Amravati University Chemistry Teachers' Association

A Textbook of
B.Sc. First year course in

Chemistry

Semester - II

As per Sant Gadge Baba Amravati University
New Syllabus (under CBCS)

PUBLICATION

A Textbook of
B.Sc. First year course in

Chemistry

Semester - II

Published by **DnyanPath Publication, Amravati (INDIA)**
The First edition published in 21st December, 2022

ISBN : 978-93-94661-55-4

DnyanPath®
Publication
Write well - Right now
ISO 9001 : 2015

Visit us
www.dnyanpath.org

Reg. Office : FFS-A, Block C, First Floor, Venus Plaza, Shegaon Naka, V.M.V. Road, Amravati, Maharashtra 444 603

Branch Office : Kalash Apartment, Near Gulmohar Hall, Pande Layout, New Sneh Nagar, khamala, Nagpur, Maharashtra 440025

Visit us : www.dnyanpath.org

Contact us : dnyanpathpub@gmail.com

Phone : 08600353712, 09503237806

Printed at - Shri Gurudeo Printers, Amravati.
Mahatma Fule Sankul, Shegaon Naka,
V.M.V. Road, Amravati, Maharashtra 444603

₹ : 200/-

AUCTA

Amravati University Chemistry Teachers' Association

A Textbook of B.Sc. First year course in

Chemistry

Semester - II

As per Sant Gadge Baba Amravati University
New Syllabus (under CBCS)

- AUTHORS -

Mr. G. D. Rawate
M.Sc., SET, NET, B.Ed.
Assistant Professor
Department of Chemistry
R. R. Lahoti Science College,
Morshi

Dr. S. V. Manohare
M.Sc., Ph.D., NET-JRF, GAT
Assistant Professor and Head,
Department of Chemistry
Adarsha Science, J.B. Arts and Birla Comm.
Mahavidyalaya, Dhamangaon Rly.

Mr. P. M. Kadam
M.Sc., NET (JRF)
Assistant Professor,
Department of Chemistry
Shri Vyankatesh Arts &
Commerce College, Deulgaon Raja

Dr. A. V. Yadgire
M.Sc., Ph.D.
Assistant Professor,
Department of Chemistry
Shri Shivaji College of Arts,
Commerce & Science, Akola

Dr. D. M. Chavhan
M.Sc., NET-JRF, Ph.D.
Assistant Professor and Head
Department of Chemistry
Indira Mahavidyalaya,
Kalamb

Dr. N. D. Gawhale
M.Sc., Ph.D., NET-JRF, SET, GAT
Assistant Professor and Head
Department of Chemistry
G. S. Tompe Arts, Commerce
and Science College, Chandur Bazar

- EDITORS -

Dr. D. B. Dupare
M.Sc., B.Ed., Ph.D.
Associate Professor
Department of Chemistry
Shri. Dr. R.G.Rathod Arts &
Science College, Murtizapur

Dr. R. P. Ganorkar
M.Sc., Ph.D.
Associate Professor
Department of Chemistry
M.Fule Arts, Commerce and Sitaramji
Chaudhari Science College, Warud

Dr. Y. S. Thakare
M.Sc., Ph.D., NET, SET
Associate Professor
Department of Chemistry
Shri Shivaji Science
College, Amravati

PREFACE

Eversince the introduction of Newly Revised and Re-structured syllabi of Chemistry (alongside other subjects), at UG and PG levels, by our University, there has been the genuine need and persistent demand by students and faculty for the quality textbooks.

I, on behalf of AUCTA, feel immensely grateful to my esteemed colleagues, who worked as the Authors and Co-authors, for their scholarly contributions that went into making this Text-book as a comprehensive and comprehensible study material for students and teachers of Chemistry. Their selfless gestures, relentless efforts and perseverance for this noble academic cause deserve a huge applaud and genuine appreciations from each one of us associted with this great subject of universal importance.

I feel immensely privileged to record my deep gratitude to our eternally reverred Gurus and timeless inspirators- Dr. W. S. Marathe, Dr V. S. Jamode and Dr. A. S. Wankhede for lending their masterly fingerprints in ironing out the creases and inadvertent errors. Their eminence, insights and expertise have definitely gone into making this book as much flawless and error-free as possible.

I very sincerely thank Mr. Sachin D. Sukalkar and Mr. Sushil M. Sukalkar of DnyanPath Publication, Amravati (India) and his colleagues for bringing out this book in a very delectable and aesthetic shape within the stipulated time-frame.

I finally acknowledge all my colleagues for their direct- indirect contributions to this Association's academic endeavour and hope that the Chemistry Teachers and Students would find this book adequately useful in accomplishing their respective objectives.

Dr. P. R. Rajput
President,
Amravati University Chemistry Teachers Association (AUCTA)

- SYLLABUS -

B.Sc. Semester - II

UNIT - I

A) **Ionic bonding:** Definition of ionic bond. Factors affecting ionic bond formation (energetic of ionic bond formation ionization energy, electron affinity and lattice energy). Born-Haber's cycle to determine lattice energy. Solvation and solvation energy, factors affecting solvation energy.

B) **Polarization:** Definition, polarizing power, polarizability, effect of polarization on nature of bond. Fajan's rules of polarization and its applications.

