the bond angles being 120°.

The alcohol formed has inverted configuration (OH group occupies a position opposite to that of Cl) when compared to the alkyl halide. The reaction is said to proceed with inversion of configuration usually referred to as *'Walden inversion'*.

7.4.2 Reactivities of alkyl halides in S_N1 and S_N2 mechanism

The relative reactivity of alkyl halides involved in S_N1 reaction has been dependent upon stability of carbocation formed by them. Therefore, the reactivity of alkyl halides follow the order.

benzyl halides, allyl halide > tertiary halides >
secondary halides > primary halides > methyl halides

Reactivity of alkyl halides in S_N2 mechanism has been governed by steric factors. When the alkyl groups are bulkier, the incoming (or) attacking nucleophile experiences steric hindrance and reduces the probability of formation of intermediate transition state. Thus, the bulkier the group, the lesser is its reactivity towards S_N2 reaction. The reactivity of various alkyl halides follow the order.

methyl halides > primary halides > secondary halides > tertiary halides

In general primary alkyl halides prefer to follow S_N2 mechanism whereas tertiary alkyl halides follow S_N1 mechanism. Secondary alkyl halides may undergo both, except in very polar solvents, where S_N2 predominates.

7.4.3 Factors influencing the mechanism of substitution

In addition to the nature of alkyl halides, various other factors influence the mechanism of nucleophilic substitution.

(a) Nature of alkyl groups in the alkyl halides

Bulky R groups favour S_N1 over S_N2, since it is difficult for the nucleophile to attack the reactive carbon ($C^{\delta+}$) due to steric hindrance. The alkyl halide is more likely to ionize before S_N2 attack can take place.

(b) Nature of the nucleophilic reagent

Strong nucleophilic reagents (e.g., OH^- and RO^-) favour S_N2 mechanism as they are powerful enough to pushout the halide ion. Weak nucleophilic reagents favour S_N1 mechanism as they can attack the already formed carbocation more readily

(c) Concentration of the nucleophilic reagent

Higher concentration of the nucleophile favours S_N2 mechanism, whereas lower concentration of the nucleophile favours S_N1 mechanism.

(d) Nature of the solvent

Polar and protic solvents favour S_N1 mechanism since they help in the ionization of alkyl halides by solvating R^+ and X^- ions. Non polar solvents favour S_N2 mechanism, as the transition state is less polar than the reactants and the nonpolar solvents can solvate the transition state more effectively than the reactants.

(e) Electrophilic catalysts

Lewis acids like H^+, Ag^+, $ZnCl_2$ and $AlCl_3$ favour S_N1 over S_N2 as they can accept the electrons from the leaving nucleophile (X^-) and helps in the ionization of R–X.

7.4.4 Distinguishing features of S_N1 and S_N2 mechanisms

S_N2 Reactions	*S_N1 Reactions*
Most of the S_N2 reactions follow second order kinetics.	All the S_N1 reactions follow first order kinetics.
The attack takes place exclusively from the back side.	The nucleophile can attack the carbon carrying the halogen from the back as well as front sides although the back side attack predominates.
Complete inversion of configuration takes place.	In case of optically active alkyl halides, partial racemisation takes place.
Reaction rate is determined mainly by steric factors.	Reaction rate is determined mainly by electronic factors.
The order of reactivities of alkyl halides is: methyl > primary > secondary > tertiary halides.	The order of reactivities of alkyl halides is: tert > sec > pri > methyl halides.
Favoured by strong nucleophiles.	Favoured by mild nucleophiles.
Favoured by high concentration of the nucleophiles.	Favoured by low concentration of the nucleophiles.
Favoured by solvents of low polarity.	Favoured by solvents of high polarity.

7.5 ELIMINATION REACTIONS

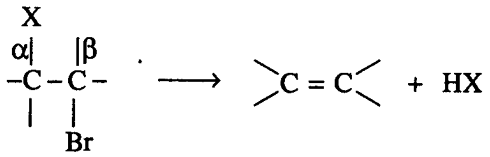
An elimination reaction is one in which a molecule loses two atoms or groups, without being replaced by other atoms or groups. Generally, an elimination reaction involves loss of atoms or groups on vicinal (adjacent) carbon atoms resulting in the formation of a π-bond between these carbon atoms. Thus, an elimination reaction is the reverse of an addition reaction.

$$CH_3CH_2Br \xrightarrow{\text{alc. KOH}} CH_2 = CH_2$$

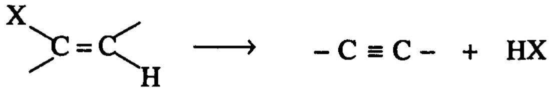
$$C_2H_5OH \xrightarrow{H^+} CH_2 = CH_2$$

Elimination reactions are mainly of two types:

(a) β-Elimination reactions: If the two atoms or groups are lost from the adjacent carbon atoms, it is called a β-elimination or 1, 2-elimination.



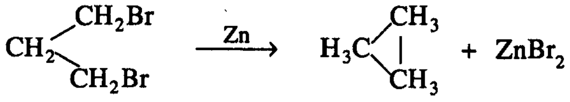
alkyl halide



vinyl halide

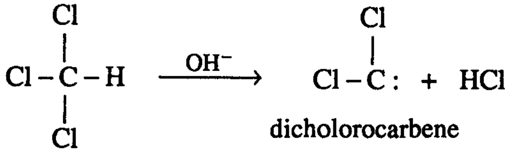
It gives rise to a new double or triple bond.

Similarly 1,3- and even 1,4-elimination are also known.



1,3–elimination

(b) α-Elimination reactions: If the two atoms or groups are lost from the same carbon atom, it is called an α-elimination or 1,1 elimination. The most common example of this type is the generation of dichlorocarbene from chloroform.



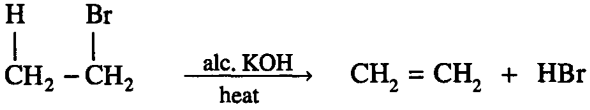
$$Cl-\overset{Cl}{\underset{Cl}{C}}-H \xrightarrow{OH^-} Cl-\overset{Cl}{C}: + HCl$$

dicholorocarbene

The carbene thus formed is not stable, but it has been trapped in various ways. Only few examples of α-elimination reactions are known.

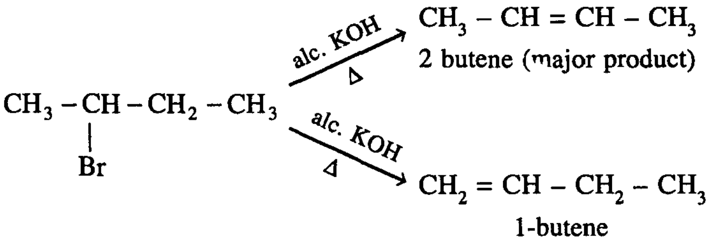
7.5.1 Elimination reactions leading to Zaitsev product (Zaitsev or Saytzeff Rule)

Alkyl halides when boiled with alcoholic potassium hydroxide produce olefins. The reaction involves the elimination of a molecule of hydrogen halide and is known as *dehydrohalogenation reaction.*



$$\underset{\mathrm{CH_2}}{\overset{\mathrm{H}}{|}}-\underset{\mathrm{CH_2}}{\overset{\mathrm{Br}}{|}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \mathrm{CH_2=CH_2} + \mathrm{HBr}$$

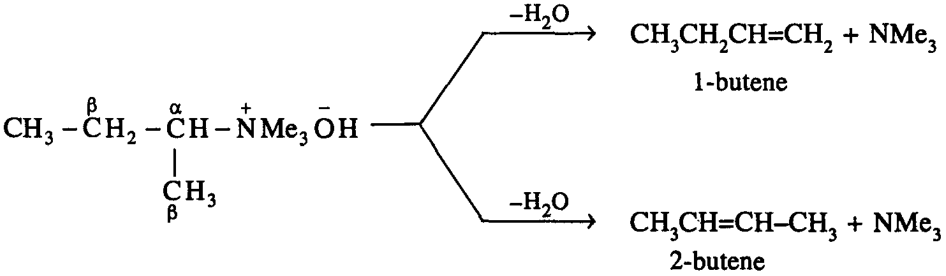
During dehydrohalogenation reaction halogen from one carbon atom and hydrogen from the adjacent (not from the same) carbon atom are eliminated in the form of HX. *If the dehydrohalogenation of alkyl halides can yield more than one alkene, then the product is the most highly substituted alkene* **(Saytzeff rule).** For example, 2 - bromobutane, when boiled with alcoholic KOH, yields 1- and 2-butenes in which the highly substituted 2-butene is the main product.



2-butene is thermodynamically more stable than 1-butene and hence it is formed predominantly. Usually 1,2 - elimination reactions involving alkyl halides and alcohols follow Saytzeff's rule.

7.5.2 Hofmann's rule

This rule deals with the structural orientation of the alkenes formed by 1, 2 - elimination reactions. The rule states that *the least substituted product is the predominant product in a 1, 2 - elimination reaction involving alkene formation.* For example, when sec - butyl trimethyl ammonium hydroxide is heated, 1-butene will be formed predominantly.



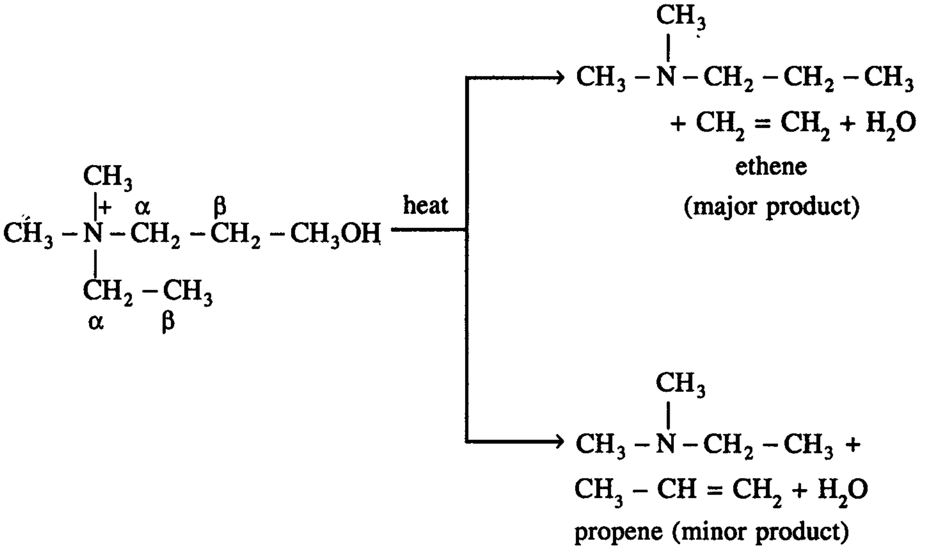
In this reaction NMe_3 (trimethyl amine) is a leaving group and the OH^- ion abstracts a proton from the β-carbon atom to form a molecule of H_2O. In the above example there are two β carbon atoms. If the CH_3 group gives up a proton, 1-butene will be formed. If the CH_2 group gives up a proton 2-butene will be formed. Formation of 1-butene as major product is explained on the basis of acidity of hydrogen atom and steric factor.

The β H of CH_3 group is more acidic and is readily abstracted by the OH^- ions than the β hydrogen of CH_2 group (Due to +I effect of ethyl group the β-hydrogen of CH_2 group is less acidic).

The steric effect makes the crowded β carbon unfavourable for giving up the H atoms. If the β - C is less crowded, the abstraction of hydrogen from that carbon by OH^- is more effective. Thus, acidity and steric factor favours formation of 1-butene over 2-butene in the above example.

Usually ammonium, sulphonium and phosphonium compounds give the Hofmann products by 1, 2 elimination reactions.

Another example is, when ethyl dimethyl-n-propyl ammonium hydroxide is subjected to pyrolysis, the least substituted (least alkylated double bond) alkene ethene, is obtained as major product (follows Hofmann's rule).



In this example, OH^- abstracts the proton preferably from the β carbon of ethyl group as it is less crowded and hence OH^- experience less steric repulsion. The removal of proton from the β carbon of propyl group is not favoured due to steric factor. Hence the major product is ethene and not propene.

7.5.3 E_1 and E_2 Eliminations

1, 2 - elimination reactions are classified under two heads, depending on the mechanism of the reaction.

E_1 reactions: *Elimination reactions in which the rate determining step involves only one species are called E_1 reactions.* These reactions generally *take place in two steps and follow first order kinetics.* (E_1 - elimination I order).

E_2 - reactions: *1, 2 - elimination reactions in which the rate determining step involves two species and take place in a single step are called E_2 elimination reactions. These reactions generally follow second order kinetics.* (E_2 – elimination II order).

Mechanism of E_1 reactions

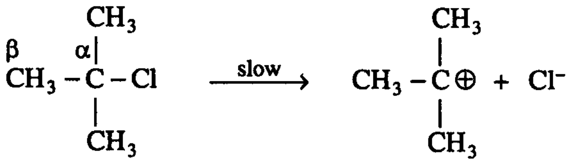
E_1 reactions take place in two steps via a carbonium ion intermediate. *The first step involves the formation of carbonium ion. It is the rate determining step.* The second step involves loss of proton from the carbon atom adjacent to the carbon bearing the positive charge. This step is relatively faster than step 1.

$$\text{rate} = k\,[\text{substrate}]$$

As the rate determining step involves only one species, these type of reactions follow I order kinetics.

For example, tertiary butyl chloride when boiled with alcoholic potassium hydroxide undergoes elimination via E_1 mechanism and yields 2-methylpropene.

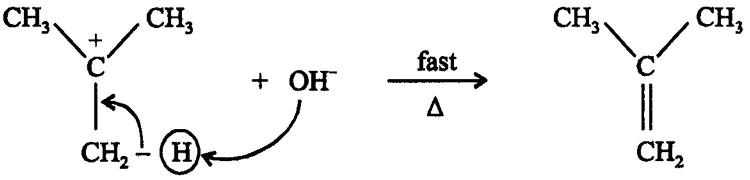
Step I. Formation of t-butyl carbonium ion



$$\overset{\beta}{CH_3}-\overset{\overset{CH_3}{\alpha|}}{\underset{\underset{CH_3}{|}}{C}}-Cl \xrightarrow{\text{slow}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\oplus + Cl^-$$

$$\text{rate} = k\,[(CH_3)_3\,C\cdot Cl]$$

Step II. Loss of proton from adjacent or β carbon.



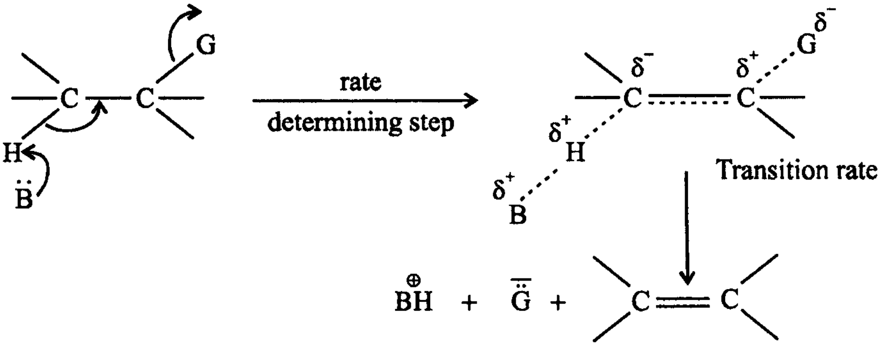
2-methyl propene

E_1 reactions generally lead to Saytzeff's products, i.e., the more substituted alkene (more stable) is formed.

The factors that influence the rate of S_N1 reactions also influence the rate of E_1 reactions. This is because in both the reactions the rate determining step is the formation of intermediate carbonium ion.

Mechanism of E_2 reactions

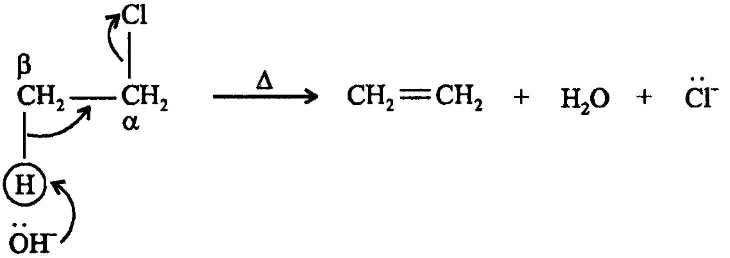
E_2 eliminations take place in single concerted step which involves breaking of two sigma bonds and formation of one π bond. An E_2 reaction is initiated by a base, which pulls out the proton.



Since the rate determining step involves both the substrate and the base, it follows second order kinetics.

rate = k [substrate] [base]

For example, ethyl chloride when boiled with alcoholic KOH yields ethene via E_2 mechanism.



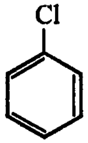
In E_2 reactions the leaving group (Cl) leaves the substrate with a pair of electrons (Cl^-), leaving a vacant p-orbital on α carbon atom of the substrate. On the other hand, an electrophile usually a proton, leaves the substrate as cation, whereby the β-carbon atom of the substrate contains a pair of electrons in the p-orbitals. The p orbitals of α and β carbon lying in the same plane undergo side ways overlap resulting in the formation of π bond.

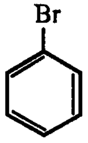
7.6 AROMATIC HALOGEN COMPOUNDS

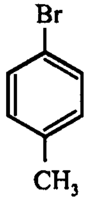
The halogen derivatives of aromatic hydrocarbons are divided into two classes namely, (a) *aryl halides* and (b) *arylalkyl halides* or *aralkyl halides.*

Aryl halides are organic compounds in which the halogen atom is attached directly to the carbon atom of the ring. For example,

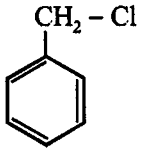
C_6H_5Cl C_6H_5Br $p\text{-}C_6H_4{<}^{Br}_{CH_3}$


chlorobenzene

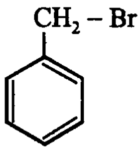

bromobenzene


p-bromo toluene

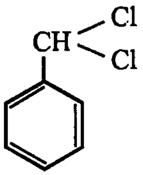
Aralkyl halides are organic compounds in which the halogen atom is attached to the carbon atom of the side chain. For example,



benzyl chloride



benzyl bromide

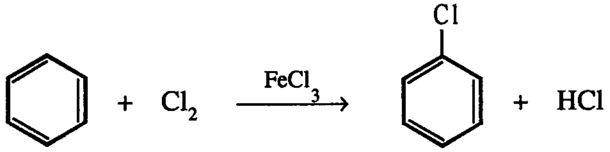


benzal chloride

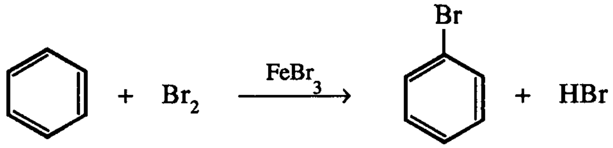
They are often referred to as side chain halogen derivatives.

7.7 PREPARATION OF ARYL HALIDES

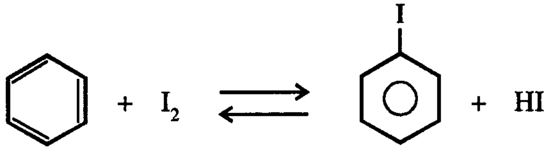
Direct halogenation: Chlorine reacts with benzene in dark and in the presence of halogen carriers (e.g., $FeCl_3$, $AlCl_3$ etc.) to give chlorobenzene.



Bromination of benzene is similar to chlorination.

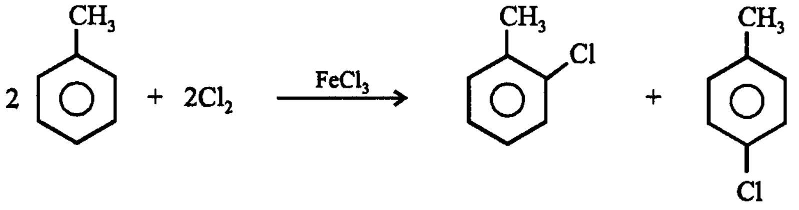


Iodination of benzene is possible only in the presence of strong oxidizing agents like iodic acid, nitric acid etc. Iodination of benzene is a reversible reaction and to prevent the backward reaction HI must be oxidized to I_2 by strong oxidizing agents like conc. HNO_3 (or) iodic acid.



$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Like benzenes, alkyl benzenes when treated with chlorine or bromine at low temperature, in the absence of light, and in the presence of a halogen carrier undergo nuclear halogenation.