C) **Valence bond theory:** Directional nature of covalent bond. Hybridization, types of hybridization to explain geometries of $BeCl_2$, BF_3, CH_4, PCl_5, SF_6 and IF_7

Periods : 14

UNIT - II

A) **VSEPR Theory:** Various rules under VSEPR theory to explain molecular geometry (following examples may be taken to explain various rules - $SnCl_2$, CH_4, NH_3, H_2O, SF_4, ClF_3, XeF_4, XeO_3, PCl_5. Limitations of VSEPR theory

B) **Molecular Orbital Theory:** Postulates of MO theory. LCAO approximation. Formation of bonding and antibonding MOs. Rules for LCAO. MO energy level diagram. Concept of bond order. MO structure of homonuclear diatomic molecules of namely He_2, H_2, N_2 and O_2. Stability sequence of species of O_2 i.e. O_2, O_2^+, O_2^{2+}, O_2 and O_2^{2-}. Paramagnetic nature of O_2. MO structure of heteronuclear diatomic molecules viz. NO, HF and CO (Coulson's structure). Explanation of important properties of CO viz. – triple bond, almost nonpolar nature, electron donor and acceptor behavior. Comparison of VB and MO theories

Periods : 14

Unit III

A) **Haloalkanes:** Vinyl chloride - Synthesis from acetylene and ethylene dichloride, reactions with aqueous and alcoholic KOH, polymerization. Allyl chloride - Synthesis from propylene, reactions with aqueous and alcoholic KOH. Allyl bromide - Synthesis from propylene using NBS, reaction with HBr. Comparison of reactivity of vinyl and allyl chloride.

B) **Haloarenes:** Chlorobenzene - Synthesis from phenol, reaction with acetonitrile. Bromobenzene - Synthesis from silver salt of benzoic acid (Hunsdiecker reaction), Wurtz-Fittig reaction. Iodobenzene - Synthesis from benzene diazonium chloride, Ullmann reaction. Benzyl chloride - Synthesis from toluene and benzene, reactions with Mg and NaCN. Comparison of reactivity of chlorobenzene and benzyl chloride, benzyne intermediate mechanism.

C) **Polyhydric alcohols:** Ethylene glycol - Synthesis from ethylene and ethylene dibromide, reactions with PCl_5, CH_3COOH and acetone, dehydrations using conc. H_2SO_4, $ZnCl_2$ and phosphoric acid. Pinacol - Synthesis from acetone and Adiketone, Pinacol-Pinacolone rearrangement (mechanism). Glycerol - Synthesis from propylene and 3-chloropropylene, reactions with HNO_3, HCl and Na, dehydration using $KHSO_4$

Periods : 14

Unit IV

A) **Phenols:** Phenol - Synthesis from toluene, cumene and salicylic acid, Kolbe's carboxylation reaction, Fries rearrangement, Reimer-Tiemann reaction, bromination, acidity of phenol.

B) **Ethers and epoxides:** Diethyl ether - Synthesis from ethanol, Williamson's synthesis, reactions with cold and hot HI and acetic anhydride. Crown ethers - Brief introduction to crown ethers and its applications. Ethylene oxide - Synthesis from ethylene, ring opening reactions with Grignard reagent, HCN and H_2S, reduction with Zn + CH_3COOH, dimerization to dioxane (mechanism). Styrene oxide - Synthesis from styrene, ring opening reactions with acid and alkali, reduction with $LiAlH_4$.

C) **Thiols and thioethers:** Ethanethiol - Synthesis from ethyl iodide, oxidations with I_2 and H_2O_2. Diethyl sulphide - Synthesis from ethyl bromide, Williamson's synthesis, desulphurization with Raney Ni, decomposition with alkali.

Periods : 14

Unit V

Crystalline state:

Symmetry in crystal, plane of symmetry, axis of symmetry and point of symmetry. Law of constancy of interfacial angles. Elements of symmetry in cubic crystals. Laws of symmetry. Law of rational indices, Weiss and Miller indices of a lattice planes, calculation of interplanar distance d(h,k,l) from Miller indices in a cubic system. Seven crystal systems and fourteen Bravais lattices, Bravais lattices of cubic system. Simple cubic system (S.C.C.), body centered cubic system (B.C.C.) and face centered cubic system (F.C.C.). Calculation of number of constituent units in S.C.C., B.C.C. and F.C.C. Ratio of interplanar distances for 100, 110 and 111 lattice planes in S.C.C., B.C.C. and F.C.C. (No geometrical derivation). Derivation of Bragg's equation for X-ray diffraction, Bragg's X-ray spectrometer 10 method for the determination of crystal structure of NaCl and KCl. Anomalous behavior of KCl towards X-ray. Numerical.

Periods : 14

UNIT VI

Chemical Kinetics:

Explanation of terms like rate of reaction, order of a reaction and molecularity. Definition with one example of zero, first and second order reaction. Half-life period of a reaction. Derivation of rate equation for first and second order reaction with equal initial concentration and different initial concentration of a reactant. Characteristics of first and second order reaction. Examples of first and second order reaction and their kinetics study with modified rate equation viz. the reactions (i) decomposition of H_2O_2, (ii) reaction between $K_2S_2O_8$ and KI, (iii) hydrolysis of methyl acetate catalyzed by acid, (iv) saponification of ethyl acetate by NaOH and (v) inversion of cane sugar. Determination of order of a reaction by integration, graphical, equifractional change, vant Hoff's differential method and Ostwald's isolation method. Effect of temperature on reaction rates. Arrhenius equation, activation energy and its determination using Arrhenius equation. Numerical.

■ ■ ■

- INDEX -

UNIT - I

A) IONIC BONDING

B) POLARIZATION

C) VALENCE BOND THEORY

UNIT - II

A) VSEPR THEORY

B) MOLECULAR ORBITAL THEORY

UNIT - III

A) HALOALKANES

B) HALOARENES

C) POLYHYDRIC ALCOHOLS

UNIT - IV

A) PHENOLS

B) ETHERS AND EPOXIDES

C) THIOLLS AND THIOETHERS

UNIT - V

CRYSTALLINE STATE

UNIT - VI

CHEMICAL KINETICS

■ ■ ■

UNIT I

IONIC BONDING, POLARIZATION AND VALENCE BOND THEORY

A) IONIC BOND

An ionic bond is formed when there is actual transfer of one or more electrons from the outermost energy shell of one atom to the outermost energy shell of the other atom.

The atom from which the electrons are transferred acquires positive charge and the atom which gains the electrons acquires negative charge. Thus the electrostatic attraction between the oppositely charged ions results in the formation of a bond called as ionic bond. An ideal example of ionic bond is between Sodium and Chlorine in the molecule, sodium chloride, which, in turns of electron transfer can be explained as follows

Sodium atom loses single electron from its outermost shell to form Na^+ ion (cation) Chlorine atom in turn accepts the electron transferred by the sodium atom to form Cl^-(anion)

$$\underset{(2.8,7)}{Na} \quad + \quad \underset{(2.8,1)}{Cl} \longrightarrow \underset{(2,8)}{[Na^+]}\ \underset{(2,8,8)}{[CT]}$$

Thus, there exists an electrostatic attractive force between positively charge sodium ion and negatively charged Chloride ion in NaCI molecule. The formation of ionic bond is favoured when

I) Metal has low ionisation energy
II) Other element has high electron affinity and
III) The resulting compound has high lattice energy.

1.1 Energetic of Ionic Bond Formation

Three types of energies are involved in the ionic bond formation. These are:

1. Ionization energy.
2. Electron affinity and
3. Lattice energy

1. Ionization energy: It is related to cation formation.

It is defined as the energy required removing an electron from an isolated gaseous atom of an element resulting in the formation of its positive ion (cation) i.e. it is the energy required for bringing about the following change:

$$M_{(g)} \longrightarrow Mg^+ + e \qquad \Delta H = +I$$

It is given the symbol, I and since energy is to be supplied in this process it is givel positive sign. The energy is measured in electron volts (e) or kilocalories (kcal) per mole

The energy required in above process is called first ionization energy. The energy required to remove one or more electron from positively charged ion to get dipositive ion called second ionization energy. In the same way third, fourth and higher ionization energy are defined. The magnitude of ionization energy is a direct measure of ease of cation formation. If its value is low, cation is readily formed. Alkali and alkaline earth metals have low value of ionization energy.

2. Electron affinity: It is related to anion formation. It is defined as the energy released when an atom of electronegative element gaseous state accepts an electron and is converted into electronegative ion (anion) i.e. it the energy released in the following process.

$$X_{(g)} + e \longrightarrow X^-_{(g)} \; ; \qquad \Delta H = -E$$

It is given the symbol E and since it is the energy released, it is given a negative sign. It is also measured in eV or kcal/mole. Similar to ionization potential there can be first, second, third electron affinities also, respectively corresponding to energy changes involved during the formation of uninegative, dinegative and trinegative ions.

Anion formation will be favoured if more energy is released in the above process i.e. if electron affinity is high. Halogens have relatively high values of electron affinity Hence they readily form anions.

3. Lattice energy: It is related to the formation of an ionic solid from its ions. Lattice energy of an ionic crystal $M^+ X^-$ is defined in the following two ways: It is defined as the energy released when exact number of gaseous cations $M^+(g)$ and gaseous anions $X^-(g)$ come close together from infinity to form one mole solid ionic crystal, $M^+ X^-(S)$

$$M^+_{(g)} + X^-_{(g)} \longrightarrow M^+X^- + \text{Energy released}$$

It is also defined as the energy required to remove ions of one mole of solid ionic crystal from their equilibrium positions in crystal to infinity.

$$M^+_{(g)} + X^-_{(g)} \longrightarrow M^+X^- + \text{Energy supplied}$$

It is represented as U

Lattice energy of an ionic solid is a measure of its stability. If the value of lattice energy is high, it means that more energy is required to separate the ions from the ionic crystal. In other words this means that the ionic crystal is stable,

1.2 Factors Favouring Tie Formation of Ionic Bond

From the above discussion we can now write the factors which will favour the ionic bond formation.

The formation of an ionic compound MX will be favored if

I) The ionization energy of element M is low

II) Electron affinity of X is high

III) Lattice energy of compound MX is high.