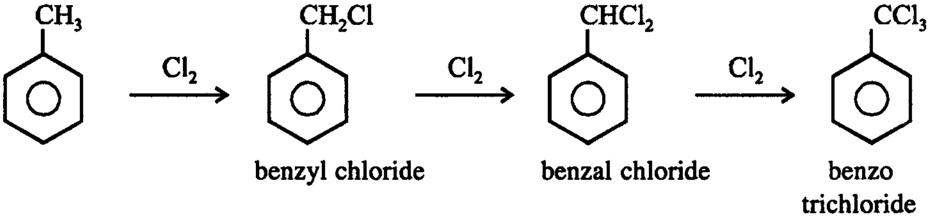


o-chlorotoluene p-chlorotoluene

7.8 PREPARATION OF ARALKYL HALIDES

Side chain halogenation: Alkyl benzenes when treated with chlorine or bromine, at high temperature, in the presence of sunlight and absence of halogen carrier undergo halogenation in the side chain.

When chlorine gas is passed through boiling toluene in the presence of sunlight benzyl chloride, benzal chloride and benzotrichloride are obtained by successively replacing one, two and three hydrogen atoms of toluene.



7.9 RELATIVE REACTIVITIES OF ALKYL, ARYL, ALLYL AND VINYL HALIDES TOWARDS SUBSTITUTION REACTIONS.

Reactivities of different type of halides can be studied by boiling them with alcoholic $AgNO_3$ solution.

$$\text{Alkyl halide} + \underset{\text{(alc)}}{AgNO_3} \xrightarrow{\Delta} \underset{\text{White precipitate}}{AgCl\downarrow}$$

$$\text{Allyl halide} + \underset{\text{(alc)}}{AgNO_3} \xrightarrow{\Delta} \underset{\text{White precipitate}}{AgCl\downarrow}$$

$$\text{Aryl halide} + \underset{\text{(alc)}}{AgNO_3} \xrightarrow{\Delta} \text{No precipitate}$$

$$\text{Vinyl halide} + \underset{\text{(alc)}}{AgNO_3} \xrightarrow{\Delta} \text{No precipitate}$$

An alkyl halide (eg methyl chloride) readily undergoes nucleophilic substitution, on boiling with alcoholic $AgNO_3$ and gives a white precipitate of silver chloride. The C – X bond in alkyl halide is polar and can be readily cleaved & hence alkyl halides undergo substitution readily.

$$CH_3Cl + AgNO_3\ \text{(alc)} \longrightarrow CH_3NO_3 + AgCl\downarrow$$

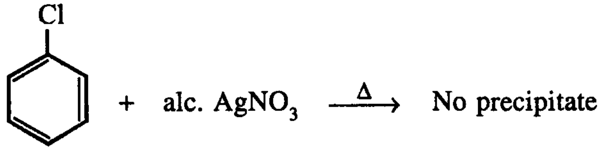
The C – X bond of an allyl halide (e.g., allyl chloride) can also be cleaved readily, as the resulting allyl carbocation is stabilized by resonance. Hence, allyl chloride gives a white precipitate of AgCl readily, when boiled with alcoholic silver nitrate solution.

$$\underset{\text{allyl chloride}}{CH_2=CH-CH_2-Cl} \xrightarrow[\Delta]{\text{alc. }AgNO_3} CH_2=CH-CH_2-NO_3 + \underset{\text{White precipitate}}{AgCl\downarrow}$$

$$[CH_2 = CH - \overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH_2]$$

resonance structures of allyl carbocation

In aryl halides and vinyl halides the C – X bond is very strong, as the lone pair of electrons on halogen atom gets delocalized which gives the C – X bond, partial double bond character. Moreover, the C–X bond is formed by $sp^2 - p$ orbital overlap. This makes the bond short and strong. Thus, it is very difficult to cleave the C–X bond of aryl and vinyl halides and they do not give white precipitate with silver nitrate solution.



$$+ \text{ alc. } AgNO_3 \xrightarrow{\Delta} \text{No precipitate}$$

$$\underset{\text{Vinyl chloride}}{CH_2 = CH - Cl} + \text{ alc. } AgNO_3 \xrightarrow{\Delta} \text{No precipitate}$$

The order of reactivity of various halogen compounds towards nucleophilic substitution is

allyl halide > alkyl halide > vinyl halide > aryl halide

IMPORTANT POINTS

- Halogen derivatives of alkanes are known as haloalkanes.
- The order of reactivity of alkyl halides is RI > RBr > RCl. C – I bond is more reactive because lower energy is required to break the bond.
- The reactivity of alkyl halides follows the order: tertiary alkyl halide > secondary > primary taking into considerations of alkyl group.
- The carbon atom of C – X bond in alkyl halides is a good target for attack by nucleophiles and gives rise to nucleophilic substitution reactions.
- The hydrolysis of primary halides by OH^- ions as nucleophile takes place through S_N2 mechanism in which product is said to have inversion in configuration.
- The hydrolysis of *t*-butyl bromide takes place through S_N1 mechanism. The secondary halides are expected to follow S_N1 and S_N2 mechanism. The order or reactivity of alkyl halides in S_N1 mechanism is allyl > benzyl > tertiary > secondary > primary > methyl carbonium ion because the rate determining step in S_N1 mechanism is the formation of carbonium ion.
- Polar solvents favour S_N1 mechanism. S_N1 mechanism is generally favoured by weak nucleophiles such as H_2O, ROH, etc. and S_N2 mechanism is favoured by strong nucleophiles such as OH^-, OR^-, etc.
- Alkyl halides also undergo eliminations reactions in the presence of a base as nucleophile. The reactivity of alkyl halides follows the order:

  tertiary > secondary > primary and RI > RBr > RCl

- Primary and secondary alkyl halides undergo dehydrohalogenation.
- 2-bromobutane on dehydrohalogenation gives 2-butene as the major product according to Saytzeff's rule.
- 1, 2 elimination reactions follow either E_1 or E_2 mechanism.
- In E_1 reactions the rate depends on the concentration of the substrate alone and follows I order kinetics. These reactions take place in 2 steps.
- In E_2 reactions, the rate depends on the concentration of the substrate and base and follows II order kinetics. These reactions take place in single step.
- Aryl halides are prepared from benzene and their homologues by direct halogenation, in the absence of light and in the presence of halogen carrier.
- Direct iodination of benzene is possible only in the presence of strong oxidizing agents like HNO_3 and HIO_3, which destroy HI and prevent the backward reaction.
- Alkyl halides undergo nucleophilic substitution readily due to polar nature of C – X bond.
- Aryl halides and vinyl halides undergo nucleophilic substitution with difficulty as the lone pair of electrons on halogen atom is involved in resonance, which leads to partial double bond character of the C–X bond.

EXERCISE

Short answer type questions:

1. What are alkyl halides? Give example.
2. How are alkyl halides classified?
3. What do you mean by chain isomerism?

   Explain chain isomerism in alkyl halides with a suitable example.
4. Give the structural formula of the positional isomer of n-propyl chloride.
5. Why is thionyl chloride preferred over hydrogen halides, in the preparation of alkyl halides from alcohols?
6. What are nucleophilic substitution reactions?
7. What are S_N1 and S_N2 reactions?
8. Arrange the following in decreasing order of reactivity towards S_N1 reaction

   CH_3CH_2Cl, $(CH_3)_3C-Cl$ and $(CH_3)_2CHCl$
9. Why do polar solvents favour S_N1 mechanism?
10. Why do strong nucleophile favour S_N2 mechanism?
11. What are elimination reactions?
12. State saytzeff rule. Illustrate with a suitable example.
13. Illustrate Hofmann's rule with an appropriate example.
14. How would you obtain (a) chlorobenzene (b) bromobenzene starting from benzene.
15. Why direct iodination of benzene is not possible?
16. Why aryl and vinyl halides do not give a precipitate with alcoholic silver nitrate solution?

Essay Type Questions:

1. Explain the mechanism of S_N1 reaction with an example.
2. Describe S_N2 mechanism.
3. Explain how S_N2 mechanism leads to Walden inversion.
4. Compare the reactivities of alkyl, aryl allyl and vinyl chlorides towards nucleophilic substitution and justify your answer.
5. Explain the mechanism of E_1 and E_2 with suitable example.

❖ ❖ ❖

Chapter 8

Thermodynamics

SYLLABUS

8.1 INTRODUCTION

Almost all naturally occurring phenomena are accompanied by energy changes. Similarly almost all chemical reactions involve either the absorption or release of heat, a form of energy. Energy is an abstract concept. Energy is not something that can be seen, touched or weighed. *It is defined as capacity to do work.* There are different forms of energy. The most common form is heat. Besides this, there is mechanical energy involved in the motion of all machinery; electrical energy used to run a motor; radiant energy inherent in light and radiation in general; chemical energy present in the fuel and so on. Though the different forms of energy appear different at first glance, they are inter-related to one another and under certain conditions can be transformed from one form to another. *A study of inter-conversion of the various forms of energy in a system constitutes the subject of thermodynamics. Thermodynamics* is also considered as a *science of the relationship between heat and other forms of energy.* The laws of thermodynamics have been developed on the basis of observation and experiments over a long period of time. Though there is no direct proof of laws, the laws can be stated in mathematical form; thus, *thermodynamics is an exact science.*

Thermodynamics is based on three concise statements, the *three Laws of Thermodynamics* that sum up our experiences with energy. Various important generalisations of physical chemistry such as Raoult's law of vapour pressure lowering, law of chemical equilibrium, the phase rule etc., can be deduced from these laws.

The absolute value of energy contained in a system of little importance in thermodynamics, whereas the energy changes associated with changes in system are of considerable importance. Of greater chemical interest is that the equilibrium position of a reacting system can be related to these energy changes and criteria for feasibility of spontaneity of a chemical reaction under a given set of conditions can be laid down.

The only limitation of thermodynamics is, it does not take into consideration the time element in these transformations. It may predict energy changes accompanying a physical process or a chemical reaction, but the rate at which such a transformation proceeds is not considered. It also does not predict the manner in which the transformation takes place.

8.2 SOME BASIC THERMODYNAMIC TERMS

Precise definitions of some of the terms frequently used in thermodynamics is necessary to understand the basic laws and concepts of thermodynamics.

System : *A thermodynamic system is the specific part of the physical universe under observation.*

Surroundings : *The surroundings are the rest of the universe outside the system.* It can affect or be affected by the system. Usually the surroundings are restricted to a region in the immediate vicinity of the system under investigation.

The system's content may range from a small quantity of any substance to the entire universe. The choice of the system and the surroundings is very arbitrary and must be defined clearly.

Boundary: The system is separated from the surroundings by a real or imaginary, rigid or non-rigid boundary.

Consider a gas in cylinder placed in the constant temperature bath maintained at say 298 K. In this case, the substance gas constitutes the system, the walls of the cylinder are the boundaries and the constant temperature bath is the surroundings.

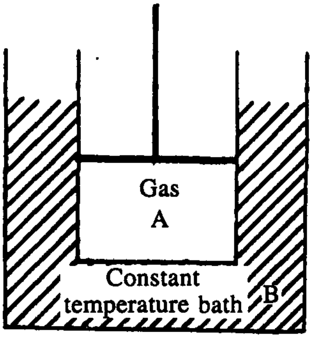
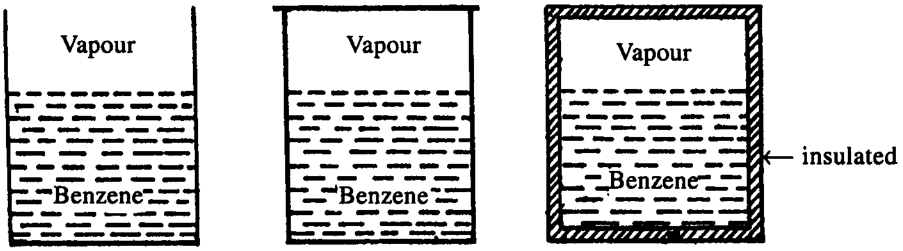


Fig. 8.1: System and surroundings

Types of systems: Even though a system is separated from the surroundings, transfer of heat, matter may be possible. Accordingly, different types of systems are possible.

Open system: *A system in which exchange of both matter and energy (in the form of heat) is possible with the surroundings.* An open container consisting of a volatile liquid, say benzene, in contact with its own vapour constitutes an open system. Energy from the surroundings is taken for the vapourisation of the liquid and the vapour can escape out of the container into the surroundings. There is exchange of both matter and energy with the surroundings.

Closed system: *A system which can exchange energy but not matter with the surroundings.*



Open system Closed system Isolated system

Fig. 8.2: Types of systems

A closed container of the above example can exchange energy with the surroundings but not mass. This will be a closed system

Isolated system: *A system in which no exchange of matter or energy is possible with the surroundings.* There can be no interaction of the system with the surroundings. Now, if the walls of the container in the earlier example are thermally insulated and the container closed, it becomes an isolated system. The system can exchange neither matter nor energy with the surroundings.

Homogeneous system consists of only one phase and its properties are uniform throughout. A mixture of gases, pure liquid, etc., forms a homogeneous system.

Heterogeneous system consists of more than one phase and its properties are not uniform as in a mixture of two immiscible liquids such as oil and water, or a solid in contact with a liquid such as ice and water.

8.2.1 Properties of a System

Certain properties are necessary to describe a system completely. These are macroscopic properties such as pressure, volume, temperature, mass etc. These defining properties of a system are referred to as *state properties or state variables* of a system. For a homogenous system, for example, whose composition is already fixed, only two of the variables, say pressure and temperature need to be specified. The third variable, volume in this case, gets automatically fixed as these variables are inter-related by the relation PV = RT. The two variables to define the system may be chosen suitably and are called *independent variables*. The third variable is known as the *dependent variable.*

These properties may be classified as *extensive* and *intensive* properties.

Extensive properties: *These are properties whose values depend on the amount of the substance or the size of the system* such as mass, volume, energy, heat capacity, etc.

Intensive properties: *These are properties whose values are independent of the amount of substance or the size of the system.* They are characteristics of the substance present in the system. Pressure, density, temperature, surface tension etc., are some examples of intensive property.

Any extensive property when expressed per unit mass of the substance becomes an intensive property. Mass and volume are extensive properties but volume per unit mass (reciprocal of density) is an intensive property.

8.2.2 Thermodynamic Equilibrium

A system is said to be in equilibrium when each of its properties has a definite value and does not change with time. The thermodynamic equilibrium implies the existence of three kinds of equilibria in the system, namely thermal, mechanical and chemical.

Thermal equilibrium: *The temperature remains constant throughout the system.* i.e., there is no flow of heat from one portion of the system to another.

Mechanical equilibrium: *No mechanical work is done by one part of the system on another.* There is no movement of particles of the constituents of the system in itself or of the system with respect to its surroundings. This is possible, if there is uniformity of pressure throughout the system.

Chemical equilibrium: *The chemical composition of a system remain the same throughout*

Thus *a system is said to be in thermodynamic equilibrium if (i) its macroscopic properties do not alter with time, (ii) there are no currents of matter and energy within the system or at its boundaries.*

8.3 THERMODYNAMIC PROCESS

In a thermodynamic process, the state of the system changes i.e., at least one of the properties (pressure, volume etc.,) of the system changes. Expansion, vaporization, sublimation are all thermodynamic processes. The *process of operation by which a change of state is brought about is called the path and property which is dependent on the path is called a path variable or a path function.*

Types of Processes

Isothermal process: In this case, the *temperature* of the system *remain constant during each step.* The system is in contact with a constant temperature bath. Heat absorbed or evolved during the process is taken from or given to the surroundings.

Isobaric process: *The pressure remains constant* in this case. When a reaction occurs in an open container which is at the atmospheric pressure (or any constant external pressure) the process is isobaric. Conversion of liquid water to vapour is an open container (constant pressure) is an example of isobaric process.

Isochoric process: The process occurs at *constant volume.* Reaction occurring is sealed cylinders are examples of isochoric processes.

A process at constant pressure is accompanied by a change in volume and vice versa.

Adiabatic process: In an adiabatic change, *no heat enters or leaves the system.* Systems in which such processes occur are thermally insulated from the surroundings. The temperature of such systems changes according to the conditions - *if the change* *is exothermic, the heat evolved remains in the system and the temperature of the system rises, if endothermic, there is a fall in the temperature of the system as the heat absorbed is supplied by the system itself.*

Distinction between Isothermal and Adiabatic Processes

Isothermal process	*Adiabatic process*
Temperature remains constant i.e., $\Delta T = 0$	Temperature changes i.e., $\Delta T \neq 0$
Internal energy of system remains constant $\Delta U = 0$	Internal energy of system varies $\Delta U \neq 0$
The system exchanges heat with the surroundings $q \neq 0$	The system does not exchange heat with the surroundings. $q = 0$.
PV = constant	PV^{γ} = constant.

Cyclic process: The process which *brings back a system to its original state after a series of changes* is called a cyclic process. For instance, a system from state A undergoes changes like

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

and then gets back to initial state A.

The final state of a system may be attained either directly or in stages. Two types of processes are recognized according to the path of a system.

Reversible process: It is a term descriptive of the idealized process. Although this cannot be realised in actual practice, it is regarded as a theoretical basis for the corresponding real process which is then said to attain reversibility. The concept of reversible process is important as certain thermodynamic calculations are possible only for reversible processes. *A reversible process consists of a series of equilibrium stages. The system can be brought back to the initial stage without producing any permanent effect in the surroundings.*

It is carried out infinitesimally slowly so that the properties of the system remain uniform at every instant. Consider a liquid in equilibrium with its own vapour. Let the liquid be contained in a cylinder fitted with a weightless and frictionless piston. The cylinder be placed in a constant temperature bath. Initially the pressure on the piston is the same as the vapour pressure P of the liquid. An infinitesimally small pressure dP is applied on the piston very slowly. This causes an infinitesimally amount of vapour to condense. The condensation of the vapour occurs at such a slow rate that the temperature of the system does not change. The heat liberated is given to the thermostat. Similarly, in the reverse process, i.e., the evaporation, is carried out very slowly by decreasing the pressure on the piston by dP, the system absorbs the same amount of heat from the surroundings. The processes, as can be seen are idealizations and require infinite time to reach the final stage.

A reversible process may also be defined as a process which may be reversed at any instant by changing the driving force by an infinitesimally small amount without leaving any permanent changes either in the system or the surroundings.

Irreversible process: A rapid evaporation or condensation brought about by a large variation in pressure on the piston causes considerable change in the temperature of the system. Such a process is irreversible in thermodynamic sense. The system has no chance to attain equilibrium as in the above case. Most of the spontaneous processes is nature are irreversible and proceed only in one direction. *Irreversible processes cannot be brought back to the initial stage without producing a permanent change in the surroundings.*

8.4 THERMODYNAMIC FUNCTIONS

8.4.1 Heat and Work

Heat: *Heat is defined as the energy that flows between two bodies that are at different temperatures.* When two systems are in thermal contact (i.e., not insulated) energy flows from the system at a higher temperature to one at a lower temperature till the temperature becomes equal or thermal equilibrium is reached. This gives us a qualitative concept of heat. Once heat flows into a system, it appears in the system as an increase in its internal energy.

Heat is generally represented by the symbol q. The algebraic sign of *q is positive,* when *heat is absorbed by the system and is negative, when heat is lost by the system.* The unit of heat is joule.

Heat is a path function.

Work: It is a common experience and *when an object possessing mass has to be moved, i.e., lifted, pushed or pulled, some force has to be exerted on the object.* This operation is described as performing work on the object. It is equal to the product of force and displacement in the direction of the force.

i.e., work = force × distance moved.

It is denoted by the symbol w and its unit is joule. The IUPAC convention is that *w is given a positive sign when work is done on the system and a negative sign when work is done by the system on the surroundings.*

Work, like heat, is a path function and depends on how the process is carried out. In thermodynamics, different types of work like mechanical work, electrical work etc., are considered.

The relation of unit of mechanical work to the thermal unit is called the *mechanical equivalent of heat.* Its numerical value is 4.185 J.

[**Note:** The sign of heat and work can be remembered this way – when heat is absorbed by the system, energy is added to it; q is positive. When work is done on the system, energy of the system increases, w is assigned a positive sign. On the other hand, when heat is evolved, by a system, energy is subtracted from it; q is negative, when the system does work on the surroundings, energy of the system decreases, w is assigned a negative sign].