1.3 Experimental determination of lattice energy using Born-Haber Cycle

The lattice energy of ionic solid like NaCl may be determined by using Born Haber cycle. It is thermochemical cycle and was devised by Born and Haber in 1919.The cycle first relates the lattice energy of crystalline solid to other known thermochemical quantities. Then make use of Hess's law to evaluate the unknown quantity. Lattice energy of Sodium Chloride may be determined by using Born Haber cycle as follows. Sodium chloride may be considered to formed from solid sodium metal and gaseous chlorine by two different method described below

Method 1: It is direct combination of solid sodium and gaseous chlorine to give solid sodium chloride. The process may be represented by following equation.

$$Na_{(S)} + \frac{1}{2} Cl_{2(g)} \longrightarrow Na + Cl^{-}_{(S)};\quad \Delta\ Hf = -414.2\ mol^{-1}$$

This equation tells us that when one mole of solid sodium combines with half mole of gaseous chlorine molecules, one mole of crystalline sodium chloride is formed. During this process 414.2 KJ $mol^{-1}$of energy is also evolved. This energy is called heat formation of sodium chloride and is represented by the symbol ΔHf.

Method 2: It involves five different steps described below

Step 1: Sublimation of Sodium: In this process I mole of solid sodium Na (s) changes gaseous sodium Na (g). The energy required for this process is S (Heat of sublimation sodium) Its value is experimentally found out to be 108.7 KJ mol^{-1}.

$$Na_{(s)} \longrightarrow Na_{(g)};\quad SNa = 108.7\ KJ\ mol^{-1}$$

Step 2: Dissociation of chlorine: In this process half mole of chlorine is dissociated intol mole of chlorine atoms. The energy required for this process is $1/2DCl_2$ (where $DCl_2$is the heat of dissociation of one mole of chlorine). Experimental value of $1/2\ DCl_2$ is 112.95 KJ mol^{-1}.

$$Cl_{2(g)} \longrightarrow Cl_{(g)};\quad {}^{1}/_{2}DCl_2 = -112.95\ KJ\ mol^{-1}.$$

Step 3: Formation of sodium ions: I mole of gaseous sodium atoms are converted sodium ions by removal of an electron from each of them. Energy required for this process isINa(Ionization energy of sodium) Its experimental value is 489.5 KJ mol^{-1}.

$$Na_{(g)} \longrightarrow Na^{+}_{(g)} + e^{-};\ INa = 489.5\ KJ\ mol^{-1}$$

Step 4: Formation of chloride ions: One mole of chlorine atoms (formed in step 2) take up electrons given by sodium and are converted to negatively charged chloride ions. Th process is accompanied by release of energy. By definition the energy released in this process is electron affinity of chlorine (Ea). Its experimental value is 351.4 KJ mol^{-1}.

$$Cl_{(g)} + e^{-} \longrightarrow Cl^{-}_{(g)};\quad ECl = -351\ KJ\ mol^{-1}$$

Step 5: Formation of ionic crystal $Na^{+}Cl^{-}_{(s)}$: Gaseous sodium and chloride ions formed in step (3) and (4) above combine to give solid sodium chloride crystal $Na^{+}Cl^{-}_{(s)}$. Energy released in this process also and by definition this is lattic energy of NaCl. It is represented as UNaCl Its value is to be determined from other values.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow Na + Cl^-; \; UNaCl = ?$$

According to Hess's law the energy change in method (1) must be equal to total of ener changes of all steps in method (2) i.e..

$$\Delta Hf = SNa + \frac{1}{2} DCl_2 + INa + ECl + UNaCl$$

$$\Delta Hf = SNa + \frac{1}{2} DCl_2 + INa + ECl + UNaCl$$

Putting the actual values we get

$$414.2 = +108.7 + \frac{1}{2}(225.9) + 489.5 - 351.4 + UNaCl$$

OR

$$UNaCl = -414.2 - 108.7 - 112.95 - 489.5 + 351.4$$

$$= -773.95 \text{ KJ mol}^{-1}$$

It can be represented as given below in figure

Examples:

1. To calculate the lattice energy of NaCI crystal the data is
   Sublimation energy (S) = 108.7 KJ mol^{-1}
   Dissociation energy for Cl (D) = -225.9 KJ mol^{-1}
   Ionization energy for Na I = 489.5 KJ mol^{-1}
   Electron affinity for Cl (E) = -351.4 KJ mol^{-1}
   Heat of formation of NaCI (ΔH) = -414.2 KJ mol^{-1}
   Substitute these values in equation.

$$Uo = +A\ H - S - 1/2D - 1 - E$$

$$Uo = -414.2 - 108.2 - 1/2\ (225.9) - 489.5 + 351.4$$

$$= 773.95 \text{ KJ mol}^{-1}$$

2. Calculate the heat of formation (ΔH) Of KF from its elements from the following da by the use of Born-Haber cycle.
   Sublimation energy of potassium (S)= - 878.8 KJ mol^{-1}
   Dissociation energy of F2 (D) = -158.9 KJ mol^{-1}
   Ionization energy of K (g) (1) = - 414.2 KJ mol^{-1}
   Electron affinity for F (g) (E) = -334.7 KJ mol^{-1}
   Lattice energy of KF (Uo) = -807.5 KJ mol^{-1}

Solution:

$$\Delta Hf = S + 1/2D + I + E + Uo$$

$$\Delta Hf = -87.8 + 1/2\ (158.9) + 414.2 + (-334.7) + (-807.5) = 560.8 \text{ KJ mol}^{-1}$$

This can be represented as:

$$K_{(s)} + \frac{1}{2}F_{2(g)} \longrightarrow KF_{(s)} + 560.8 \text{ KJ mol-1}$$

3. Calculate the heat of formation (ΔH) of MgF2, from its elements using the Born Haber cycle. The thermochemical data are as follows.
   Sublimation energy of magnesium (S) = 146.4 KJ mol^{-1}
   Dissociation energy of F, (D) = 158.9 KJ mol^{-1}
   Ionization energy of Mg (g) (I) = 2184.0 KJ mol^{-1}
   Electron affinity for F (g) (E) = -334.7 KJ mol^{-1}
   Lattice energy of MgF: (Uo) = -2922.5 KJ mol^{-1}
   Substituting these values in the expression for MgF_2

$Mg_{(s)} + F_{2(g)} \longrightarrow MgF_2 + 1102.6$ KJ mol-1

$\Delta Hf = S+D+I+2E+Uo$

Here D will be used instead of D because of the following process

$F_{2(g)} + D \longrightarrow 2F_{(g)}$

Also 2E is taken in place of E because of the following change.

$2F_{(g)} + 2e \longrightarrow 2F_{(g)}$

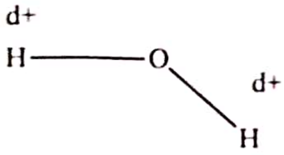
$\Delta Hf = 146.4 + 158.9 + 2184.0 + 2(-334.7) - 2922.5$

$= -1102.6$ KJ mol^{-1}

1.4 Solvation of Ions and Solvation Energy

The interaction that takes place when a substance is introduced in a solvent and the energy change associated with this process is called Solvation and energy change associated with this process is called solvation energy.

Let us consider the various changes that take place when an ionic solute like sodium chloride is added to a polar solvent like water. Water is called a polar solvent because in its molecule the oxygen atom is partly negatively charged and each hydrogen atom is partly positively charged as shown below;



When sodium chloride is introduced in such a solvent, the negative ends of water molecule attract the positive ions, and the positive ends attract the negative ions of the crystal. These attraction forces exerted by the water molecules weaken the existing among the ions in the crystal. Hence some of the ions in the crystal are pulled away from their positions in crystal lattice as shown in the figure

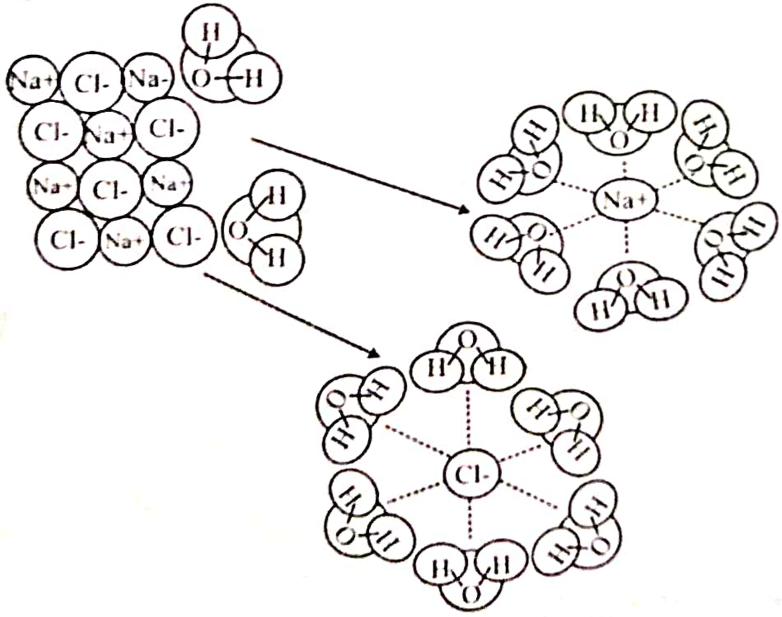


Fig. 1.1 : Dissolution of sodium Chloride in water

Once the Na and CT ions are broken away from the ionic lattice, following tw processes occur simultaneously.

1) Each sodium ion is surrounded by a definite but unknown number of wate molecules, say x, with their negative ends (oxygen ends) pointing towards it.

$Na^+ + xH_2O = [Na(H_2O)]^+$

This process is called solvation of sodium ion and the energy change associate with it is called solvation energy of sodium ion, (ΔHs)Na+. The chemical specie $[Na(H2O)]^+$ is called solvated or acquated sodium ion and may also be represented a $[Na(aq)]^+$

2) Each chloride ion is surrounded by definite but unknown number of water molecule say y, with their positive ends (hydrogen ends) pointing towards it.

$Cl^- + \ y\,H_20 \ = [Cl(H_2O)]^-$

The process is called solvation of chloride ion and the energy change associate with it is called solvation energy of chloride ion, (ΔHs)Cl. The chemical specie $[Cl(H20\ )y]^-$ is called solvated or aquated chloride ion and may also be represented a $[Cl(aq)]^-$