Sign conventions for heat and work

Heat absorbed by a system	+q
Heat evolved by a system	–q
Work done on a system	+w
Work done by a system	–w

8.4.2 State Functions

A state functions is a property of a system that depends only on its present state, determined by variable such as pressure, temperature and is independent of any previous history of the system. History of the system means the previous conditions under which it existed. Thermodynamic functions like internal energy U, enthalpy H, entropy S etc., are all state functions. The change in their values depends only upon the initial and final states of the system. *State functions give exact or perfect differentials.*

8.4.3 Exact or Perfect Differential

Consider a quantity z, dependent upon two variables x, y so that z may be mathematically expressed as

$$z = f(x, y)$$

The quantity z can be completely defined by considering two mutually perpendicular axes as the axes of co-ordinates. Any particular point A has co-ordinates x, y and hence z has a definite value. When the system changes from state A to state B, the value of quantity z at B is independent of the path followed, if dz is a perfect differential. Thus the integral of dz can be written as a difference of the quantity z in the final and initial states. In other words,

$$\int_A^B dz = Z_B - Z_A$$

Since the *integral is path independent, the differential is called perfect or exact differential.*

Internal energy U, is a state function, so that when the system moves from state A to state B,

$$\int_A^B dU = U_B - U_A = \Delta U$$

and dU is the exact differential.

The quantities heat and work are not state functions. The integral of their differentials in going from state A to state B depends on the path chosen.

$$\int_A^B dw = w \text{ and not } w_B - w_A$$

Similarly, $$\int_A^B dq = q \text{ and not } q_B - q_A$$

Such differentials are called *inexact differentials.*

If an infinitesimal amount of heat q is absorbed by a system and an infinitesimal amount of work w is done on the system, the infinitesimal change in internal energy is given by,

$$dU = q + w$$

dU is an exact differential while q and w are not, being path dependent. The sum of two inexact differentials can be an exact differential.

8.5 INTERNAL ENERGY U

Every substance or system is associated with a certain amount of energy called the internal or intrinsic energy. It is the energy associated with a system by virtue of its molecular constitution and the motion of its molecule. The exact magnitude of internal energy i.e., its absolute value is extremely difficult to measure and is not known. In thermodynamic systems, when any energy change occurs, change in internal energy simulataneously takes place. The change in internal energy is independent of the path followed and depends only on its initial and final states of the system. In other words, *internal energy, U is a state function and dU is a perfect differential. It is also an extensive property.*

In thermodynamics, change in internal energy accompanying a process is important rather than the actual value, and this can be measured easily.

8.6 I LAW OF THERMODYNAMICS

This is basic law of nature and is merely the law of conservation of energy.

Different ways of stating the I law are:

(1) *Energy may be transformed from one form to another but it can be neither be created not destroyed.*

(2) *Energy in one form, if it disappears, will make its appearance in an exactly equivalent amount in another form.*

(3) *It is impossible to construct a self–acting or a perpetual motion machine which could produce work without consuming any energy.*

(4) *Energy can be neither created not destroyed so that in an isolated system, the total amount of energy always remains constant.*

8.6.1 I Law of Thermodynamics and Internal Energy

The internal energy of a system may be represented by a point on P–V diagram, i.e., the system is subjected to only changes in pressure and volume. Let the system be initially in state A and then brought to state B along path I.

Change in internal energy accompanying this process $\Delta U = U_B - U_A$ (Path I).

Let it be brought back to state A along path II. Let the change in internal energy in this case be

$$-\Delta U' = U_A - U_B \text{ (Path II)}$$
$$\Delta U' = U_B - U_A \text{ (Path II)}$$

U_A and U_B are internal energy of the system in states A and B respectively. Accordingly to the I Law of thermodynamics, the net change in internal energy should be zero, otherwise it would be possible to construct a perpetual motion machine.

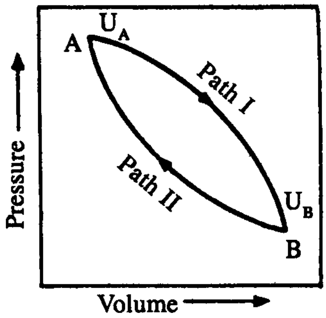


Fig. 8.3: Change in internal energy in a system

Supposing the changes in internal energies were path dependent then, $\Delta U \neq \Delta U'$and by suitable arrangement of the above process it would be possible to create energy (or destroy). Suppose $\Delta U > \Delta U'$, a coupling of the process.

$$A \xrightarrow{\text{path I}} B \xrightarrow{\text{path II}} A$$

a surplus energy equal to $\Delta U - \Delta U'$ would be obtained as the system returns to its original state. By repeating the above cycle continuous energy would be obtained and a perpetual motion machine would be possible. This is contrary to the I Law of thermodynamics. Hence $\Delta U = \Delta U'$.

Thus the internal energy changes accompanying a process is a function only of the initial and final states of the system and is independent of the path or the manner in which the change is brought about. *Internal energy is a state function.*

8.6.2 Mathematical Expression for the I Law of Thermodynamics

Consider a system whose internal energy is U_1. Let the system absorb q joules of heat. The internal energy of the system increases to $U_1 + q$.

Let an amount of work w, be done on the system which also adds on to the internal energy of the system.

If the internal energy of the system in the new state is U_2 then

$$U_2 = U_1 + q + w$$
$$\text{or } U_2 - U_1 = q + w$$
$$\text{i.e., } \boxed{\Delta U = q + w}$$

where ΔU is the change in internal energy of the system.

$\Delta U = q + w$ is the mathematical form of I Law of thermodynamics

The first law provides a means for determining the change in internal energy and not the absolute value of the internal energy.

The first law however has nothing to say about how much heat is evolved (or absorbed) or how much work is done except that the above equation is obeyed.

Internal energy is a state function, so that when the system changes through a series of states and is brought back to its initial state, there is no change in internal energy.

In other words, in a cyclic process, change in internal energy is zero.

$$\text{i.e.,} \quad \oint dU = 0$$

(the circle indicates integration around a cycle).

Cyclic integrals of q and w are not zero as they are path dependent functions.

8.6.3 Mechanical Work

In thermodynamics, most often the work is mechanical and sometimes electrical. Expansion of gas is a good example of mechanical work.

Consider a gas enclosed in a cylinder provided with a weightless frictionless piston. Let P be the pressure of the gas so that the force exerted by the gas on the piston is, F = PA where A is the area of cross-section of the piston. This may be balanced by an equal force F_{ext} acting on the piston, as shown in the figure.

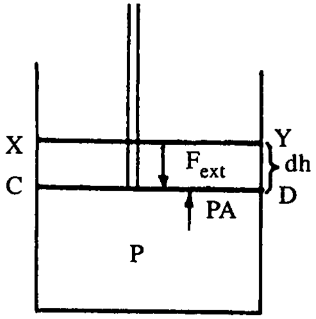


Fig. 8.4: Mechanical work

Let the piston move outward through a distance dh i.e., from CD to XY due to a small change in the external pressure. Eventually a small amount of work, w is done by the system.

$$\begin{aligned} w &= \text{force} \times \text{distance} \\ &= F \times dh \\ &= -P_{ext}\, Adh \\ &= -P_{ext}\, dV \qquad (Adh = dV, \text{ the change in volume}) \end{aligned}$$

In general for a change in volume from V_1 to V_2 the work done is given by,

$$w = \int_{V_1}^{V_2} PdV \quad (P_{ext} \text{ is written as P})$$

$$\Delta V = V_{final} - V_{initial}$$

$$\text{or} \quad w = -P\Delta V$$

P is a variable factor

From I law of thermodynamics

$$\begin{aligned} dU &= q + w \\ &= q - PdV \end{aligned}$$

Work is a path function and has different values for different processes.

1. *At constant volume:* No mechanical work is done by the system i.e., dV = 0

$$\therefore \quad dU = q$$

Thus in this case, the heat absorbed by the system is utilised completely to increase the internal energy of the system.

2. *Expansion into vacuum:* In this case, the gas is expanding against zero external pressure i.e, $P = 0$.

$$\text{Again} \quad dU = q$$

3. *Adiabatic change:* No heat enters or leaves the system i.e, $q = 0$.

$$\therefore \quad dU = w$$

The work done on a closed system in an adiabatic process goes to increase the internal energy of the system and is equal to the increase in internal energy of the system. If the system does work on its surroundings, the internal energy of the system decreases, both dU and w are negative.

4. *Cyclic process:* The initial and final states of the system are same i.e, $dU = 0$.

$$\therefore \quad q = -w$$

In a cyclic process, the heat absorbed is used up by the system to do work on the surroundings.

Maximum work: *The work done in a reversible process is a definite quantity and is also the maximum obtained from the system undergoing the given change.* For a reversible change, the internal pressure P is only infinitesimally different from the external pressure and hence there is always an equilibrium established. The magnitude of the work depends on the magnitude of the external pressure i.e., $P \pm dP$. Maximum work, therefore is done when these two opposing pressures differ by an infinitesimally small amount i.e., when the process is thermodynamically reversible.

8.7 ENTHALPY, H

Constant pressure processes are more common in chemistry than constant volume processes as most reactions in chemistry are carried out in open vessels.

If only pressure – volume work is done and the pressure is constant being equal to the external pressure then the work done on the system equals $-P\Delta V$

The I law of thermodynamics may be written as

$$\Delta U = q_p - P\Delta V$$

where q_p is the heat absorbed for the constant pressure process.

$$\Delta U = U_2 - U_1 = q_p - P(V_2 - V_1)$$

where U_2 and V_2 are respectively the internal energy and volume of the system in the final state and U_1 and V_1 are the internal energy and volume of the system in the initial state.

The above expression may also be written as

$$(U_2 + PV_2) - (U_2 + PV_2) = q_p$$

The heat absorbed q_p is given by the difference of two quantities of the system in its final and initial states. A new function is introduced called enthalpy which is defined by

$$H = U + PV$$

Enthalpy is defined as the heat content of the system.

Since enthalpy is being defined in terms of the other thermodynamic quantities, it is also a state function and $\Delta H = \Delta U + P\Delta V$

$$\text{or} \quad \Delta H = \Delta U - w$$

The heat absorbed in a process at constant pressure is equal to the change in enthalpy if the only work done is reversible pressure–volume work.

For an infinitesimal change.

$$dH = q_p$$

dH is an exact differential.

Enthalpy like internal energy is an extensive property.

In the case of chemical reactions, *the change in enthalpy of a reaction at a constant temperature and pressure (called the enthalpy of reaction) is obtained by subtracting the enthalpy of the reactants from the enthalpy of the products.*

$$\text{i.e.,} \quad \Delta H = H_{\text{products}} - H_{\text{reactants}}$$

8.8 HEAT CAPACITY

Heat is necessary to rise the temperature of a given substance which depends on the temperature range. *The heat capacity of a system is defined as the heat required to rise the temperature of the system through 1° celsius (or one kelvin)* and is denoted by C. It varies with temperature and is more accurately defined in the differential form. If the temperature of the system rises by dT when a small amount of heat dq is supplied, then heat capacity,

$$C = \frac{dq}{dT}$$

Heat capacity is thus defined as the rate of change of heat with temperature. dq not being an exact differential, the value of the heat capacity depends on the path of the process.

Heat capacity at constant volume

$$C_v = \frac{dU + PdV}{dT}$$

$$\therefore \quad C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\text{since} \quad P\,dV = 0$$

Thus heat capacity at constant volume is the rate of change of internal energy with temperature.

Heat capacity at constant pressure,

$$C_P = \frac{dU + PdV}{dT}$$

$$\therefore \quad dH = dU + PdV \text{ at constant pressure,}$$

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P$$

$$\text{or } C_P = \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

Thus *heat capacity at constant pressure is the rate of change of enthalpy with temperature.*

The heat capacities for 1 mole of a gas are termed molar heat capacities and are denoted by C_P and C_V.

8.8.1 Relation Between C_P and C_V in Gaseous System

When a gas is heated at constant volume, ΔV is zero i.e., no work is done. All the heat absorbed by the system is used to increase the internal energy of the system. Consider 1 mole of an ideal gas whose temperature is raised by 1° at constant volume. The increase in internal energy itself gives the molar heat capacity at constant volume, C_V.

On the other hand, when the system is heated at constant pressure, the gas expands and does some external work. Energy must be supplied to the system for doing external work as well as to increase the internal energy. Thus the heat capacity at constant pressure is greater than heat capacity at constant volume.

The difference between the two is given by work done by one mole of the gas in expansion when heated through 1°.

The work done by the gas in expansion at constant pressure is given by,

$$-w = P\Delta V$$

For one mole of a gas, $PV = RT$

On rising the temperature from T° to $(T + 1)^\circ$ the volume changes from V to $(V + \Delta V)$ at constant pressure, P. Thus

$$P(V+\Delta V) = R(T + 1)$$

Subtracting $PV = RT$ from the above equation,

$$P(V + \Delta V) - PV = R(T + 1) - RT$$

$$\text{or } \quad P\,\Delta V = R$$

Thus the work done by 1 mole of gas in expanding at constant pressure when heated through 1° is equal to R, the gas constant.

$$\text{i.e., } \boxed{C_P - C_V = R}$$

For n moles of the gas, $C_P - C_V = nR$

Alternatively, $H = U + PV$

Differentiating with respect to temperature,

$$\therefore \frac{dH}{dT} = \frac{dU}{dT} + \frac{d}{dT}(PV)$$

For an ideal gas PV = RT

Since, $C_P = \frac{dH}{dT}$ and $C_V = \frac{dU}{dT}$

$$\therefore \quad C_P = C_V + \frac{d}{dT}(RT)$$

$$\text{or} \quad C_P = C_V + R$$

or $C_P - C_V = R$ for one mole of gas and $C_P - C_V = nR$ for n moles of a gas.

For monoatomic gases

$$C_V = \frac{3}{2} R \text{ and,}$$

$$C_P = \frac{5}{2} R$$

The ratio of heat capacities γ for monoatomic gases is given by

$$\gamma = C_P / C_V = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.67$$

For gases like helium, argon and most metallic vapours γ is found to be approximately 1.67 over a wide range of temperatures.

In the case of diatomic gases like H_2, O_2, N_2 etc., the value of C_V has been experimentally found to be $\frac{5}{2}$ R at ordinary temperature. Thus C_P for diatomic gases is $\frac{7}{2}$R.

$$\text{and} \quad \gamma = C_P / C_V = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.4$$

The above value is in good agreement for diatomic gases at room temperature.

8.9 REVERSIBLE ISOTHERMAL EXPANSION OF A GAS

In an isothermal process, the temperature remains a constant during the entire operation. Consider an ideal gas contained in a cylinder fitted with a frictionless weightless piston placed in a thermostat. Let the pressure of the gas be P. During expansion let the external pressure be reduced by a very small quantity dP and let the volume change during reversible expansion be dV. The work done, w by the gas in the reversible expansion is given by

$$w = -(P - dP)dV$$

$$= -(PdV - dP.dV) = -P\,dV + dP \cdot dV$$

$dP \cdot dV$ being the product of two very small quantities, is extremely small and can be neglected. Thus

$$w = -P\,dV$$

Total work done W by the gas, when the volume changes from V_1 to V_2 is then given by $\int_{V_1}^{V_2} w$

$$\int_{V_1}^{V_2} w = -\int_{V_1}^{V_2} PdV$$

PV = RT for one mole of an ideal gas under reversible conditions, so that

$$P = \frac{RT}{V}$$

$$-\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} RT\,\frac{dV}{V}$$

$$= -\,RT\int_{V_1}^{V_2}\frac{dV}{V}$$

$$\text{i.e.,}\quad W = -\,RT\,ln\,\frac{V_2}{V_1}$$

$$\text{or}\quad \boxed{W = -2.303\,RT\log\frac{V_2}{V_1}}$$

$$\boxed{\text{For n moles of an ideal gas } W = -nRT\ln\frac{V_2}{V_1} = -2.303\,nRT\log\frac{V_2}{V_1}}$$

At constant temperature $P_1V_1 = P_2V_2$ (Boyle's law)

$$\therefore\quad \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore\quad \boxed{W = -2.303\,nRT\log\frac{P_1}{P_2} = 2.303\,nRT\log\frac{P_2}{P_1}}$$

The work done during an isothermal reversible compression is given by the same expression as above with the opposite sign.

dU or $\Delta U = 0$ for an ideal gas in an isothermal process.

Thus $\quad Q = W$

Thus heat absorbed or evolved in a isothermal change is the same work done on or by the system.

Example 1 : *Calculate the work done when 2 moles of an ideal gas expands isothermally and reversibly from a volume of 10^{-3} m^3 to a volume 10^{-2} m^3 at 290K. (R = 8.314 JK^{-1} mol^{-1}).*

$$\text{Work done} = -2.303\ nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 2\ \text{mol} \times 8.314\ JK^{-1} \times 290\ K \times \log \frac{10^{-3} m^3}{10^{-2} m^3}$$

$$= -2.303 \times 2\ \text{mol} \times 8.314\ JK^{-1} \times 290\ K \times \log 10$$

$$= -11105\ J$$

$$\boxed{\text{Work done} = -11105\ J}$$

Example 2 : *Calculate the work done when one mole of an ideal gas expands isothermally, reversibly from a pressure of 100 kNm^{-2} to 20 kNm^{-2} at 300 K.*

$$\text{Work done} = -2.303\ nRT \log \frac{P_1}{P_2}$$

$$= -2.303 \times 1\ \text{mol} \times 8.314\ JK^{-1} \times 300K \times \log \frac{100\, kNm^{-2}}{20\, kNm^{-2}}$$

$$= -2.303 \times 1\ \text{mol} \times 8.314\ JK^{-1} \times 300K \times \log 5$$

$$= -4015.16\ J$$

$$\boxed{\text{Work done} = -4015.16\ J}$$

Example 3: *Calculate q, w, ΔU and ΔH for the isothermal reversible expansion of 5 moles of an ideal gas from an initial pressure of 1 atm at constant temperature of 350 K.*

$$\text{Work done} = -2.303\ nRT \log \frac{P_1}{P_2}$$

$$= -2.303 \times 5\ \text{mol} \times 8.314\ JK^{-1} \times 350\ K \times \log \frac{10\ \text{atm}}{1\ \text{atm}}$$

$$= -2.303 \times 5\ \text{mol} \times 8.314\ JK^{-1} \times 350\ K \times \log 10$$

$$= -33507.5\ J$$

For an isothermal reversible expansion

$$\Delta U = 0$$

For I law of thermodynamics $\Delta U = q + w$

$$\therefore \quad q = -w$$

Hence $q = -(-33507.5J) = 33507.5J$

At constant temperature PV is constant so that

$$\Delta(PV) = 0$$

$$\Delta H = \Delta U + P\Delta V = 0$$

$$\boxed{\begin{array}{r} q = 33507.5\ J \\ \Delta U = 0,\ \Delta H = 0,\ w = -33507.5\ J \end{array}}$$

Example 4 : *Calculate w and ΔU for the conversion of 1 mole of water at 373 K to steam at 101.3 Nm^{-2} pressure. Enthalpy of vapourisation of water at 373 K is 40.67 $kJmol^{-1}$.*

Heat required to convert 1 mole of water to steam at 373 K, q = 40.67 kJ

$$\text{Pressure P} = 101.32 \text{ kNm}^{-2}$$

$$\text{Volume of 1 mole of liquid water} = 18 \text{ cm}^3$$

$$\text{Volume of 1 mole steam at 373 K} = \frac{0.0224 \text{ m}^3 \times 373 \text{ K}}{273 \text{ K}} \quad \text{since } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$= 0.0306 \text{ m}^3$$

(1 mole of steam at NTP occupies a volume of 0.0224 m^3)

$$\text{Work done} = -P(V_2 - V_1)$$

$$= -101325 \text{ Nm}^{-2} \times (0.0306 \text{ m}^3 - 18 \times 10^{-6} \text{ m}^3)$$

(18×10^{-6} m^3 can be neglected being a very small quantity)

$$= -101325 \text{ Nm}^{-2} \times 0.0306 \text{ m}^3$$

$$= -3100.5 \text{ J}$$

$$\Delta U = q + w$$

$$= 40670 \text{ J} + (-3100.5 \text{ J})$$

$$\boxed{\Delta U = 37569.5 \text{ J}}$$

Example 5: *Calculate the minimum work required to compress 20 g of O_2 from 10 m^3 to 5 m^3 at 273 K. How much heat is evolved in the process?*

$$\text{20 g of oxygen} = \frac{20}{32} \text{ mol} = 0.625 \text{ mol}$$

$$\text{Work done} = -2.303 \text{ nRT} \log \frac{V_2}{V_1}$$

$$= -2.303 \times 0.625 \text{ mol} \times 8.314 \text{ JK}^{-1} \times 273 \text{ K} \times \log \frac{5 \text{ m}^3}{10 \text{ m}^3}$$

$$= 2.303 \times 0.625 \text{ mol} \times 8.314 \text{ JK}^{-1} \times 273 \text{ K} \times \log 2$$

$$= 983.37 \text{ J}$$

Minimum work required to compress = 983.37 J
Heat evolved in the process = 983.37 J

8.10 REVERSIBLE ADIABATIC EXPANSION OF A GAS

In an adiabatic process, there is no exchange of heat between the system and the surroundings, i.e., q = 0.