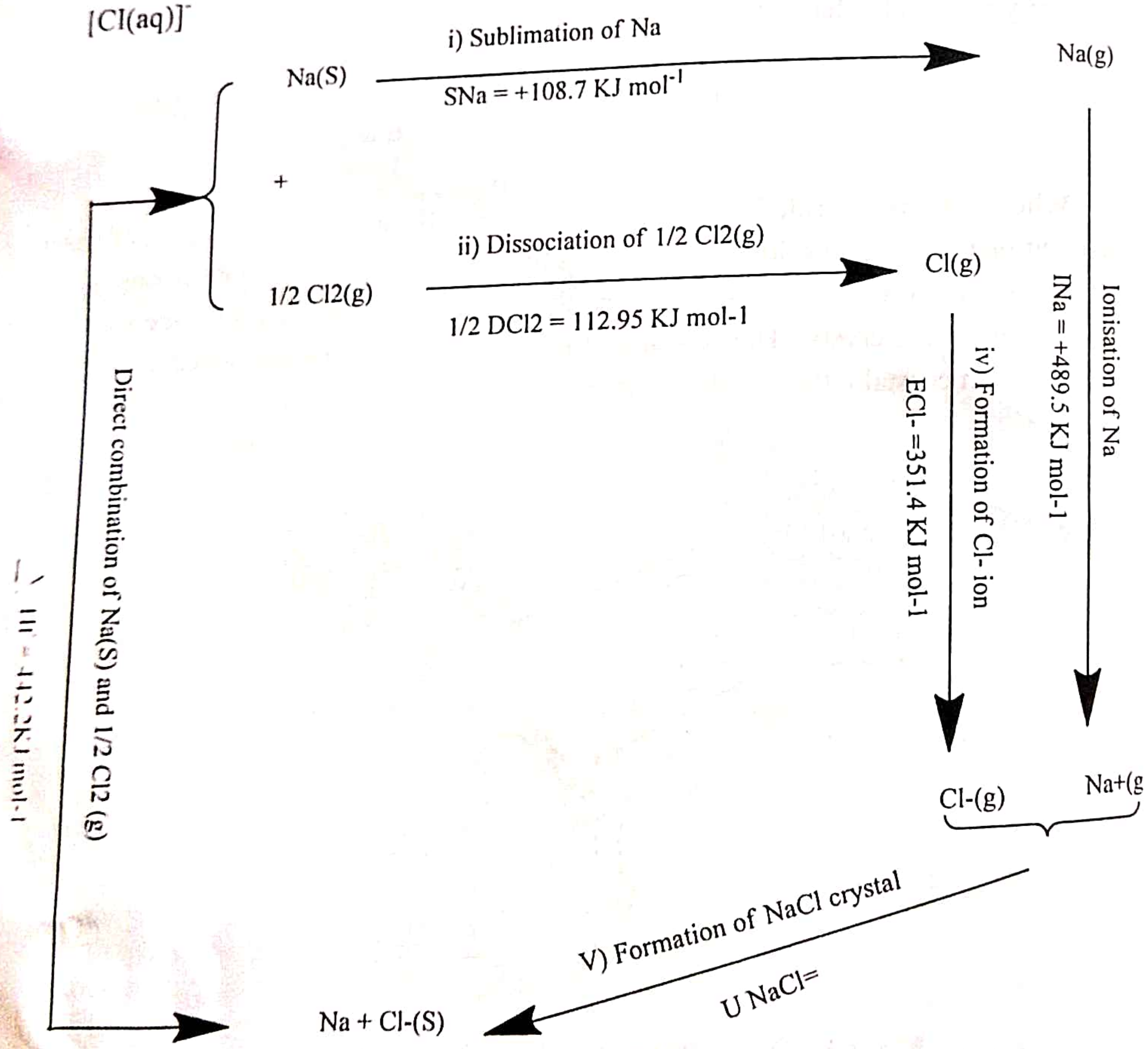


Fig. 1.2 : Born-Haber cycle for determination of salvation energy.

1.5 Calculation of Solvation Energy

The energy changes during solvation of sodium and chloride ions may be calcul using a Born-Haber type cycle as given in figure 1.6

Here L is the heat of solution of NaCl at infinite dilution (i.e. the total amount of evolved or absorbed when one mole of sodium chloride dissolved in such a large excess of water, that further addition of water does not produce any heat change).

UNaCl is the lattice energy of NaCL.

$(\Delta Hs)Na$. and $(\Delta Hs)Cl^-$ are the solvation energies of sodium and chloride ions. Since heat of solution of NaCl at infinite dilution (L) and lattice energy of NaCl (UNaCl) are experimentally known, the solvation energies Na+ and Cl- ions can be calculated from following relation.

$$L = UNaCl + (\Delta HS)Na^+ + (\Delta\ Hs)Cl^-$$

It gives us the sum of solvation energies of sodium and chloride ions. There purely thermochemical way to separate this sum into two parts corresponding to sodium chloride ions.

1.6 Factors affecting solvation and solvation energy

1) **Solvation energy and lattice energy:** The dissolution of an ionic compound in polarsolvent is favoured if the attraction between solvent molecules and ions, exceeds the attraction among the ions in a crystal lattice or in other words if the energy of solvation of ions exceeds the lattice energy of the crystal.

2) **Dielectric constant and solvation energy:** For a given ion and the solvent the dielectric constant and the solvation energy are related by following equation, called Bornequation.

   $H = C_2/2r\ (1-1/D)$

   Here,

   D = dielectric constant of the solvent.

   R = ionic radius and or

   H = Solvation energy of gaseous ion,

   C = charge on the ion,

   From this equation it is evident that increase in the magnitude of dielectric constant increases the solvation energy.

3) **Ionic size:** Both solvation energy and lattice energy are increased by decreases in cation and anion size. It is therefore difficult to relate solubility to size of ion. However the two opposite charges are not of the same magnitude and in general other factors being equal solubility increases with increase in cation or anion size.