I law of thermodynamics becomes dU = w or dU = – PdV

If the external pressure is zero i.e., adiabatic expansion in vacuum, no work is done and there is no change in energy

During adiabatic expansion dV is positive and the gas does work on the surroundings which is negative. There is drop in temperature as internal energy is converted to work.

For an ideal gas,

$$dU = C_V\, dT$$

Assuming C_V to be a constant over the temperature range,

$$\Delta U = U_2 - U_1 = C_V(T_2 - T_1)$$

$$\text{and} \quad w = C_V(T_2 - T_1)$$

In adiabatic expansion $T_2 < T_1$, so that work done by the gas is negative

$$\text{Since} \quad dU = C_V dT \quad \text{and} \quad dU = -P\, dV$$

$$C_V\, dT = -PdV$$

$$\text{and} \quad C_V\, dT = -RT\frac{dV}{V} \qquad (\because PV = RT)$$

$$C_V\frac{dT}{T} = -R\frac{dV}{V}$$

$$\text{or} \quad \frac{C_V}{R}\frac{dT}{T} = -\frac{dV}{V}$$

For a process where the initial volume V_1 at initial temperature T_1 changes to final volume V_2 at temperature T_2, the above expression becomes

$$\frac{C_V}{R}\int_{T_1}^{T_2}\frac{dT}{T} = -\int_{V_1}^{V_2}\frac{dV}{V}$$

C_V is assumed to be constant.

$$\frac{C_V}{R}\ln\frac{T_2}{T_1} = -\ln\frac{V_2}{V_1}$$

$$\frac{C_V}{R}\ln\frac{T_2}{T_1} = \ln\frac{V_1}{V_2}$$

$$\text{or} \quad \ln\frac{T_2}{T_1} = \frac{R}{C_V}\ln\frac{V_1}{V_2}$$

$$\ln\frac{T_2}{T_1} = (\gamma - 1)\ln\frac{V_1}{V_2} \qquad [\text{since } R = C_P - C_V$$

$$\therefore R/C_V = \frac{C_P - C_V}{C_V} = \gamma - 1]$$

Taking antilogarithms on both sides of the equation

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

$$T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$$

$$\boxed{TV^{\gamma-1} = \text{Constant}}$$

For an ideal gas

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Hence $$\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1}$$

Substituting for $\frac{T_2}{T_1}$ as $\left(\frac{V_1}{V_2}\right)^{\gamma-1}$

$$\frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}\frac{V_1}{V_2}$$

$$= \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$P_2V_2^{\gamma} = P_1V_1^{\gamma}$$

$$\boxed{PV^{\gamma} = \text{constant}}$$

Alternatively, $C_V\, dT = -P\, dV$

Total work done,

$$W = \int_{V_1}^{V_2} PdV = \int_{T_1}^{T_2} C_V dT$$

$$\boxed{W = C_V\,(T_2 - T_1)}$$

For n moles of the gas, the work is given by,

$$\boxed{W = nC_V\,(T_2 - T_1)}$$

Example 6: *5 moles of an ideal gas are allowed to expand adiabaticdlly and reversibly at 300 K from a pressure of 1000 kNm^{-2} to a final pressure of 100 kNm^{-2}. Calculate the final temperature of the gas and the work done by the gas, $C_V = \frac{3}{2}R$.*

Since $C_V = \frac{3}{2}R$, $C_P = \frac{5}{2}R$

and $$\gamma = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.67$$

For an adiabatic expansion of an ideal gas

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

Substituting,

$$\left(\frac{100\text{k Nm}^{-2}}{1000\text{k Nm}^{-2}}\right)^{1.67-1} = \left(\frac{T_2}{T_1}\right)^{1.67}$$

$$\therefore \quad \left(\frac{T_2}{T_1}\right)^{1.67} = \left(\frac{1}{10}\right)^{0.67}$$

Taking logarithms and solving

$$\frac{T_1}{T_2} = 2.5188$$

$$T_2 = \frac{T_1}{2.5188}$$

$$= \frac{300\text{ K}}{2.5188} = 119.1\text{ K}$$

$$\boxed{\text{Final temperature of the gas} = 119.1\text{ K}}$$

$$\text{Work done by the gas W} = n\,C_V\,(T_2 - T_1)$$

$$= 5\text{ mol} \times \frac{3}{2} \times 8.314\text{ JK}^{-1}\text{mol}^{-1}\ (119.1\text{ K} - 300\text{ K})$$

$$= -5\text{ mol} \times \frac{3}{2} \times 8.314\text{ JK}^{-1}\text{mol}^{-1}\ 180.9\text{ K}$$

$$= -11280\text{ J}$$

$$\boxed{\text{Work done} = -11280\text{ J}}$$

Example 7: *One mole of an ideal gas ($C_V = 12.55$ JK^{-1} mol^{-1}) at 400 K is compressed adiabatically and reversibly to one fourth its original volume. Calculate the final temperature of the gas R = 8.314 JK^{-1} mol^{-1}.*

$$\text{Since} \quad C_P = C_V + R$$

$$= (12.55 + 8.314)\text{JK}^{-1}\text{mol}^{-1}$$

$$= 20.864\text{ JK}^{-1}\text{mol}^{-1}$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{20.864\text{ JK}^{-1}\text{mol}^{-1}}{12.55\text{ JK}^{-1}\text{mol}^{-1}}$$

$$= 1.67$$

For an adiabatic expansion

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Substituting, $T_2 = 400\text{K} \times \left(\frac{4\ \text{Vdm}^3}{\text{Vdm}^3}\right)^{1.67-1}$

$$= 400\ \text{K}\ (4)^{0.67}$$

$$\boxed{\text{Final temperature} = 1012.6\ \text{K}}$$

Example 8: *4 g of helium gas at 300 K expands adiabatically from a volume of 10 dm³ to a volume of 20 dm³. Calculate q. Assume* $C_V = \frac{3}{2}R$.

Since the process is adiabatic q = 0

$$C_V = \frac{3}{2}R$$

$$\therefore \quad C_P = \frac{5}{2} \quad \text{and} \quad \gamma = 1.67$$

4.0 g helium is 1 mole of the gas

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Substituting the values

$$T_2 = 300\ \text{K} \times \left(\frac{10\ \text{dm}^3}{20\ \text{dm}^3}\right)^{1.67-1}$$

$$= 300\ \text{K} \times (0.5)^{0.67} = 188.5\ \text{K}$$

$$\boxed{\text{Final temperature} = 188.5\ \text{K}}$$

Work done by the gas $W = n\, C_V\, (T_2 - T_1)$

$$= 1.0\ \text{mol} \times \frac{3}{2} \times 8.314\ \text{JK}^{-1}\text{mol}^{-1}\ (188.5\ \text{K} - 300\ \text{K})$$

$$= -1.0\ \text{mol} \times \frac{3}{2} \times 8.314\ \text{JK}^{-1}\text{mol}^{-1} \times 111.5\ \text{K}$$

$$\boxed{\text{Work done} = -1390.5\ \text{J}}$$

8.11 VARIATION OF HEAT OF REACTION WITH TEMPERATURE - KIRCHHOFF'S EQUATION

Making use of I law of thermodynamics, Kirchhoff in 1858 deduced mathematical expressions to define the variation of heat of reaction with temperature. The enthalpies of reaction i.e., ΔH generally vary with temperature. The exact influence of temperature can be worked out as follows:

Consider a simple reaction,

$$A \rightarrow B$$

Let the above reaction proceed at temperature T_1, accompanied by heat change ΔH_1. The product B at temperature T_1 be brought to temperature T_2 which involves absorption of heat equal to $C'_P(T_2 - T_1)$ where C'_P is the mean molar heat capacity of the products.

The total heat change accompanying the above process is

$$\Delta H_1 + C'_P (T_2 - T_1)$$

The same reaction may be carried out by initially raising the temperature of the reactants to T_2 from T_1. The reaction is then allowed to proceed at temperature T_2.

In this case, heat absorbed in the first step = $C_P (T_2 - T_1)$ where C_P is the mean molar heat capacity of the reactants, and

heat change accompanying the reaction at T_2 is ΔH_2. The total heat change accompanying the above process is therefore

$$\Delta H_2 + C_P (T_2 - T_1)$$

In both the cases, the reactant A at temperature T_1, is changed to product B at temperature T_2. Obviously the two energy changes must be equal.

$$\begin{aligned} \Delta H_1 + C'_P (T_2 - T_1) &= \Delta H_2 + C_P (T_2 - T_1) \\ \Delta H_2 - \Delta H_1 &= C'_P (T_2 - T_1) - C_P (T_2 - T_1) \\ &= (C'_P - C_P) (T_2 - T_1) \\ \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} &= C'_P - C_P = \Delta C_P \end{aligned}$$

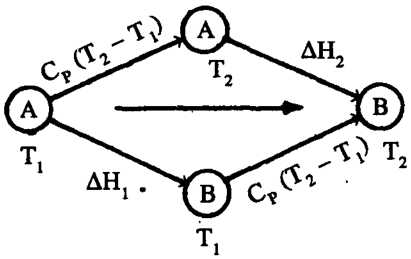


Fig. 8.5: Conversion of A at T_1 to B at T_2

ΔC_P is the difference in the molar heat capacities of the products and reactants at constant pressure.

ΔH_2 and ΔH_1 are the changes in enthalpies of the reaction at temperatures T_2 and T_1 respectively.

$$\boxed{\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)}$$

The above equation is known as *Kirchhoff's equation.*

Similarly, at constant volume,

$$\boxed{\Delta U_2 - \Delta U_1 = \Delta C_V (T_2 - T_1)}$$

These equations are useful in calculating the heats of reactions at other temperatures knowing ΔH at any given temperature.

The molar heat capacities are assumed to remain a constant over the temperature range $T_1 \rightarrow T_2$. The variation of heat capacities with temperature must also be taken into account when the enthalpies are measured over a wide range of temperatures.

Alternatively, for the reaction $A \rightarrow B$, $\Delta H = H_B - H_A$

On differentiating ΔH with respect to temperature,

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left(\frac{\partial(H_B)}{\partial T}\right)_P - \left(\frac{\partial(H_A)}{\partial T}\right)_P$$

$$= (C_P)_B - (C_P)_A$$

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \Delta C_P$$

Integrating it, $$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P dT$$

i.e., $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$ (assuming ΔC_P to be a constant over this range of temperature)

Similarly at constant volume,

$$\Delta U = U_B - U_A$$

$$\left(\frac{\partial(\Delta U)}{\partial T}\right)_V = \left(\frac{\partial U_B}{\partial T}\right)_V - \left(\frac{\partial U_A}{\partial T}\right)_V$$

$$= (C_V)_B - (C_V)_A = \Delta C_V$$

Integrating it,

$$\int_{T_1}^{T_2} d(\Delta U) = \int_{T_1}^{T_2} \Delta C_V dT$$

$$\Delta U_2 - \Delta U_1 = \Delta C_V (T_2 - T_1)$$

Example 9: *Calculate the enthalpy change at 348 K for the reaction.*

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow \frac{1}{2}HCl(g) \qquad \Delta H^o_{298K} = 92.2kJ$$

The mean heat capacities over this temperature range for

$H_2(g) = 28.51\ JK^{-1}\ mol^{-1}$

$Cl_2(g) = 32.23\ JK^{-1}\ mol^{-1}$

$HCl(g) = 28.47\ JK^{-1}\ mol^{-1}$

$$\begin{aligned}
\Delta C_P &= C_P(HCl) - \frac{1}{2}C_P(H_2) - \frac{1}{2}C_P(Cl_2) \\
&= 28.47 - \frac{1}{2}(32.33) - \frac{1}{2}(28.51)\ JK^{-1}\ mol^{-1} \\
&= -1.97\ JK^{-1}\ mol^{-1} \\
\Delta H_2 &= \Delta H_1 + \Delta C_P\ (T_2 - T_1) \\
&= -92.2\ kJ + (-1.97 \times 10^{-3} kJ)\ (348 - 298)
\end{aligned}$$

$$\boxed{\Delta H_{348K} = -\ 92.299\ kJ}$$

IMPORTANT POINTS

- The subject of thermodynamics deals with the study of interconversions of various forms of energy. It is also considered as a science of the relationship between heat and other forms of energy.
- Thermodynamics is based on three law of thermodynamics. It is an exact science.
- A thermodynamic system is the specific part of the physical universe under observation.
- The surroundings are the rest of the universe outside the system. It can affect or be affected by the system.
- Open system is a system which can exchange both matter and energy with the surroundings.
- Closed system is one in which exchange of energy is possible with the surroundings but not of matter.
- Isolated system is a system in which no exchange of matter or energy is possible with the surroundings.
- Macroscopic properties such as pressure, volume, temperature, composition are needed to describe a system. These are called state variables or state properties of a system.
- Properties whose values depend on the amount of the substance or the size of the substance are called extensive properties (Mass, volume, energy etc.)
- Properties whose values are independent of the amount of the substance or the size of the system are called intensive properties. (density, temperature etc.)
- A system is said to be in equilibrium when each of its properties has a definite value and does not vary with time.
- Thermodynamic equilibrium means the existence of thermal, mechanical and chemical equilibrium in a system.
- In thermal equilibrium, the temperature remains constant through the system. In mechanical equilibrium, there is no mechanical work done by one part of the system on another. The chemical composition of the system remains constant throughout in chemical equilibrium.

- The state of a system changes in a thermodynamic process.
- The process by which change of a system is brought about is called a path. A property which is dependent on a path called a path variable.
- In isothermal process, the temperature of the system remains constant.
- In isobaric process, the pressure of the system remains constant.
- In isochoric process, the volume of the system remains constant.
- In an adiabatic process, no heat enters or leaves the system. The temperature of the system changes
- The process which brings back a system to its original state after a series of changes is called a cyclic process.
- A reversible process consists of a series of equilibrium stages. The system can be brought back to the initial stage without producing any permanent effect on the surroundings. It is carried out infinitesimally slowly.
- Irreversible process is carried out rapidly and this system cannot be brought back to the initial stage without producing any permanent effect on the surroundings.
- Heat is defined as the energy that flows between two bodies at two different temperatures. It is represented by the symbol q.
- Heat is a path function. By convention heat absorbed by a system is positive and heat evolved by a system is negative.
- Work is equal to the product of force and displacement in the direction of the force. It is denoted by the symbol w.
- According to the modern convention, w is positive when work is done on the system and negative when work is done by the system.
- Work is path function and depends on how the process is carried out.
- The numerical value of mechanical equivalent of heat is 4.185J.
- A state function is a property of system which depends only on its present state and not on any previous history of system. The change in their values depends only upon the initial and final states of the system.
- State functions give perfect or exact differentials.
- Internal energy or intrinsic energy U, is the energy associated with a system by virtue of its molecular constitution and motion of its molecules.
- Absolute value of the internal energy for any substance is difficult to measure.
- Change in internal energy dU in any process can be measured.
- dU is perfect differential and U is an extensive property.
- I law of thermodynamics is merely the law of conservation of energy. It is stated as – energy can neither be created nor destroyed so that in an isolated system, the total amount of energy always remains constant.
- Another statement of I law is – energy in one form, if it disappears, will make its appearance in an exactly equivalent amount in another form.
- Change in internal energy is path independent and is given by $U_{final} - U_{initial}$.
- Change in internal energy in a cyclic process is zero.

- Mechanical work i.e., work done during expansion is PΔV.
- Work is a path function and varies for different processes.
- Work done at constant volume is zero.
- Work done in an adiabatic process is dU.
- The work done in a reversible process is maximum.
- Enthalpy H, is defined as the heat content of the system. It is an extensive property and dH is an exact differential.
- For a chemical reaction, the change in enthalpy of a reaction ΔH at constant temperature and pressure is called the enthalpy of reaction and is equal to $H_{products} - H_{reactants}$.
- Heat capacity C of a system is the heat required to raise the temperature of the system by 1°.
- Heat capacity depends on the path of the process.
- C_P and C_V are molar heat capacities at constant pressure and constant volume respectively.
- For one mole of an ideal gas, the difference between C_P and C_V is R (gas constant).
- The enthalpies of reaction vary with temperature. The variation of ΔH with temperature is given by Kirchhoff's equation.

IMPORTANT MATHEMATICAL RELATIONS

I Law of thermodynamics

$$dU = q + w$$

$$dU = U_{final} - U_{initial}$$

$$w = -P\Delta V$$

$$dU = q - P\Delta V$$

$$H = U + PV$$

$$dH = dU - w$$

$$\Delta H = H_{products} - H_{reactants}$$

$$C_P - C_V = R \text{ for 1 mole of an ideal gas}$$

$$C_V = \frac{3}{2}R \text{ and}$$

$$C_P = \frac{5}{2} \text{ (for a monoatomic gas)}$$

Reversible isothermal expansion

$$W = -2.303\ nRT \log V_2/V_1$$

$$W = -2.303\ nRT \log P_1/P_2$$

$$dU = \Delta U = 0 \text{ for ideal gas}$$

Reversible adiabatic expansion

$$q = 0$$

$$dU = C_V dT$$

$$dU = -PdV$$

$$w = C_V(T_2 - T_1)$$

$$TV^{\gamma-1} = \text{constant}$$

$$PV^{\gamma} = \text{constant}$$

Kirchoff's equation

$$\Delta H_2 - \Delta H_1 = \Delta C_P(T_2 - T_1)$$

EXERCISE

Short Answer Type Questions:

1. Define the following terms –

   (i) thermodynamic system (ii) closed system (iii) isolated system (iv) open system. Explain.
2. What are homogeneous and heterogeneous systems?
3. Name the system where (i) there is no exchange of matter and energy and (ii) there can be exchange of energy but not of matter, between the system and surroundings.
4. What is meant by an intensive property? Explain with an example.
5. What is meant by an extensive property? Explain with an example.
6. Classify the following as extensive and intensive properties –

   (i) mass (ii) density (iii) volume (iv) temperature (v) energy (vi) enthalphy (vii) viscosity.
7. How are intensive and extensive properties related?
8. What is an adiabatic process? Explain.
9. Distinguish between —
   - (a) extensive and intensive property.
   - (b) open and closed system.
   - (c) isothermal and adiabatic processes
   - (d) reversible and irreversible processes.
10. Define and explain the terms (i) heat and (ii) work.
11. Mention the sign conventions used for heat and work.
12. What is the state function? Explain with an example.
13. What do you understand by the statement – "internal energy is a state function"?
14. On what concept (or law) is the first law of thermodynamics based?
15. State I law of thermodynamics.
16. Give the mathematical form of I law of thermodynamics and explain the terms involved.
17. The I law of thermodynamics is represented as $\Delta E = q + w$ where E is a state function but q and w are not. Substantiate.
18. Define enthalpy and change in enthalpy.
19. Give an expression for the change in enthalpy in the case of a chemical reaction.
20. Define molar heat capacity of a substance.

21. Define molar heat capacities under different conditions. What is its unit?
22. Why is C_P more than C_V for an ideal gas?
23. How are C_P and C_V related?

Essay Type Questions:

1. Explain the different types of systems in thermodynamics.
2. Name the properties required to describe a system. What is meant by dependent and independent variables?
3. What is meant by thermodynamic equilibrium?
4. Explain the different types of thermodynamic processes.
5. What is meant by a reversible process? Are naturally occurring spontaneous processes reversible? Why is the concept of reversible process important?
6. Explain the terms exact and inexact differentials.
7. Deduce the mathematical form of I law of thermodynamics.
8. Derive a relation between C_P and C_V.
9. Derive an expression for the molar heat capacity of an ideal gas.
10. Derive an expression for the work done in the reversible isothermal expansion of an ideal gas.
11. Derive an expression for the work done in the reversible adiabatic expansion of an ideal gas.
12. Derive Kirchhoff's equation.
13. Derive an expression for the variation of ΔH with temperature at constant volume.
14. Deduce an expression for the effect of temperature on the enthalpy of a reaction.

PROBLEMS

1. Calculate the work done when 1 mole of an ideal gas expands isothermally and reversibly from a volume of 1 dm^3 to a volume of 15 dm^3 at 300 K.
2. 15 moles of an ideal gas expands reversibly from 105 dm^3 to 1050 dm^3 at 290 K. How much heat would be absorbed in the process?
3. One mole of an ideal gas is allowed to expand against a confining pressure that is all times infinitesimally less than the gas pressure, from an initial pressure of 10 atm to a final pressure of 0.4 atm at 273 K. How much work is done by the process and what is the heat absorbed in the process?
4. The heat capacity of a gas at constant volume is 28 $JK^{-1}mol^{-1}$. What will be the heat capacity of the same gas at constant pressure?
5. Assuming nitrogen gas to be an ideal gas, calculate the work done by 20 g of nitrogen gas in expanding isothermally and reversibly from a volume of 10 dm^3 to 20 dm^3 at 300 K. What are q, ΔU and ΔH for the process?
6. Calculate the minimum work necessary to compress 64 g of O_2 from a volume of 10 dm^3 to 5 dm^3 at 250 K. How much heat is evolved in this process?
7. 3 moles of He gas at 100 kNm^{-2} are compressed reversibly and isothermally to 300 kNm^{-2} at 400 K. Calculate q, w and ΔU assuming ideal behaviour.
8. Calculate work done when 3 moles of a gas is expanded reversibly and isothermally from 6×10^5 Nm^{-2} to 2×10^5 Nm^{-2} at 298 K.