4) **Ionic charge:** With increasing cation or anion charge, the lattice energy increases much more rapidly than the solvation energy. This results in decrease of solubility.

5) Electronic configuration of cations and their polarising effect:
   a) If the anion is more readily polarised by the cation, than is the solvent, the lattice energy will increase more than solvation energy and the solubility will decrease.
   b) If the solvent is more readily polarised by the cation, the solubility will increase. The ions having pseudo inert gas configuration Ag+ , Pb++, Hg++, etc. have high anion polarising effect, hence their salts (AgCl, PbCl2, HgCl2)) have lower solubility in water. As compared to these, the alkaline earth cations(Ca++, Ba++ etc.) having inert gas type configuration, have low anion polarising effect, hence their halides CaCl2, BaCl2, are readily soluble in water.

****

B) POLARIZATION

1.7 Polarization, Polarizing power, Polarizability

Anions are larger in size than cations and therefore their electron clouds are l tightly held. In an ionic molecule, when a cation approaches nearby anion closely, positive charge on the cation tends to attract the electron cloud of the anion toward its due to electrostatic force of attraction existing between them. At the same time the cati also tend to repel the positively charged nucleus of the anion. The combined effect these two forces is that the electron cloud of the anion no longer remains symmetrical is elongated towards the cation. This phenomenon is called distortion, or deformation polarization of the anion by the cation and anion is said to be polarized. Thus "t **distortion of the symmetrical electron charged cloud of an anion by the cation termed as polarization".**

For example, the large iodide ion by itself is perfectly symmetrical. Howev when a small positively charged lithium ion comes close to the iodide ion, the electr cloud on the anion is pulled towards the positive lithium ion. The iodide ion is said to polarized and the process is called polarization.

The polarization effect produces covalence in LiI molecule because there is sor electron density in between the nuclei as in the sharing of electrons in a covalent bo .The power or ability of a cation to polarize (distort) a nearby anion is known polarizing power and the tendency of the anion to get distort or polarize by cation known as polarizability.

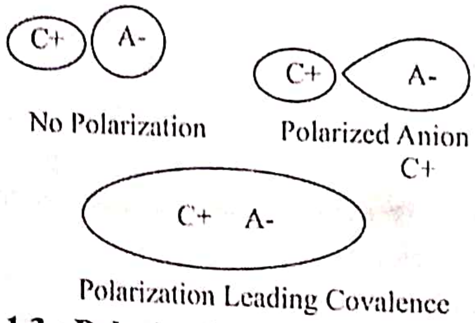


Fig. 1.3 : Polarization of cation by anion

The anion also has similar effect on the cationi.e.thecation is also polarized by tl anion, but since anion is usually large and cation is small, the polarization of cation n much and is considered as negligible. Extensive polarization would be witness whe cation penetrates the anionic electron cloud giving a covalent bond. Compoun consisting of large negative ions and small positive ions, the polarization leads to parti covalent character in ionic compounds.

Examples of such ionic covalent compounds are $FeCl_3$, $AlCl_3$, LiBr, etc.

1.8 Effect of Polarization on Nature of Bond (Covalent Character in ionic Compounds)

The nature of bond (ionic) formed between cation and anion in an ionic molecules' depends upon the effect of polarization of one ion upon the other. If the degree of polarization is quite small or negligible, then the bond remains largely ionic

While, if the degree of polarization is large, electrons are drawn from negative ion toward the positive ion, resulting in a high concentration of electrons between the two nuclei and a large degree of covalent character results. Consequently, greater the polarization greater is the covalent character induced in the ionic bond.

1.9 Fajan's Rules of Polarization

Kazimierz Fajan's in 1923 gave simple approach to explain partial covalent character in ionic bond. He explained the variation of non-polar character in ionic compounds in terms of polarization effects. Following factors determine the extent of polarization (polarizing power of cation and polarizability of anion) of an anion by a cation, that is, the extent of covalent character induced in an ionic compound. These factors are suggested by Fajan's and hence are called **Fajan's Rules.**

1. The cations with high charge and small size have high polarizing power

The cations having high positive charge and small size attracts the electron cloud of the anion more strongly towards itself than the cation with low positive charge and igger size and hence polarizes the anion more strongly. In other words, induced covalent haracter in ionic compounds increases with decrease in size of cation and or increase with charge on the cation. The polarizing power of a cation is directly proportional to its harge and inversely proportional to its size. The polarizing power of a cation is generally xpressed in terms of a parameter called ionic potential which is the ratio of the effective uclear charge of the cation and its size. Thus higher the ionic potential of a cation, the reater would be its polarizing power and greater would be induced covalent character in nic compound. This is confirmed by the gradual decrease in melting points as follows.
onsider compounds with cations of different charges but of nearly the same size. For ample NaBr (m.p.=755°C), $MgBr_2$ (m.p.=700°C) and $AlBr_3$ (m.p.=498°C). The larizing power of Al ion is greater than that of Mg^{2+} ion which, in turn, is greater than at of Na^+ ion. Therefore NaBr has the least covalent character and highest meting point hereas $AlBr_3$ has maximum covalent character and lowest melting point of the three mpounds.