9. Calculate the work done when 2 moles of an ideal gas is compressed at 298 K from 10 m^3 to 5 m^3 isothermally and reversibly. How much heat is evolved during the process?
10. Calculate ΔU, q and w for 10 moles an ideal gas expanding isothermally and reversibly from a pressure of 1.21×10^5 Nm^{-2} at 273 K.
11. Calculate the work done when 2 moles of an ideal gas expands isothermally and reversibly from a volume of 10^3m^3 to a volume of 10^5 m^3 at 298 K.
12. 100g of nitrogen initially at 298 K and 10 atmospheric pressure expands adiabatically to a pressure of 1 atm. Calculate the final temperature if $C_P = \frac{7}{2}R$.
13. To what pressure must a given volume of nitrogen originally at 375 K and 100 kPa pressure be compressed in order to rise its temperature to 673 K. $\gamma = 1.4$.
14. 10 g of O_2 gas at 373 K expand reversibly and adiabatically from a volume of 3 dm^3. Calculate the final temperature and work done on the gas. Assume $C_V = \frac{5}{2}R$.
15. 10 g of N_2 gas at 290 K are compressed adiabatically and reversibly from 8 dm^3 to 5 dm^3. Calculate the final temperature and work done on the gas. Assume $C_V = \frac{5}{2}R$.
16. The enthalpy change accompanying the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$ at 300 K was found to be – 45.92 kJ. Calculate the enthalpy of the reaction at 323 K. The molar heat capacities at constant pressure over this temperature range for N_2, H_2 and NH_3 are 28, 45, 28.32 and 37.07 JK^{-1} mol^{-1} respectively.
17. At 298 K, the enthalpy of formation of liquid water is –285.6 kJ mol^{-1}. What is the enthalpy of formation at 373 K, given
    C_P of H_2 = 28.80 JK^{-1} mol^{-1}; C_P of O_2 = 29.13 JK^{-1} mol^{-1};
    C_P of H_2O = 75.24 JK^{-1} mol^{-1}
18. Calculate the enthalpy of the reaction
    $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ at 1500 K from the following data
    ΔH at 298 K = –136.79 kJ mol^{-1}
    C_P of C_2H_4 = 11.83 JK^{-1} mol^{-1}; C_P of H_2 = 28.80 JK^{-1} mol^{-1}
    C_P of C_2H_6 = 9.405 JK^{-1} mol^{-1}

ANSWERS

1. –6755.64 J
2. 83.290 kJ
3. W = –7303.3 J, q = 7303.3 J
4. 36.31 JK^{-1} mol^{-1}
5. W = –1235 J, q = 1235, ΔU = ΔH = 0
6. 2881.9J, –2881.9 J
7. W = 16.06J, q = –16.06J, ΔU = 0
8. –8.167 kJ
9. 3.435 kJ
10. ΔU = 0, w = –52.28 kJ, q = +52.28 kJ
11. –22.82 kJ
12. 154.3 K
13. 774.36 kPa
14. q = 0, w = –1984.12 J
15. 350 K, w = 445.4 J
16. – 46.37 kJ
17. –283.21 kJ mol^{-1}
18. – 174.32 kJ mol^{-1}

Chapter 9

Liquid Mixtures

SYLLABUS

9.1 TYPES OF SOLUTIONS
9.2 SOLUBILITY
9.3 SOLUTIONS OF GASES IN LIQUIDS
9.4 LIQUID MIXTURES
9.5 THE DISTRIBUTION LAW

There are very many reasons for preparing solutions. Most chemical reactions are carried out in solutions as they are faster. Solutions have certain useful properties compared to the individual constituents. Alloys, for example, which are solutions of two or more metals (sometimes, a nonmetal and metals) find better applications than metals themselves. Transportation of certain gases become more convenient when dissolved in a suitable solvent. Acetylene is transported dissolved in acetone. The solutions are also useful when the boiling point or freezing point of a pure substance need to be modified. Freezing mixture (salt in ice) brings down the temperature of ice to 251 K.

9.1 TYPES OF SOLUTIONS

A solution is defined as a *homogeneous mixture of two or more substances.* Depending upon the physical state of the solute and the solvent, different types of solutions are possible. Table 9.1 gives a list of the common types of solutions.

When one of the component happens to be a liquid, this component is often referred to as the *solvent* while the other components like a gas or a solid is the *solute*. When all the components are of the same state, the one in the largest amount is the solvent.

Table 9.1: Types of Solutions

Solute	*Solvent*	*Examples*
Gas	Gas	Air
Gas	Liquid	Aerated water (soda water) Carbonated beverages
Gas	Solid	Hydrogen gas in palladium
Liquid	Liquid	Ethanol in water Benzene in toluene
Solid	Liquid	Salt in water
Solid	Solid	Brass, Bronze

A solution is said to be *saturated if it contains the maximum amount of the solute in a given amount of the solvent at that temperature. An unsaturated solution obviously contains less than the maximum amount of solute. In supersaturated solution, the amount of solute present is more than in a saturated solution and is therefore not very stable.*

9.2 SOLUBILITY

The solubility of a substance varies widely. Water is a good solvent for a number of substances but does not dissolve many organic compounds. The solubility of a substance in another depends on factors like

- *(i) nature of solute and solvent*
- *(ii) temperature and*
- *(iii) pressure.*

Two factors namely, enthalpy of solution ΔH_{sol} and entropy of solution ΔS_{sol} govern the dissolution of a substance in a solvent. *A negative enthalpy of solution is always favourable for solution formation.* The entropy factor, ΔS_{sol} also plays an important role. In fact, solution formation is largely governed by this factor. Entropy is a measure of disorder or randomness. *The process of solution is always accompanied by an increase in disorder or randomness.* When enthalpy of solution is highly endothermic, no solution is formed i.e., the solute does not mix with the solvent.

In the case of gases, the only factor of importance is the increase in disorder. Hence gases are always miscible.

As a general rule, "*like dissolves like*". i.e., *chemically similar substances dissolve in each other*. Organic compounds which are generally nonpolar dissolve in organic solvents which are also nonpolar. Similarly polar molecules (inorganic compounds) dissolve in polar solvents such as water. This can be easily understood as chemically similar compounds are in a similar environment and are able to mix freely. Solutes and solvents which are not chemically similar are not able to tolerate each other, so there is no tendency to dissolve. Between the two extremes, a considerable number of intermediate stages of similarity exists and wide ranges of solubilities of substances in one another are encountered. There are other factors like solvation energy, hydrogen bonding which also influence solubility to some extent.

The effect of temperature on solubility is quite marked and depends on the enthalpy of solution. A substance that dissolves with evolution of heat at saturation shows a decrease in solubility with increase in temperature. On the other hand, if a substance dissolves with absorption of heat, the solubility increases with increase in temperature.

The effect of pressure on solubility plays a prominent role only where gases are involved and has little effect in the cases of liquids and solids.

9.3 SOLUTIONS OF GASES IN LIQUIDS

Most of the gases that are soluble in water and other liquids generally form true solutions. The amount of gas dissolved depends upon the pressure, the temperature, the nature of the gas and the nature of the solvent.

9.3.1 Factors influencing the Solubility of a Gas

Solubility of gas is expressed as mass of the gas per unit volume of solvent.

1. Nature of the gas and nature of the solvent : Generally speaking, *the gases which are easily liquefied, are more soluble in common solvents.* Thus carbon dioxide is more soluble in water than hydrogen or oxygen is. Also gases that form ions in aqueous solutions are more soluble in water than in other solvents. Thus, hydrogen chloride which is highly soluble in water, is not soluble in benzene. Though, chemical similarity is not a criterion, frequently chemical similarity between the gas and the solvent leads to a higher solubility. This can be seen in the high solubility of organic compounds in non–polar (organic) solvents.

2. Effect of temperature : *At constant pressure, the solubility of a gas decreases with increase in temperature.* Because of this property, many dissolved gases may be removed from a solution by boiling.

3. Effect of pressure: Pressure has a marked influence on the solubility of a gas in a given solvent.

9.3.2 Henry's Law

After a series of experiments, William Henry (1803) found a quantitative relationship between the pressure and the solubility of a gas.

This *relation* called **Henry's law** may be stated as *the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the solution at constant temperature.*

If *m* is the mass of gas dissolved in unit volume of the solvent and *P* the pressure of the gas in equilibrium with the solution at constant temperature *T*, then

$$m \propto P$$

or

$$m = kP$$

where *k* is the proportionality constant known as *Henry's law constant.*

Henry's law constant depends only on temperature.

When several gases are dissolved simultaneously in a solvent, above equation is valid for each gas independently. Thus the solubility of each gas from a mixture of gases is directly proportional to the partial pressure of the gas in the mixture . The value of k is of course, different for different gases.

Henry's law may also be stated as *the volume of a gas that dissolves in a fixed volume of a liquid at constant temperature is a constant and is independent of the pressure of the gas.*

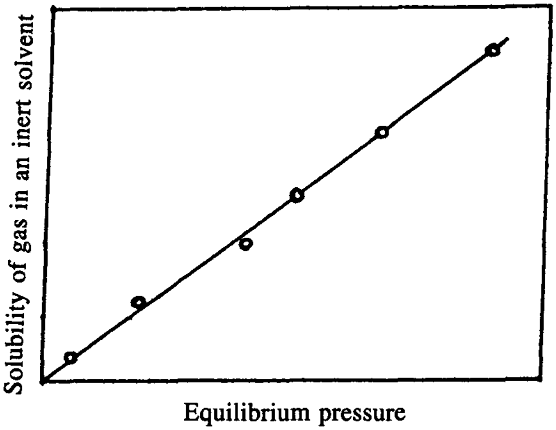


Fig. 9.1 : Variation of solubility of a gas with pressure

The ideal gas equation

$$PV = nRT \text{ can be written as}$$

$$PV = \frac{m}{M}RT \text{ (m is the mass and M is the mol.wt. of the gas)}$$

$$\therefore V = \frac{m}{p}\frac{RT}{M}$$

$\frac{m}{p}$ is a constant from Henry's law, $\frac{RT}{M}$ is a constant for a gas at constant temperature, so that V is also a constant. If Henry's law is valid, then the graph of solubility of a gas against equilibrium pressure at constant temperature should be a straight line (Fig. 9.1).

9.3.3 Limitations of Henry's Law

Henry law is applicable to ideal gases and approximately to real gases.

Most gases obey Henry's law provided,

(i) the pressure is not too high. This is so because ideal gas behaviour is approached only at low pressure;

(ii) the gas is not highly soluble; and

(iii) the gas does not dissociate or enter into chemical combination with the solvent.

For instance, Henry's law is not applicable in the following cases:

(i) Hydrogen chloride gas which dissociates in water into ions as,

$$H_2O + HCl \rightleftharpoons H_3O + Cl^-$$

(ii) Ammonia which enters into chemical combination as

$$NH_3 + H_2O \rightleftharpoons NH_4\,OH$$

(iii) To the solution of carbon dioxide in water at low temperature and pressure of 1000 – 10000 kPa. In the case of CO_2, however Henry's law is applicable at 373 K. The deviation at low temperature being attributed partly to compound formation between carbon dioxide and water.

9.3.4 Applications of Henry's Law

1. Effervescence is observed when a bottle of soda or beer is opened. This is because before sealing, the beverage is pressurized with a mixture of air and carbon dioxide. Because of the high pressure in the gas mixture more CO_2 dissolves in the drink. On opening the seal as the pressure drops down to atmospheric pressure, the excess dissolved gas escapes causing effervescence

2. The study of the solubility of the gases under different pressures in blood or lipids fats is of considerable physiological importance for deep water divers and mountaineers.

For example, when a diver at a depth of 15 m or so breathes in compressed air from a supply tank, more than normal nitrogen dissolves in the blood and other body fluids due to the higher pressure at that depth. When the diver ascends quickly, the partial pressure decreases and the excess dissolved nitrogen escapes forming bubbles in the bloodstream. These bubbles restrict blood flow and cause death. This condition is known as "*bends*". A mixture of helium–oxygen is used in compressed gas tanks in recent times, instead of air (oxygen–nitrogen mixture) as the solubility of helium is very low in blood.

3. When a mixture of gases is brought in contact with a solvent each gas dissolves in proportion to its own partial pressure independent of the pressure of the other gases. Henry's law is applicable to each gas independently irrespective of the presence of the other gases. Thus a dissolved gas can be merely removed from the solution by bubbling in a gas of indifferent solubility.

Ammonia from its aqueous solution can be expelled by bubbling in a gas like nitrogen which is insoluble.

9.4 LIQUID MIXTURES

In a binary system of two liquids, depending upon the nature of the two liquids, the miscibility of one in the other varies. Accordingly three types of binary liquid mixtures are possible.

1. Completely miscible liquid pairs
2. Partially miscible liquid pairs
3. Completely immiscible liquid pairs

9.4.1 Completely Miscible Liquid Systems

In *completely miscible liquids, the relative amounts of the constituents can be varied to any extent and the constituents mix freely and only a single phase exist.*

Ideal Solutions : Similar to the concept of ideal gases, in the theory of solutions, the concept of ideal solutions can be visualized. In an ideal gas, the intermolecular forces of attraction are assumed to be completely absent. Since liquids exist only because of molecular interactions, in an ideal solution the molecules can be expected to be of similar size and intermolecular attraction. Thus, in an ideal solution A in B, the forces of attraction between A and A, A and B, B and B should be the same.

9.4.2 Raoult's law of Ideal Solutions:

According to this law, *the partial vapour pressure of a volatile constituent of a solution at constant temperature is equal to the product of the vapour pressure of the pure constituent and its mole fraction in the solution.*

In a binary solution A and B, if the number of moles of A and B are n_A and n_B respectively then the mole fractions of $A(X_A)$ and $B(X_B)$ are given as

$$X_A = \frac{n_A}{n_A + n_B} \quad \text{and}$$

$$X_B = \frac{n_B}{n_A + n_B}$$

In a binary solution, $X_A + X_B = 1$

If P_A and P_B are the partial pressures of the two components A and B in the solution, P_A^o and P_B^o are the vapour pressures of pure components A and B respectively, then according to Raoult's law.

$$P_A = X_A P_A^o \quad \text{and}$$

$$P_B = X_B P_B^o$$

If the vapour behaves like an ideal gas, then the total pressure above the mixture is

$$\begin{aligned} P &= P_A + P_B \\ &= X_A P_A^o + X_B P_B^o \end{aligned}$$

An ideal solution obeys Raoult's law exactly at all concentrations and temperatures. For any given system, at a given temperature P_A^o and P_B^o are constant. Hence a plot of partial pressure of each constituent P against its mole fraction X, in solution should be a straight line. Also, the total pressure of the ideal solution lie on a straight line joining P_A^o and P_B^o.

Calculation of the vapour pressure above the mixture is then very simple.

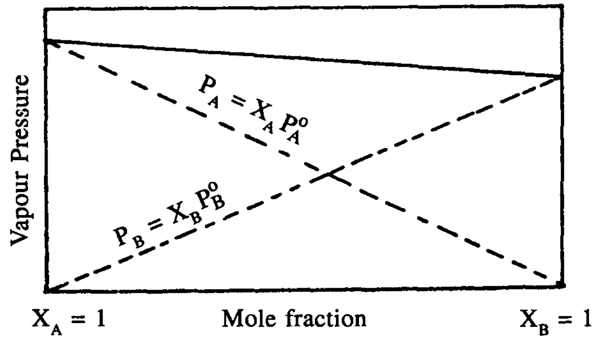


Fig. 9.2: Vapour pressure of an ideal solution

A more careful statement of *an ideal solution, however, includes specification that no volume change should occur and that no heat should be evolved or absorbed on mixing of the two components.*

i.e, $\Delta V = 0$

and $\Delta H_{mix} = 0$

Also, the properties are expected to be strictly additive.

Just as the ideal gas laws form a useful basis for understanding the specific deviation shown by real gases, so also the concept of ideal solutions is useful in understanding the behaviour of non–ideal solutions.

Only a few binary miscible liquid systems obey Raoult's law throughout the complete range of concentrations. Examples of this type are carbon tetrachloride–silicon tetrachloride, ethylene dibromide-ethylene dichloride, benzene–ethylene dichloride, chlorobenzene-bromobenzene, hexane-heptane etc. Most systems, however deviate from Raoult's law to a greater or lesser degree depending on the nature of the liquids and the temperature. These are called *real or non–ideal solutions.* Completely miscible binary solutions can be divided into three categories.

In Fig. 9.3, 9.4, 9.5 behaviour of miscible liquid pairs of the three types are shown. The dotted lines in all these graphs indicate ideal behaviour.

Type I: *Solutions of this type show small positive deviations from ideal behaviour. The total pressure is at all times intermediate between those of the two pure components.* Fig. 9.3 gives a graphical representation for the cyclohexane–carbon tetrachloride system. CCl_4–benzene, benzene–toluene, water–methanol are other liquid pairs showing similar behaviour.

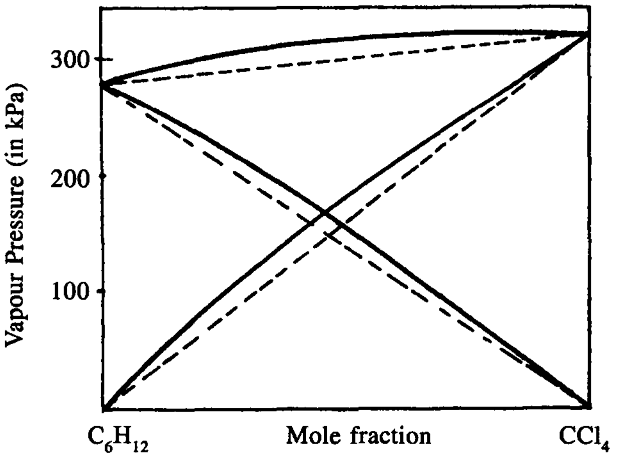
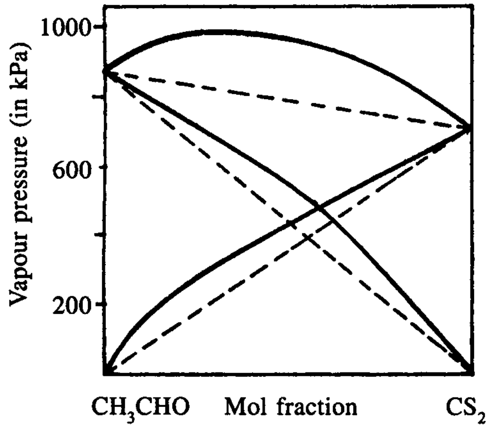


Fig. 9.3: Vapour pressure of the system cyclohexane-carbon tetrachloride at 313 K

Type II: *Solutions of this type show large positive deviations from Raoult's law. The total vapour pressure rises to a maximum which is above the vapour pressure of either of the pure constituents.* (Fig. 9.4) Examples of this type are acetaldehyde–carbon disulphide, ethanol–chloroform, water–ethanol etc.

Type III: In this cases, *large negative deviations from Raoult's law are seen and the total vapour pressure curve shows a minimum i.e., the vapour pressures of certain composition of the solution are below the vapour pressures of either of the pure* *components* (Fig. 9.5). Acetone–chloroform, water–sulphuric acid, water–nitric acid, etc., show this type of behaviour.



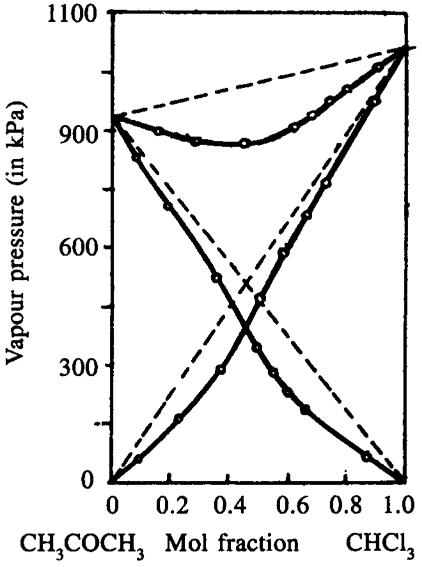


Fig. 9.4: Vapour pressures of the system methanol-carbon disulfide at 308 K

Fig. 9.5: Vapour pressures of the system acetone-chloroform at 328 K

In the above graphs, it can be seen that the vapour pressure curves becomes nearly straight lines when mixture contains a large amount of one of the components. This is a case of a very dilute solutions and ideal behaviour is expected; Raoult's law is obeyed.

9.4.3 Vapour Pressure–Composition Curves of Binary Solutions

It is convenient to show two lines on a vapour pressure diagram – one of the lines showing the vapour pressure changes with the composition of the liquid mixture while the other shows how the composition of the vapour changes. Since the vapour is always richer in the more volatile component, the two lines are generally different. In other words, the composition of the vapour differs from that of the solution from which it distills over. Such diagrams are important in the study of distillations.

For ideal solutions the vapour composition that is in equilibrium with a liquid of mole fraction X_A can be easily calculated. In the case of non–ideal solutions on the other hand, the composition of the vapour in equilibrium with a given solution is calculated from the experimentally determined vapour pressures of the two components.

The vapour pressure – composition curves correspond to conditions of constant temperature. In all the cases, the vapour – composition curves lie below the liquid – composition curves (Fig. 9.6).

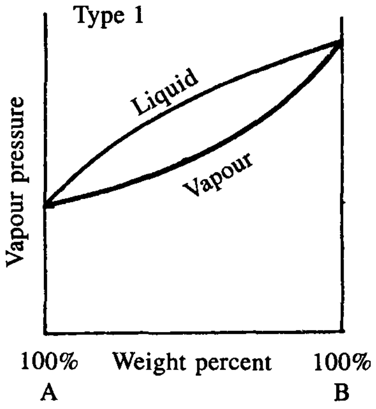


Fig. 9.6(a)

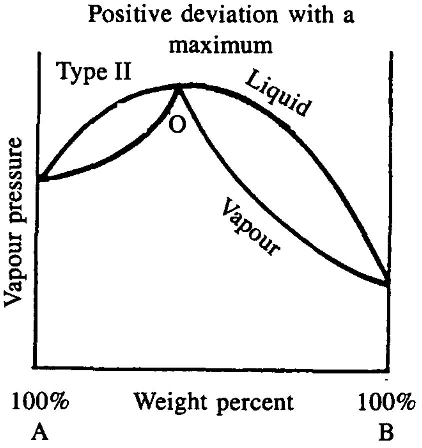


Fig. 9.6(b)

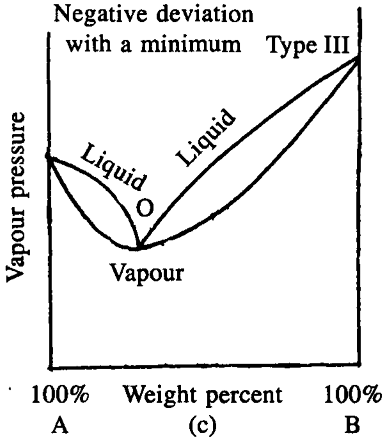


Fig. 9.6(c)

Fig. 9.6(a), (b), (c) Types of Vapour Pressure Composition diagrams

In *solution of type II* where the curves show a maximum, the vapour composition and the liquid composition curves are in contact at the point of maximum vapour pressure. At this point the compositions of the solution and the vapour are identical. The non-ideality arises due to interaction between the components.

The system shows a higher vapour pressure than predicted by Raoult's law. One of the components like water, alcohols exists in associated state and the other is more or less inert. Due to mixing, the extent of association is lowered and the enthalpy change is positive.

A similar situation is seen in *type III solutions*. The vapour pressure is lower than the predicted value according to Raoult's law and the interaction could be similar to acid-base or hydrogen bond formation.

This leads to liberation of heat, i.e., negative enthalpy of mixing as against zero enthalpy of mixing in an ideal solution. Even the entropy of mixing in the above cases is different from that of the ideal case.

A completely miscible mixture consisting of two liquids A and B, when heated under constant pressure will boil at a temperature when its total vapour pressure becomes equal to the external pressure. If P represents the external pressure, then the condition for boiling may be written as

$$P = P_A + P_B$$

where P_A and P_B are the total pressures of A and B respectively.

Since solutions of different compositions have different vapour pressures, it must follow that these solutions will boil at different temperatures. In general, a solution of higher vapour pressure will boil at a relatively lower temperature.

The temperature–composition or boiling point–composition curves can be drawn. The shapes of the curves depend on the behaviour of the system as a function of temperature at constant pressure.

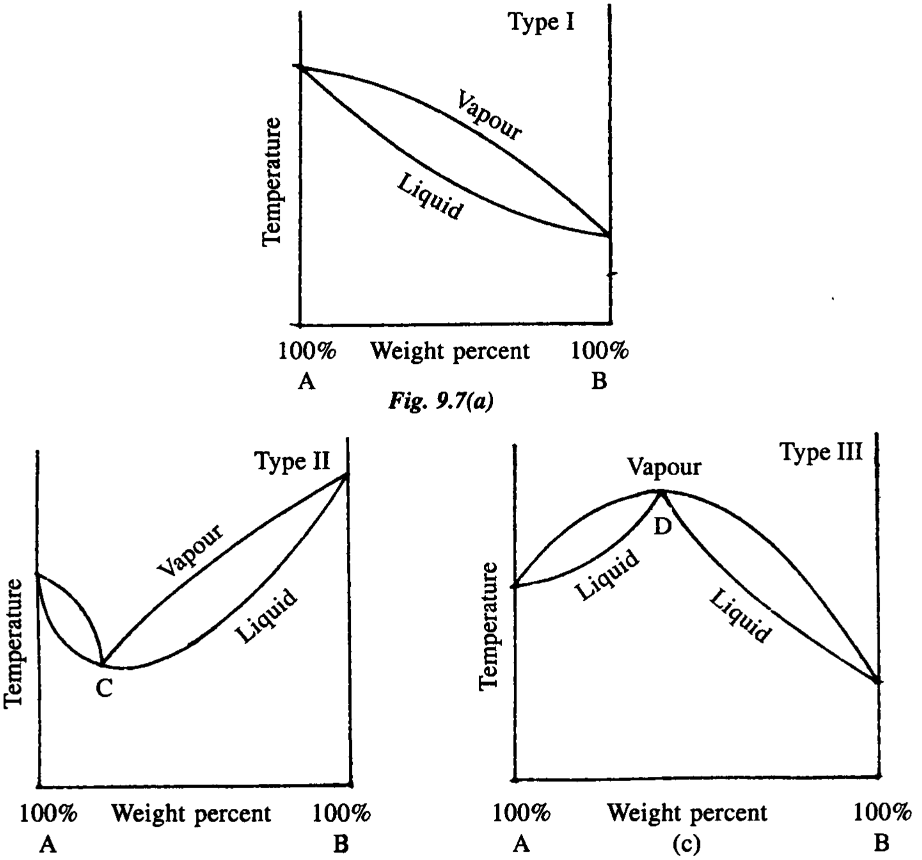


Fig. 9.7(a)

Fig. 9.7(b)

Fig. 9.7(c)

Fig. 9.7 (a), (b), (c) Boiling point-Composition curves of Binary Solutions

In *solutions of type I*, the vapour pressure of A is the lowest in the system and that of B is the highest. Solutions of different compositions of A and B have vapour pressures intermediate between the two. Consequently, at constant pressure, the boiling point of A will be the highest in the system, that of B the lowest in the system. Solutions of the different compositions of A and B have boiling points intermediate between the two. Also the vapour coming off form any particular composition has a larger proportion of the volatile constituent B than the corresponding liquid.

In Type II the vapour of the system is maximum for composition C, and hence such a solution will boil at the lowest temperature leading to a minimum in the boiling point curve.

In Type III solutions on the other hand, the solution of composition D has the lowest vapour pressure in the system and the boiling point curve exhibits a maximum.

9.4.4 Distillation of Binary Liquid Solutions

The behaviour of the three types of solutions on distillation at constant pressure is different since their boiling point diagrams are different.

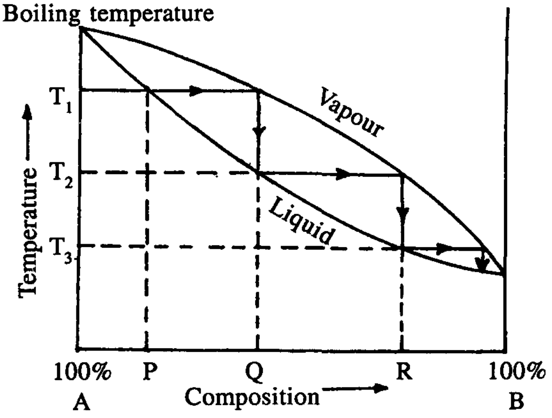


Fig. 9.8: Distillation behaviour of solutions of type I

Type I: On heating a solution of composition P no boiling starts until temperature T_1 is reached. At this temperature, the vapour coming off the solution of composition P is richer in the more volatile component B and has the composition Q (Fig. 9.8). Since the vapour is richer in the component B, the residue will be richer in the less volatile component A. On heating the residue boils at a temperature higher than T_1. The vapour coming off is richer in B and the residue is richer in A. By distilling the residual solution again, a final residue of pure A is obtained.

If the vapour coming off the solution be condensed i.e., the vapours of the original solution of composition P be condensed and again distilled, the solution will boil at a lower temperature T_2. the vapour coming over is again richer in B than the original, in this case of composition R. The vapours on condensing and distilling boils at a temperature T_3. By continuing this process of condensing and redistilling the vapours, distillate consisting essentially of pure B can be obtained. Thus by repeated distillation of a binary solution of type I, it is possible to separate the constituents into a residue of the less volatile constituent A and a distillate of the more volatile constituent B.

The above process of separating mixtures by repeated distillations and condensation in a discontinuous manner would be extremely complicated and tedious. Instead the separation is performed in a continuous manner, using a distilling apparatus called the *fractionating column.* This process is termed as *fractional distillation.*

On a commercial scale, the fractionating column consists of belts and plates provided at different heights dividing the column into different compartments.

The liquid mixture is heated in the still at the bottom. As the vapours enter the first compartment A, partial condensation occurs. The condensate containing more of the high boiling component, collects on the plate while the vapour containing more of the volatile constituent pass on the next compartment B.

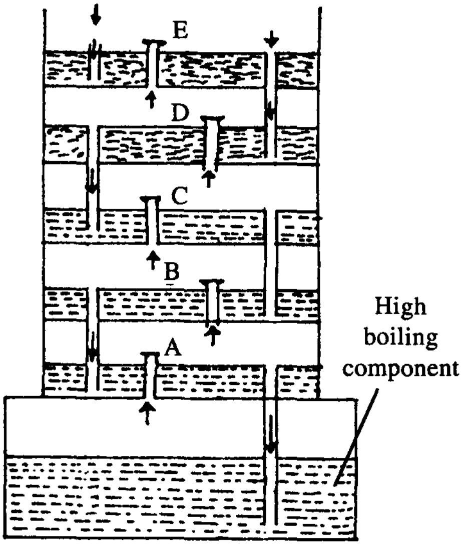


Fig. 9.9: Bell and plate type fractionating column

This continues and eventually the vapours of the more volatile constituent escape at the top while the high boiling component collects at the bottom.

Type II: The distillation behaviour of solutions of type II shows a minimum at C. The liquid and vapour phases at this point have the same composition.

If a solution of composition between A and C such as x is distilled, the solution boils at temperature T, and the vapour coming off has more of the more volatile component B than the original solution x. The composition of the residue in the flask will therefore shifts towards A and boil at a temperature higher than T. If the distillation is continued, then eventually residue of pure A, boiling at temperature T_A is obtained.

The vapour of the original solution x contains more of the more volatile component B and has a composition x'. When the vapours are condensed and redistilled repeatedly, a vapour of composition C is eventually obtained. This vapour when condensed and redistilled will distill over having the same composition as C. Thus no further separation is possible by distillation.

Only one of the pure components can be separated depending upon the composition of the original mixture, by complete fractional distillation in this case.

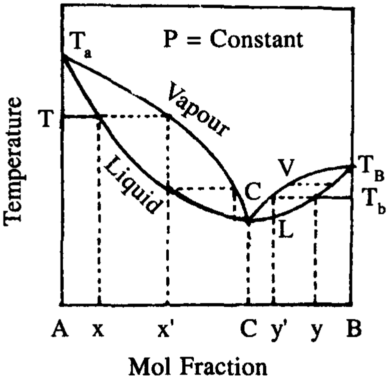


Fig. 9.10: Distillation behaviour of solutions of type II

On the other hand, if a solution of composition between C and B, for example y, is distilled, the solution boils at T_b and the vapour coming off is richer in A than the original solution y. On repeated distillation the residue will tend towards pure B while the distillate towards C. Such a solution on complete distillation will yield pure B in the residue and a constant boiling mixture of composition C in the distillate. In this case, pure A cannot be recovered by distillation.

Type III: The behaviour of solution of type III is similar to that of type II discussed above. The only difference being that the residue tends towards the maximum boiling mixture of composition D while the distillate tends towards pure constituents either A or B.

Since the constant boiling mixture is least volatile, it has the maximum boiling point and is obtained as residue.

To start with if the liquid mixture has composition between A and D, say 'a' the vapour obtained on distillation is richer in the component A than the original mixture. The composition of the residue shifts towards D. Repeated distillation gives a residue of the constant boiling mixture of composition at D. The vapour has a composition a', which on condensing and redistilling finally gives a distillate of pure A. Pure B cannot be obtained by distillation of this mixture.

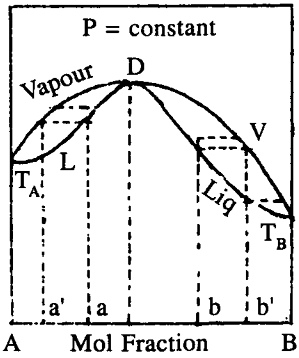


Fig. 9.11: Distillation behaviour of solutions of type III

A mixture of composition 'b' lying between D and B on distillation will yield a vapour richer in component B than the original solution. The residue, as before shifts towards D and eventually a residue containing the constant boiling mixture is obtained. The distillate on the other hand, on repeated condensation and distillation gives off vapours of pure B. In this case, pure A cannot be separated by distillation.

As in type II solutions, only one of the pure components can be separated by fractional distillation of the mixture.

Thus in binary solutions of type II and type III showing large deviations from Raoult's law with a maximum or a minimum in the boiling point curve, *it is not possible to separate the two components by fractional distillation. In both the cases, on complete fractional distillation the mixture can only be separated into a constant boiling mixture of composition C or D and one of the pure constituents, A or B depending upon the composition of the original mixture.*

9.4.5 Azeotropic Solutions

The *constant boiling mixtures obtained during fractional distillation of non–ideal solutions are called azeotropic solutions.* The composition of an azeotropic solution is a constant at given pressure. On varying the pressure, both the composition and the boiling point changes. This shows that an azeotrope is not a chemical compound but only a mixture. 100% pure constituents may be obtained by other methods. For example, ethyl alcohol and water form an azeotrope containing 95.6% alcohol boiling at 351.2 K. In order to obtain pure alcohol calculated amount of benzene is added to the above mixture. A ternary mixture containing 18.5% alcohol, 7.4% water and 74.1% benzene distills over at 337.6 K; this continues till water is completely removed. The next fraction is a binary mixture of 67.6% benzene and the rest alcohol boiling over at 340.8 K. Pure alcohol is left behind as residue which boils at 351.3 K.

Methods like preferential adsorption treatment with a chemical which attacks only one of the component, like quick–lime used to remove water from rectified spirit, or fractional extraction can also be used.

Table 9.2: Boiling points and composition of Azeotropes
$P = 101.3\ kNm^{-2}$

Type	*Liquid A*	*Liquid B*	*P.(K)*	*Weight % of A*
Minimum	H_2O (373 K)	C_2H_5OH (351.3 K)	351.2	4.4
boiling point	H_2O	C_3H_7OH (370.2 K)	360.7	28.3
	CH_3OH (337.7 K)	$CHCl_3$ (334.2 K)	326.5	12.5
	C_2H_5OH	C_6H_6	341.2	32.4
	CH_3COOH (391.5 K)	$C_6H_5CH_3$ (383.6 K)	378.4	28.0
Maximum	HCOOH (273.8 K)	H_2O	380.1	77.5
boiling point	HCl (189 K)	H_2O	381.6	20.2
	HBr (200 K)	H_2O	399.0	47.6
	HNO_3 (359 K)	H_2O	393.5	68.0
	$CHCl_3$	CH_3COCH_3 (329.4 K)	381.6	80.0

9.4.6 Partially Miscible Liquid Pairs

There are quite a number of *liquid pairs which show only limited miscibility in each other. They are partially miscible.* This is similar to the solution of a sparingly soluble salt in a liquid. For example, when a small amount of phenol is added to water at room temperature and shaken, a solution of phenol in water is obtained. However, on adding a larger amount of phenol two liquid layers separate – one a solution of phenol in water and the other a solution of water in phenol. *Each layer is a saturated solution of one in the other.* At a constant temperature, the composition of the two layers, although different from each other, remain constant as long as the two phases are present. The two layers in equilibrium are called *conjugate solutions*. The addition of any one of the liquids merely changes the relative volumes of the two layers and not their composition. Gradual addition of phenol causes the water layer to diminish in size which finally disappears and only a layer of water in phenol remains. The mutual solubility of the two liquids varies in a characteristic manner with temperature. In this case, the mutual solubility goes on increasing as the temperature is increased until a homogenous solution is obtained. This *temperature at which the two liquids become completely miscible is called the mutual solubility temperature (M.S.T.) for that particular composition of the two liquids.*

Understanding partial miscibility of some liquids

During mixing, there is more disorder and entropy increases. In the case of partially miscible liquids, enthalpy of mixing ΔH is positive i.e., endothermic which is unfavourable. In such a situation, the two liquids mix only if ΔS > ΔH. When one of the components is very large ΔS is sufficiently positive to overcome the unfavourable ΔH and the two liquids are miscible. Large proportions of both the components lead to a situation where ΔH is too endothermic to be overcome by ΔS at room temperature. The liquids do not form a homogenous solution. However, as the temperature is increased. TΔS > ΔH and the two liquids become miscible.

This can be observed in phenol–water system. A very small amount of water is miscible in phenol and the reverse is also true. Beyond a certain concentration phenol and water do not mix at room temperature.

9.4.7 Variation of mutual solubility with temperature in phenol–water system

The variation of mutual solubility of phenol and water with temperature is as shown in Fig. 9.12. At any one temperature in the curve, the composition of each layer is fixed by points A and B.

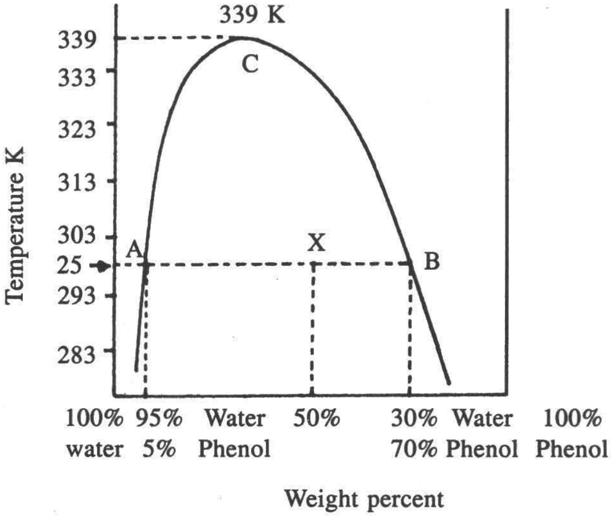


Fig. 9.12: Mutual solubility of phenol-water system

The composition of phenol in water is given by point A while, that of water in phenol is given by B at that temperature. The line joining the two points A and B is called the *tie line*. With increase of temperature as seen from the curve, the composition of the two layers approach each other. At 339 K, the two layers merge into one homogeneous solution. This temperature is called the *critical solution temperature (C.S.T) or the consolute temperature of the system.* Above this temperature, it is seen that the two liquids are miscible with each other in all proportions and only a single layer of liquid results.

Since this temperature is the *maximum* on the *mutual solubility temperature – composition curve*, it is termed the *upper critical temperature or upper consolute temperature.*

Any solution of phenol and water of composition and temperature represented by a point within the curve ACB consists of two layers.

The proportion by weight of the two layers can be easily calculated using *lever rule*. Accordingly for a system of composition say 50% of phenol,

$$\frac{\text{Weight of aqueous layer}}{\text{Weight of phenol layer}} = \frac{XB}{AX}$$

Any composition at a given temperature represented by points on the left of the curve AC or the right of the curve CB consists of only one layer. All compositions between pure water and point A yield a solution of phenol in water. Within the dome shaped area ACB, the system is heterogenous and two liquid phases exist, while in the area outside the dome only a single liquid layer, i.e., a homogeneous system exists, *The upper critical solution temperature may, therefore be defined as the temperature above which the two partially miscible liquids become miscible in all proportions*. For phenol–water system the temperature is 339 K.

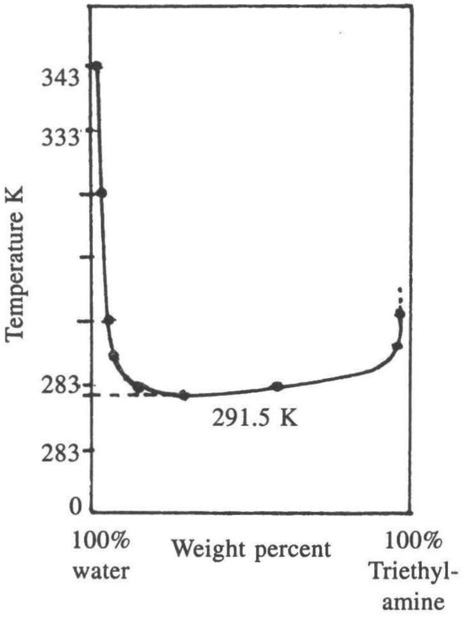


Fig. 9.13: Mutual solubility of triethylamine in water

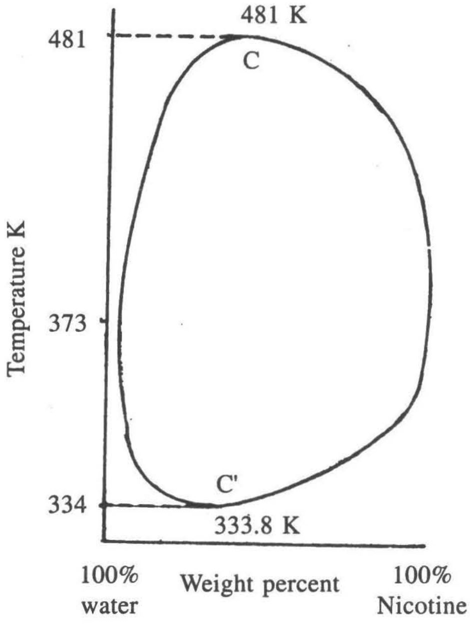


Fig. 9.14: Mutual solubility of nicotine in water

Triethylamine–Water system: There are a few miscible liquid pairs where the mutual solubility is found to increase with decrease in temperature. In the case of triethylamine–water system for example, at or below 291.5 K the two liquids are completely miscible. Above this temperature, the two liquids are only partially miscible in all proportions. *The temperature below which two partially miscible liquids become completely miscible is called the lower critical solution temperature* since the curve confining the area of partial miscibility exhibits a minimum (Fig. 9.13).

Nicotine–water system: This system exhibits upper as well as lower critical solution temperatures. Within the enclosed area, the two liquids are only partially miscible and a heterogeneous system exists. (Fig. 9.14)

Outside this area, there is a homogeneous phase. The upper or maximum critical solution temperature is 481 K while the lower or minimum is 333.8 K indicated by C and C' respectively. The composition corresponding to C and C' are the same and is equal to 34% nicotine.

The critical solution temperature of this system is affected by pressure. On applying external pressure to the system, the upper and lower critical solution temperature approach each other until a pressure is reached when the two liquids becomes completely miscible.

There are also certain liquid pairs like ether–water which do now show an upper or a lower critical solution temperature. They are only partially miscible in each other at all temperatures.

The critical solution temperature is affected considerably by the presence of foreign substances. A foreign substance soluble in only one of the liquids decreases the mutual solubility resulting in an increase in the critical solution temperature. For example, 0.15 M KCl raises the critical solution temperature of phenol–water system by about 12 K. On the other hand, if the foreign substance dissolves in both the liquids uniformly, the mutual solubility is increased and the critical solution temperature is lowered. For example, 0.083 M sodium oleate decreases the critical solution temperature of phenol–water system by 9.3 K.

Table 9.3: Critical Solution temperatures of some partially miscible liquid systems

Liquid Pairs	*Critical solution temperature*	
	Upper	*Lower*
Phenol – Water	339 K	–
Phenol – isopentane	336.5 K	–
Methanol – Cyclohexane	322.1 K	–
Methanol – Carbon disulphide	313.5K	–
Aniline – Hexane	332.61 K	291.5 K
Water – Triethylamine	–	291.5 K
Water – Diethylamine	416 K	–
Nicotine – Water	481 K	333.8 K
Glycerol – 3–Toluidine	393 K	280 K

9.4.8 Completely Immiscible Liquid Pairs

In the case of completely immiscible or almost completely immiscible liquid pairs, the addition of one liquid to the other no way affects the properties of either liquid. Each liquid behaves as if the other is not present. Accordingly, in mixture of two immiscible liquids, each liquid exerts its own pressure corresponding to the pure liquid at the given temperature. The total vapour pressure of the two pure liquids at that temperature. Thus

$$P = P_A^o + P_B^o$$

where P_A^o and P_B^o are the vapour pressures of the two pure liquids A and B at that temperature. The pressure exerted by each liquid and hence the total pressure do not depend on the actual or relative amounts of liquids present.

Any system boils at a temperature when its total vapour pressure becomes equal to the external pressure. In this case, since the two liquids together can reach any given total pressure at a lower pressure lower than either liquid alone, it is obvious *that the mixture boils at a lower temperature lower than the boiling point of either of the two liquids present in the mixture.* Further since at any given temperature there is no change in the partial vapour pressure of the component liquids, *the boiling point of all possible compositions of any two immiscible liquids remains the same as long as the two liquids are present.*

When one of the liquids is boiled away the temperature rises to T_A or T_B depending upon which liquid (A or B) is left behind.

The relative proportions of the two liquids in the distillate can be calculated, since the number of moles of each component in the vapour phase is proportional to its vapour pressure. At the boiling point T, if n_A and n_B are the number of moles of the two liquids A and B in the vapour phase, then

$$n_A \propto P_A^o \quad \text{and}$$

$$n_B \propto P_B^o.$$

or

$$\frac{n_A}{n_B} = \frac{P_A^o}{P_B^o}$$

$$\frac{n_A}{n_B} = \frac{W_A/M_A}{W_B/M_B}$$

where W_A and W_B are the actual weights of the two liquids A and B in the distillate, and M_A and M_B are the respective molecular weights.

$$\frac{P_A^o}{P_B^o} = \frac{W_A/M_A}{W_B/M_B} = \frac{W_A M_B}{W_B M_A}$$

or

$$\frac{W_A}{W_B} = \frac{P_A^o M_A}{P_B^o M_B}$$

The above equation relates directly the ratio of the weights of the two components present in the distillate of a mixture of two immiscible liquids to the molecular weights and vapour pressure of the two pure components. Examples of such pairs include water–cyclohexane, water–nitrobenzene, water–bromobenzene, water–aniline, etc.,

9.4.9 Steam Distillation

Distillation of immiscible liquids is utilized industrially and in the laboratory as it involves the lowering of boiling points of the components. Purification of organic liquids which either have very high boiling point or tend to decompose when heated to their boiling points can be suitably carried out using the above principle. The other liquid is generally water and the process is known as *steam distillation*. The immiscible mixture of the liquid and water is either heated directly or by passing the vapours of steam into the liquid. The vapours distilling over are condensed and separated. In this manner it is possible to distill many organic liquids of high boiling point at temperatures below 373 K i.e., the boiling point of water.

Example 1: *At a pressure of 101.3 kNm^{-2} a mixture of water and nitrobenzene distills over at 372 K. The vapour pressure of water at 372K is 97.70 kNm^{-2}. Estimate the proportion by weight of nitrobenzene in the distillate.*

$$\frac{\text{Weight of nitrobenzene } W_A}{\text{Weight of water } W_B} = \frac{P^o_A M_A}{P^o_B M_B}$$

$$\begin{aligned}
\text{Molar mass of nitrobenzene} &= 0.123\ \text{kgmol}^{-1} \\
\text{Molar mass of water} &= 0.018\ \text{kgmol}^{-1} \\
\text{Total pressure} &= 101.3\ \text{kNm}^{-2} \\
P^o_B &= P - P^o_A = 101.3\ \text{kNm}^{-2} - 97.70\ \text{kNm}^{-2} \\
&= 3.60\ \text{kNm}^{-2}
\end{aligned}$$

$$\therefore \quad \frac{W_A}{W_B} = \frac{3.60\ \text{kNm}^{-2}}{97.70\ \text{kNm}^{-2}} \times \frac{0.123\ \text{kgmol}^{-1}}{0.018\ \text{kgmol}^{-1}}$$

$$W_A : W_B = 0.252 : 1.0$$

∴ Proportion of nitrobenzene in the distillate

$$= \frac{\text{Wt. of nitrobenzene}}{\text{Total wt of water and nitrobenzene}} \times 100$$

$$= \frac{0.252}{1.252} \times 100$$

$$= 20.13$$

$$\boxed{\text{Proportion by weight of nitrobenzene} = 20.2\%}$$

Example 2: *In a steam distillation of an insoluble oil, the mixture boils at 368K when the external pressure is 100kNm^{-2}. The vapour pressure of water at this temperature is 84.0 kNm^{-2}. If the molar mass of water and oil are 0.018 kNm^{-2} and 0.380 kNm^{-2} respectively, calculate the amount of steam required to distill 0.1kg of oil.*

$$\frac{\text{Weight of steam } W_A}{\text{Weight of oil } W_B} = \frac{P^o_A M_A}{P^o_B M_B}$$

$$P_A^o = 84.0\ \text{kNm}^{-2}$$

$$P_B^o = 100 - 84.0 = 16\ \text{kNm}^{-2}$$

$$\therefore \quad \frac{W_A}{W_B} = \frac{84.0\ \text{kNm}^{-2}}{16.0\ \text{kNm}^{-2}} \times \frac{0.018\ \text{kgmol}^{-1}}{0.380\ \text{kgmol}^{-1}}$$

Weight of oil in the distillate = 0.1 kg

Weight of steam in the distillate be W_A

$$\therefore \quad W_A = \frac{84.0\ \text{kNm}^{-2}}{16.0\ \text{kNm}^{-2}} \times \frac{0.018\ \text{kgmol}^{-1}}{0.380\ \text{kgmol}^{-1}} \times 0.1\ \text{kg}$$

$$= 0.0248\ \text{kg}$$

i.e,. $\boxed{\text{Weight of steam necessary to distill 0.1 kg of oil is 0.0248 kg}}$

Example 3: *Two immiscible liquids, water and an organic liquid are boiled at 97.89kNm^{-2} pressure and the mixture boils at 363K. The ratio of the weight of organic liquid to water collected in the distillate is 2.47. Calculate the molecular weight of organic liquid if vapour pressure of water at this temperature is 70.11 kNm^{-2}.*

Vapour pressure of organic liquid = $97.89\ \text{kNm}^{-2} - 70.11\ \text{kNm}^{-2}$

$$= 27.78\ \text{kNm}^{-2}$$

$$\frac{\text{Weight of organic liquid}}{\text{Weight of water}} = \frac{P_A^o M_A}{P_B^o M_B}$$

$$\text{i.e., } 2.47 = \frac{22.78\ \text{kNm}^{-2} \times M_A}{70.11\ \text{kNm}^{-2} \times 0.018\ \text{kgmol}^{-1}}$$

$$M_A = \frac{2.47 \times 70.11\ \text{kNm}^{-2} \times 0.018\ \text{kgmol}^{-1}}{27.78\ \text{kgmol}^{-1}}$$

$$= 0.1122\ \text{kgmol}^{-1}$$

$$\text{Relative molar mass} = \frac{0.1122\ \text{kgmol}^{-1}}{0.001\ \text{kgmol}^{-1}}$$

$$= 112.2$$

$\boxed{\text{Molecular weight of organic liquid} = 112.2}$

9.5 THE DISTRIBUTION LAW

Iodine is soluble both in water and carbon tetrachloride. When a solution of iodine is shaken with carbon tetrachloride it is found to that the brown aqueous solution turns to pale brown while the carbon tetrachloride layers acquires a deep purple colour. Iodine distributes itself between water and carbon tetrachloride layers. The distribution of iodine in two layers is such that the ratio of the concentration of iodine in the two layers at a given temperature.

$$\text{i.e., } \frac{\text{Concentration of iodine in } CCl_4 \text{ layer}}{\text{Concentration of iodine in aqueous layer}} = \text{constant, K}$$

Such distribution of a solute between any two immiscible or only slightly miscible solvents can be accomplished with any solute. A number of experiments were carried out by Berthelot and Jungfleish (1972) and a formulation known as distribution law was put forward.

"*A solute distributes itself between two non-miscible solvents in contact with each other in such a way that the ratio of its concentrations in the two layers (C_1 / C_2) is a constant irrespective of its total amount.*"

Nernst (1891) pointed out later that the ratio C_1/C_2 is a constant only when the solute exists in similar molecular species in both the solvents i.e., the solute has the same molecular weight in both the solvents.

Nernst distribution law is stated as – *when a solute distributes itself between two non–miscible solvents in contact with each other, there exists for similar molecular species at a constant temperature, a constant ratio of distribution between the two solvents irrespective of the amounts of the solute and the liquids.*

$$C_1/C_2 = K$$

C_1 and C_2 refers to the concentration of similar molecular species in the two liquids at a constant temperature. Conventionally, the higher concentration term is kept as the numerator so that $K > 1$. *K* is the *distribution coefficient* or *partition coefficient* of the solute between the two solvents. Use of activities, particularly in concentrated solutions leads to accurate distribution coefficient values.

9.5.1 Condition for the Validity of Distribution Law

The distribution law is found to be valid only under the following conditions.

1. *Constant temperature:* The numerical value of K varies with temperature. This can be easily understood since variation of temperature causes a change in the solubility of the solute in the two solvents. The distribution coefficient of benzoic acid between chloroform and water is 1.773 at 283 K and 2.262 at 313 K.

2. *Dilute solutions:* As the concentration of the solute increases, the deviations from the distribution law becomes more and more pronounced. This may be due to stronger forces of attraction existing among the solute molecules in a concentrated solution.

3. *Mutual solubility of the two liquids:* The two liquids must be immiscible or only very sparingly soluble. Further, addition of a solute should not alter the mutual solubility of the two liquids.

For example, if a solute added decreases the mutual solubility of the two liquids, the mutual solubility eventually becomes zero and the partition coefficient becomes equal to the ratio of the solubilities of the solute in pure solvents. If the mutual solubility is increased by the solute as in the case of malonic acid increasing the mutual solubility of ether and water, the concentrations of the solute in the two layers tend to become equal and the partition coefficient then becomes one. The concentration at this point is known as constant concentration. If the addition of the solute increase the solubility of the first in the second, and decreases that of the second in the first the distribution coefficient keeps changing with every addition of the solute.

4. *Similar molecular species of the solute:* The solute must remain in the same molecular state in both the solvents. The law does not hold good if there is association or dissociation of the solute in either or both the solvents.

5. *No chemical interaction between the solute and the solvent.*

9.5.2 Deviation from Distribution Law due to Molecular Complexity

Nernst pointed out that distribution law is applicable only where the solute exists as normal molecules in both the solvents. If a solute were to dissociate into simple molecules or associate to more complex molecules then the distribution law is not valid. In such cases, the concentration terms in the distribution law should refer to the concentrations of the particular species common to both. Thus if a substance A dissolves in one solvent as normal molecules and with partial association (or dissociation) in the other, then the partition coefficient for the distribution if given by the ratio of the total concentration of A in the first solvent and the concentration of the unassociated (or dissociated) molecules in the second.

1. Association of the solutes in one of the solvents:

Let X represent the molecular formula of the solute.

Let the solute remain as X in the first solvent and let it be associated in the second solvent.

Let the total concentration of the solute in the first and second solvents be C_1 and C_2 respectively.

In the second solvent an equilibrium exists between the associated and the unassociated molecules. If n molecules of the solute are polymerised, then

$$(X)_n \rightleftharpoons nX$$

Applying law of mass action to the above chemical equilibrium,

$$K_{eq} = \frac{[X]^n}{[(X)_n]}$$

where K_{eq} is the equilibrium constant

$$[X]^n = K_{eq}[(X)_n]$$

$$\text{or} \quad [X] = \sqrt[n]{K_{eq}[(X)_n]}$$

[X] corresponds to the concentration of the solute in the unassociated form in the second solvent. If the solute is largely associated in the second solvent, then the total concentration of the solute molecules in the second solvent C_2 may be considered to be the concentration of the associated molecules $[(X)_n]$.

$$[X] = \sqrt[n]{K_{eq}C_2}$$

Since the distribution law is valid only for concentrations of similar molecular species in the two phases.

$$K = \frac{C_1}{[X]}$$

Substituting for [X]

$$K = \frac{C_1}{\sqrt[n]{K_{eq}\, C_2}}$$

$$\text{or} \quad K\sqrt[n]{K_{eq}} = \frac{C_1}{\sqrt[n]{C_2}} \qquad [\because K_{eq} \text{ is a constant}]$$

$$\therefore \boxed{\frac{C_1}{\sqrt[n]{C_2}} = \text{constant, } K'}$$

K′ is the distribution or partition coefficient in the above case.

A typical example of this type of system is the distribution of benzoic acid between water and benzene. Benzoic acid exists as a dimer in benzene and hence partition coefficient,

$$K = \frac{C_{water}}{\sqrt{C_{benzene}}}$$

Distribution of benzoic acid between water and benzene

Benzoic acid C_{water}	$C_{benzene}$	$\frac{C_w}{C_b}$	$\frac{C_w}{\sqrt{C_b}}$
0.15	0.24	0.062	0.096
0.19	0.41	0.048	0.096
0.29	0.97	0.030	0.093

2. ***Dissociation of the solute in any one of the solvents:***

Let X represent the molecular formula of the solute.

Let the solute remain as normal molecules in solvent I and be dissociated in solvent II.

Let C_1 and C_2 be the total concentration of the solute species in solvents I and II respectively.

If α is the degree of dissociation, then at equilibrium, in solvent II,

$$\begin{array}{ccc} (X) & \rightleftharpoons & A + B \\ C_2(1-\alpha) & & C_2\alpha \quad C_2\alpha \end{array}$$

The concentration of the undissociated molecules of the solute is given $C_2(1 - \alpha)$.

Distribution law is applicable to the concentration of the solute species of similar molecular nature in the two solvents.

Hence $$\boxed{\frac{C_1}{C_2(1-\alpha)} = \text{constant, K}}$$

In case, the solute is dissociated in both the solvents but to different extents, say α_1 in solvent I and α_2 in solvent II, then

$$\boxed{\text{Partition coefficient } K = \frac{C_1(1-\alpha)}{C_2(1-\alpha)}}$$

Example 4: *Different amounts of iodine are shaken with equal volumes of carbon tetrachloride and water mixture. The concentration of iodine in the two layers are found to be*

CCl_4 layer (C_1)	*4.85*	*3.42*	*2.96*
Aqueous layer (C_2)	*0.57*	*0.40*	*0.35*

Show that these results illustrate the distribution law.

According to distribution law K which is C_1 / C_2 should be a constant

(i) $C_1 = 4.85, \quad C_2 = 0.57$

$$\therefore C_1 / C_2 = 4.85 / 0.57$$
$$K = 85.1$$

(ii) $C_1 = 3.42, \quad C_2 = 0.40$

$$\therefore C_1 / C_2 = 3.42 / 0.40$$
$$K = 85.5$$

(iii) $C_1 = 2.96, \quad C_2 = 0.35$

$$\therefore C_1 / C_2 = 2.96 / 0.35$$
$$K = 84.6$$

Since the value of K in each case is the same, distribution law is illustrated.

Example 5: *Experiments in the study of the ratio of distribution of phenol between water and chloroform gave the following results.*

Concentration in aqueous solution (C_1)	*4.85*	*3.42*	*2.96*
Concentration in chloroform solution (C_1)	*0.57*	*0.40*	*0.35*

What conclusion regarding the molecular nature of phenol in chloroform solution can be drawn from the above results?

Phenol if exists as normal molecules in chloroform solution, then C_1 / C_2 would be a constant. If it is associated as a dimer, then $\frac{C_1}{\sqrt{C_2}}$ should be a constant:

C_1	C_2	$\frac{C_1}{C_2}$	$\frac{C_1}{\sqrt{C_2}}$
0.094	0.254	0.3701	0.1865
0.163	0.761	0.2142	0.1868
0.254	1.850	0.1373	0.1867

Since $\frac{C_1}{\sqrt{C_2}}$ remains a constant it follows that phenol molecules are in the form of dimers in chloroform solution.

9.5.3 Applications of Distribution Law

1. *Determination of molecular complexity and molecular weight:* The constant value of K is given by different expressions depending upon the molecular state of the solute in the two immiscible solvents. Thus it is possible to know the molecular state of the solute in the given solvent and also calculate its molecular weight. The following table is highly useful in relating to the molecular state of the solute in the two solvents.

Concentration in		*Distribution law*	*Molecular state in*	
Phase 1	*Phase 2*	*expression*	*Phase 1*	*Phase 2*
C_1	C_2	$\frac{C_1}{C_2}$	Normal	Normal
C_1	C_2	$\frac{C_1}{\sqrt[n]{C_2}}$	Normal	Association
C_1	C_2	$\frac{C_1}{C_2(1-\alpha)}$	Normal	Dissociation
C_1	C_2	$\frac{C_1(1-\alpha)}{C_2(1-\alpha)}$	Dissociation	Dissociation

The state of aggregation gives an idea about the relative molecular mass of the solute in each phase.

2. *In analysis:* When the analysis of a substance is solvent A is difficult, the analysis may be carried out in another solvent B in which it is relatively easy. In such a case, the distribution of the substance between the two solvents is carried out and the substance analysed for in solvent B. From the results of analysis in B, the distribution coefficient K for the substance in the two solvents, the volumes of A and B used etc., the weight of substance originally present in A can be calculated. For example, an extremely dilute solution of iodine in water can be easily analysed using CCl_4 or CS_2. Iodine distributes itself to a larger extent in CCl_4 or CS_2 than in water. The CCl_4 or CS_2 layer turns distinctly violet enabling the analysis.

3. *Study of complex ions:* The formulae of the complex ions formed can be easily determined using distribution law. For example, in the case of iodine in contact

with KI solution, a complex tri-iodide is formed. the formula of the complex ion as well as the equilibrium constant for the reversible reaction can be determined using distribution law.

4. *Process of extraction:* This perhaps is the most important application of distribution law. Extraction of a substance is important both in the laboratory and in industry. It is widely used in the extraction of organic substances from aqueous solution and in the purification. In the industry, extraction is used to remove various impurities associated with a product. In all these cases, it is important to know how much solvent and how many treatments are needed to effect a particular degree of separation.

In order to separate a solute X from a solution (in solvent B), the solution is treated with another solvent A in which X is more soluble. Solvent A is chosen such that it is immiscible with the solution (solvent B).

The mixture is shaken vigorously and allowed to stand for some time. The two layers are then separated. In the solvent layer A, much of solute X passes into solution from which it can be recovered. The impurities insoluble in solvent A are left behind in the solution. The solvent A can be used again and again.

In order that the extraction process be efficient, the distribution coefficient of the solute between the added solvent and the solvent in which it is already dissolved should be very high. Normally organic solutes are highly soluble in organic solvents like ether, chloroform, benzene, etc., compared to their solubility in water and this method is particularly useful for the extraction of organic substances from their aqueous solution.

It is also seen that the efficiency of the extraction process is greatly improved by using the given volume of solvent in a number of instalments than in one single operation.

Let the value of K for a solute between the added solvent A and solvent B of the solution, say water, be 2.

$$\text{i.e.,}\quad K = \frac{C_A}{C_B} = 2$$

X be the amount of the organic solute present in 1 dm^3 of water and if 1 dm^3 of solvent A is being used for extraction, then

$$K = \frac{C_A}{C_B} = \frac{x}{X - x} = 2$$

where x is the amount of the solute passing into solvent A.

$$x = 2(X - x)$$

$$x = \frac{2}{3}X$$

Thus 66.7% of the solute gets extracted. If the same volume of the solvent A is being used in two installments of 0.5 dm^3 each, then at the end of first extraction, the amount of solute extracted x_1 can be calculated as follows:

$$K = \frac{\frac{x_1}{0.5\ \text{dm}^3}}{\frac{(X - x_1)}{1\ \text{dm}^3}} = 2$$

$$2(X - x_1)\ 0.5 = x_1$$

$$\text{or } x_1 = \frac{X}{2}$$

In other words 50% of the solute is extracted and 50% of it still remains in the solvent B. Adding the second instalment of 0.5 dm^3 of solvent A, an amount x_2, can be extracted. Again

$$K = \frac{\frac{x_2}{0.5\ \text{dm}^3}}{\frac{(0.5X - x_2)}{1\ \text{dm}^3}}$$

$$\text{or } x_2 = 2(0.5X - x_2)0.5$$

$$x_2 = \frac{X}{4}$$

Thus the total amount extracted at the end of the two operations adds up to $(x_1 + x_2) = \frac{3}{2}X$. In other words it has been possible to extract 75% of the solute which is more than the amount extracted in a single operation. In general a larger amount of the solute can be extracted using a given volume of solvent in many instalments rather than in a single operation.

A formula showing the efficiency of solvent extraction under different conditions can be deduced.

When a substance distributes itself between two solvents without the complications of association, dissociation or reaction with the solvent, the weight of substance extracted is calculated as follows:

Consider a solution of solute X present in solvent 1.

Let the amount of solute X be W in V dm^3 of the solvent.

Let it be extracted with v dm^3 of solvent 2 and the partition coefficient of X between solvents 2 and 1 be K.

At the end of first operation let W_1, of solute remain in solvent 1.

$$K = \frac{(W - W_1)/v}{W_1/V}$$

$$KW_1v = (W - W_1)V = WV - W_1V$$

$$W_1(Kv + V) = WV$$

$$W_1 = \left(\frac{V}{K_v + V}\right)W$$

Out of W_1, if W_2 of solute remain unextracted at the end of second operation, then

$$K = \frac{(W_1 - W_2)/v}{W_2/V}$$

$$KW_2v = (W_1 - W_2)V = W_1V - W_2V$$

$$W_2(Kv + V) = W_1V$$

$$W_2 = \left(\frac{V}{K_v + V}\right)W_1$$

Substituting for W_1,

$$W_2 = \left(\frac{V}{K_v + V}\right)\left(\frac{V}{K_v + V}\right)W$$

$$W_2 = \left(\frac{V}{K_v + V}\right)^2 W$$

In general , the amount W_n of the solute remaining unextracted at the end of n operations is given by,

$$W_n = \left(\frac{V}{K_v + V}\right)^n W$$

In order W_n be small, n should be large. Since the volume of the added solvent 2, used for extraction is a constant, i.e., (n × V is a constant), it follows if n is large v is small. In other words, by using small volumes of solvent in larger number of instalments, the extraction is made more efficient.

It is for this reason, that in washing of precipitates it is most effective to use a small quantity at a time and repeat the process a large number of times. The process is considered as the distribution of the impurity between the wash liquid and the precipitate.

The above principle is made use of in the *desilverisation of lead by Parke's process*. Silver is extracted from the ore argentiferous lead using molten zinc in which it is 300 times more soluble than in molten lead. Molten lead and molten zinc behave as the two immiscible solvents and the process is carried out at 1073 K. The upper zinc layer is richer in silver from which silver is removed by distilling off zinc. By repeating this extraction three or four times, almost whole of silver is removed from argentiferous lead.

In the qualitative analysis of iodide and bromide ions, the halogen is set free in aqueous medium. The solution is then shaken with a few drops of carbon tetrachloride or carbon disulphide, when most of the halogen passes into the organic solvent. The organic layer acquires a colour due to dissolved bromine or iodine which can be easily identified.

IMPORTANT POINTS

- A solution is a homogeneous mixture of two or more substances. The component present in the larger proportion is the solvent. The component present in relatively smaller proportion is called a solute.
- Depending upon the physical state of the solute and the solvent different types of solutions are possible.
- The solubility of a substance depends on nature of solute and solvent, temperature and pressure.
- Two factors that govern the process of solution are enthalpy of solution ΔH_{sol} and entropy of solution ΔS_{sol}.
- A negative enthalpy of solution favours solution formation.
- The process of solution is always accompanied by an increase in disorder or randomness.
- Chemically similar substances dissolve in each other – "like dissolves like".
- Effect of temperature on solution depends on the enthalpy of solution.
- Effect of pressure on solution is important only where gases are involved.
- The amount of gas dissolved in a solvent depends on pressure, temperature and nature of gas and the solvent. Solubility of a gas is expressed as mass of the gas per unit volume of the solvent.
- Gases which are easily liquefiable like CO_2 dissolve easily in water.
- At constant pressure, the solubility of a gas decreases with increase in temperature.
- The effect of pressure on the solubility of a gas is illustrated by Henry's law.
- Henry's law is stated as – the solubility of a gas in liquid is directly proportional to the partial pressure of the gas above the solution at constant temperature.
- Henry's law may also be stated as – the volume of a gas that dissolves in a fixed volume of a liquid at constant temperature is a constant and is independent of the pressure of the gas.
- Henry's law is applicable to real gases only approximately.
- The study of the solubility of the gases in blood or lipid fats under different pressures is of importance for deep water divers and mountaineers.
- Three types of binary liquid mixtures are possible namely – completely miscible, partially miscible and completely immiscible liquid pairs.
- In completely miscible liquid pairs, the liquid constituents mix freely and only a single phase exists.
- Raoult's law of ideal solutions is stated as – the partial pressure of a volatile constituent of a solution at constant temperature is equal to the product of the vapour pressure of the pure constituent and its mole fraction in the solution.
- In the formation of an ideal solution there is no volume change and no enthalpy change.

- An ideal solution obeys Raoult's law at all concentrations and temperatures.
- Completely miscible liquid systems can be divided into three categories depending upon the extent to which they deviate from ideal behaviour.
  - Type I solutions show small positive deviations from ideal behaviour. The total pressure of solutions is at all times intermediate between that of the two pure components.
  - Type II solutions show large positive deviations from Raoult's law. The total vapour pressure for a certain composition shows a maximum which is above that of either of the pure components.
  - Type III solutions show large negative deviations from Raoult's law. The total vapour pressure shows a minimum for a certain composition which is lower than that of either of the pure components.
- On distillation, the vapour that distills over has a composition which is different from that of the solution. The vapour is richer in the more volatile component.
- The completely miscible liquid system will boil at temperature when the total vapour pressure becomes equal to the external pressure i.e., $P = P_A + P_B$.
- Solutions of different compositions of type 1 have boiling points intermediate between that of the pure components.
- On fractional distillation, it is possible to obtain both the components in a pure state.
- Solutions of type II show a minimum boiling point which is lower than that of either of the pure components.
- Solutions of type III shows a maximum boiling point which is higher than that of either of pure components.
- Fractional distillation of solutions of type II and III give one of the pure components and a constant boiling mixture.
- The constant boiling mixtures obtained during fractional distillation are called azeotropic solutions.
- Partially miscible liquid system consists of liquid pairs which have only limited solubility in each other.
- A considerable amount of both the liquid results in two separate layers – each a solution of one liquid in the other. Each layer is a saturated solution of one in the other.
- The mutual solubility of two liquids varies with change in temperature.
- For every composition of the liquid pair, there is a temperature at which the two liquids becomes completely miscible. This is called the mutual solubility temperature.
- The upper critical solution temperature (CST) is that temperature above which the two liquids become completely miscible in all proportions. Phenol–water system shows a lower CST.
- The lower critical solution temperature is the temperature below which two partially miscible becomes completely miscible in all proportions. Triethylamine–water system shows a lower CST.
- Nicotine–water system shows both an upper and lower CST.

- In completely immiscible liquid pairs, the presence of a liquid in no way affects the properties of the other liquids. The mixture boils at a temperature which is lower than that of either of the two liquids. Also, the boiling point of all possible compositions of any two immiscible liquid pairs is the same.
- In steam distillation, a mixture of water and organic liquid distills over. This is used as a method of purification of organic liquids especially those liquids which may tend to decompose at a temperature lower than their normal boiling points.
- Nernst distribution law is stated as – when a solute distributes itself between two nonmiscible solvents in contact with each other, there exists for similar, molecular species, at a constant temperature, a constant ratio of distribution between the two solvents irrespective of the amounts of the solute and the liquids.
- The distribution law is valid at constant temperature and for similar molecular species in dilute solutions. There should not be any chemical interaction between the solute and the solvents.
- Association or dissociation of the solute in one of the solvents changes the constant ratio.
- Distribution law is extremely useful in analysis, study of complex ions and solvent extraction of a substance.
- The efficiency of solvent extraction of a substance is greatly increased by a larger number of extractions than a single extraction.
- Desilverisation of lead by Parke's process is based on the principle that silver is more soluble in molten zinc than in molten lead.

IMPORTANT MATHEMATICAL RELATIONS

Henry's law, $m = kP$

m is the mass of gas dissolved in unit volume of solvent and P is equilibrium pressure of component A

Raoult's law of ideal solutions, $P_A = P_A^o X_A$ where P_A is partial vapour pressure of component A

P_A^o is vapour pressure of pure solvent.

X_A is mole fraction component A

Total vapour pressure

$P = P_A + P_B = P_A^o X_A + P_B^o X_B$

For a completely immiscible liquid pair,

Total vapour pressure $P = P_A^o + P_B^o$

$$\frac{W_A}{W_B} = \frac{P_A^o M_A}{P_B^o M_B}$$

W_A and W_B are the weights of solvents A and B in the distillate of a completely immiscible liquid pair, M_A and M_B are the respective molecular weights.

Nernst distribution law, $K = \frac{C_1}{C_2}$

C_1 and C_2 are the concentrations of solute in solvents A and B, K is the partition coefficient. If a solute is associated in one of the solvents.

$$K = C_1/\sqrt[n]{C_2}$$

If a solute is dissociated in one of the solvents,

$$K = C_1/C_2(1-\alpha)$$

EXERCISE

Short Answer Type Questions:

1. What is the change in entropy during a dissociation process?
2. Discuss the factors that influence the solubility of a gas in a liquid.
3. What is the effect of pressure on solubility of gases?
4. State and name the law relating the solubility of a gas and pressure.
5. State Henry's law of gas solubility? What are the limitations of Henry's law?
6. Show that the volume of gas dissolved is independent of pressure at constant temperature.
7. What are the different types of binary liquid mixtures known? Given an example for each.
8. What is an ideal solution? Give an example.
9. Mention the conditions for the formation of ideal solutions.
10. State Raoult's law of ideal solutions. What are its limitations?
11. What is a non–ideal solution? How many types of non–ideal solutions are you familiar with? Give one example for each.
12. Classify the following pair of liquid mixtures into ideal and non–ideal solutions –

    (i) ethyl alcohol–water (ii) hydrochloric acid–water (iii) acetone–water (iv) benzene–toluene.
13. Draw the vapour pressure – composition curves of all types of completely miscible liquid systems.
14. Which type of solutions can be completely separated into their components by distillation?
15. Certain binary liquid mixtures cannot be separated into individual components by fractional distillation. Explain why?
16. What is an azeotropic solution?
17. Explain why absolute alcohol cannot be obtained by fractional distillation of rectified spirit.
18. What are partially miscible solutions? Give an example.
19. Define (i) upper critical solution temperature (ii) lower critical solution temperature
20. What is the effect of a salt on the mutual solubility of phenol and water?
21. What is the principle of steam distillation? How is this method useful in purification of aniline?
22. State Nernst distribution law.
23. What are the limitations of the distribution law?
24. Mention any two application of distribution law.

Essay Type Questions:

1. Write a note on the application of Henry's law.
2. What do you understand by the term ideal solution? How does the volume and enthalpy vary in the formation of an ideal solution?
3. Describe the distillation of binary liquid solution which behaves almost ideally.
4. What is the principle of fractional distillation? With the help of boiling point – composition curve, explain the separation of an ideal binary liquid mixture.
5. Describe the distillation behaviour of a binary liquid mixture which exhibits a maximum in their boiling point curves.
6. A mixture of two liquids exhibits a minimum in their boiling point curves. Describe what happens during the distillation of the above mixture.
7. Write a note on azeotropic solutions.
8. Discuss the phenol–water system. Sketch the variation of mutual solubility of this system with temperature.
9. State and explain distribution law. What are its limitations?
10. Explain why it is more economical and efficient to extract in several stages using small volume of solvent than extraction in a single operation.
11. Prove that a multiple extraction with the same amount of solvent is more beneficial than a single extraction.
12. How does the distribution of solid between two immiscible liquids help to determine the molecular state of the solid (dissociation or association) in one of the liquids and to what extent?

PROBLEMS

1. Water and propanol (b.p. 370.2 K) form an azeotropic mixture boiling at 360.7 K with 71.7% of alcohol. Which component can be obtained pure by fractional distillation of a mixture containing 50% by weight of each?
2. An organic compound immiscible with water is steam distilled under normal pressure (101.3 kNm^{-2}). At the temperature of distillation the vapour pressure of water is 94.64 kNm^{-2}. Calculate the weight percent of the liquid that is present in a given amount of the distillate. Molar mass of the organic compound = 0.204 $kgmol^{-1}$.
3. A mixture of chlorobenzene and water boils at 363.3 K under a pressure of 98.661 kNm^{-2}. The vapour pressure of water is 70.66 kNm^{-2} at this temperature. What is the proportion of the two liquids in the distillate?
4. Nitrobenzene can be steam distilled at atmospheric pressure at 372.2 K. Calculate the amount of steam necessary to distill 50g of nitrobenzene. The vapour pressure of water at this temperature is 98.5 kNm^{-2}.
5. In steam distillation of an organic compound, the mixture boils at 372.2 K under normal pressure. The distillate contains 10% by weight of the organic liquid and the remaining water. What is the molecular weight and vapour pressure of the organic liquid at this temperature? The vapour pressure of water at this temperature is 70.11kNm^{-2}.

6. A pair of miscible liquids boils at 363 K when external pressure is 97.83 kNm^{-2}. The distillate contains 73% by weight of the organic liquid and the remaining water. What is the molecular weight and vapour pressure of the organic liquid at this temperature. The vapour pressure of water at this temperature is 70.11 kNm^{-2}.
7. Iodobenzene is purified by steam distillation at normal pressure when the mixture boils at 371 K. The vapour pressure of water at this temperature is 94.64 kNm^{-2}. Calculate the ratio of the two liquids in the distillate. Molar mass of iodobenzene = 0.204 gmol^{-1}.
8. In a steam distillation of an insoluble oil the mixture boils at 368 K and the distillate contains 80% by weight of the oil. The external pressure is 100.63 kNm^{-2} and the vapour pressure of water at this temperature is 84.51kNm^{-2}. Calculate the molecular weight of the oil
9. The following data shows the concentration of solutions of iodine in CS_2 and in water in equilibrium at 290 K.

Concentration of iodine in CS_2 (C_1) g/cm^3	1.64	1.29	0.63	0.39
Concentration of iodine in H_2O (C_1) g/cm^3	0.0041	0.0032	0.0016	0.0010

10. Solution of a weak organic acid in benzene was shaken with water. At equilibrium the following results are obtained.

Concentration of benzene layer	1.33	3.18	4.85
Concentration in aqueous layer	0.83	1.27	1.45

Show that in benzene, the acid exists mainly in form of dimers.

11. Succinic acid was shaken in a mixture of water and ether. The concentration of the acid in the two layers are as follows:

Concentration in ether layer	0.046	0.130	0.220
Concentration in aqueous layer	0.244	0.710	1.210

12. The molar concentration of acetic acid distributed between water and CCl_4 are as follows

Aqueous layer (C_1)	2.51	3.99	5.35
CCl_4 layer (C_2)	0.146	0.363	1.66

13. Solution of a weak organic acid in benzene was shaken with water. At equilibrium, the following pairs of results were obtained for the concentration of acid in benzene layer (C_1) and concentration of acid in water layer.

C_1	6.35	9.7
C_2	2.54	3.14

14. On shaking the various amounts of iodine with equal volumes of carbon tetrachloride and water mixture, the concentration of iodine in the two layers was found to be:

CCl_4 layer	6.12	12.24	15.2	22.38
H_2O layer	0.072	0.143	0.178	0.26

Show that these results illustrate the distribution law.

15. The distribution coefficient of alcohol between water and CCl_4 is 40.98. How will 1g of alcohol distribute itself between 20 cm^3 of water and 50 cm^3 of CCl_4.
16. At 293 K, SO_2 was permitted to distribute itself between 0.2 dm^3 of $CHCl_3$ and 0.075 dm^3 of water. When equilibrium was established the $CHCl_3$ layer contained 0.14 mole of SO_2 and the water layer 0.05 mole. Calculate the distribution coefficient at this temperature.

ANSWERS

(2) 44.25%
(3) 5 : 2 (approx)
(4) 256.5 g
(5) 0.0594 kg mol^{-1}
(6) 0.123 kg mol^{-1}, 27.72 kNm^{-2}
(7) 7/9 (approx)
(8) 0.380 kg mol^{-1}
(11) 5.42
(15) 0.9425 g in water
(16) $\frac{C_{CHCl_3}}{C_{H_2O}} = 1.05$

* * *