Consider compounds with cations of same charges but of different sizes. For mple, Na^+ and Ca^{2+} have almost similar ionic radii but $CaCl_2$ (m.p.=772°C) has higher alent character than NaCl (m.p.= 800°C) because of higher charge on Ca^{2+} has that of $^+$ Similarly, with identical charges on cations, $BeCl_2$, (m.p. 405°C) relatively more alent than $CaCl_2$ (m.p. 772°C) because of smaller ionic size Be^{2+} as compared to Ca^{2+}

The anions possessing high negative charge and larger size are easily arizable

Covalent character induced in ionic compound due to polarization of the anion n increase in size and charge on the anion. High negative charge and size of anion, n these factors, would decrease the hold of the nucleus of the ion on its electron charge d and therefore can be easily distorted by a cation Let us consider anions of different s forming compounds with the same cation 2. LiF (m.p. =870°C), LiCl (m.p.=613°C), LiBr (m.p.=547^{0}C), LiI (m.p.=466^{0}C) because of differences of sizes, the polarizability (the anions is in the order: $I^- > Br^- > Cl^- > F^-$. Hence, LiI has the maximum and LiF has th minimum covalent character. As a result LiI has the minimum and LiF has the highe melting point of all lithium halide compounds.

AgF is soluble in water whereas AgCl is not. This is because the Cl^- ion, due t its ge size, is polarized by Ag ion to a greater extent than the F ion. As a result, th boding in AgCl is predominantly covalent whereas in AgBr is mainly ionic. Therefor AgF being an ionic compound is soluble in water whereas AgCl, being covale compound, is insoluble in water. Similarly $AlCl_3$ is covalent while AlF_3, is ionic. Als CaF_2, shows minimum and CaI_2 shows maximum covalent character.

Similarly, the polarizability of anion also increases with increase in its negati charge. 'Thus among fluorides and oxides of a metal cation, since O^{2-} ion is mor polarized than F^- ion, oxides are more covalent than fluorides.

3. Electronic configuration of cation

Cations with pseudo noble gas configuration in their valence shell ($ns^2np^6nd^{1}$ have higher ionic potential or polarizing power than those cations with noble ga configuration (ns^2np6). This is because d electrons of pseudo inert gas configuratio shield nuclear charge of cation less effectively (poorly) than s and p electrons of ine configuration. 'Thus cations with pseudo inert gas configuration possess more positiv charge than the cations having inert gas configuration. Consequently such cations with l electron configuration will leads to greater polarization of the anion.

For example Hg^{2+} and Ca^{2+} ions have the same charge and nearly the same siz ionic radii being 1.16 A and 1.14 A, respectively), yet Hg ion with [Xe]$4f^{14}$ $5d^{10}$ 6S configuration has more polarizing power than Ca^{2+} ion with [Arl configuration. This i reflected in melting points of their compounds as $HgCl_2$ (m.p. 276^{0}C) and CaCl (m.p.= 772^{0}C).

Also, Cu+ cation ($3S^23p^63d^{10}$) has greater polarizing power than Na^+ ($2S^22P^6$ although both have same charge and size. Hence NaCl is ionic whereas CuCl have som covalent character. This is evident from the increase in their m.p. as shown below.

NaCl = 800^{0}C and CuCl = 442^{0}C

Similarly AgCl (m.p.=455^{0}C) is more covalent than KCl (m.p.= 776^{0}C) and $AuCl_3$ m.p. = 170^{0}C) is more covalent than RbCl (m.p. = 776^{0}C).

Thus from the above discussion, Fajans' rules given above can be summarized saying that,

1. The molecules containing high positive charge on cation, high negative charge on anion, small cation or large anion are covalent in character.
2 The molecules containing low positive charge on cation, low negative char on anion, large cation or small anion show ionic character.
3. The molecules having cations with 18 electrons valence shell configuration (Cu^+, Ag^+, $Au3^+$ etc) are more covalent than those having 8 electrons (Na^+, K^+, Rb^+ etc.) valence shell configuration.

1.10 Applications of the Concept of Polarization (Fajan's rules)

The concept of polarization is useful in assessing.

1. The degree of covalent character in an ionic compound.
2. The tendency of cation to form complexes.
3. The tendency of cation towards solvation.
4. Solubility of salts.
5. Melting points of salts.
6. Nature of oxides.
7. Thermal stability of carbonates
8. Bond energy
9. Diagonal relationship
10. Nature of anhydrous halides.

****

C. COVALENT BONDING

The idea that, two electrons can be shared between two atoms and forms covalent bond between them was first introduced in 1916 by the American chemist G.N. Lewis. He described the formation of such bonds as a resulting from the tendencies of certain atoms to combine with one another in order to have the electronic structure of corresponding noble-gas atom. This idea cannot explain the stability, reactivity geometry of covalent molecule.

In the covalent bond one has to understand what types of forces exist which keep the electron pairs in contact between the two atoms. This idea has been explained the basis of wave mechanics. Two wave mechanical theories of the covalent bond have been put forth to explain the nature of the covalent bond.

A) Valence bond theory (VBT)

B) Molecular Orbital Theory (MOT)

Valence bond theory was first proposed by Heitler and London in 1927. In this theory, the overlapping of atomic orbitals forms a molecule and molecule is composed of atoms which retain their individual character when linked to the other atoms. This theory was later on extended by Pauling and Slater in 1931 to account for the directional characteristics of the covalent bond, which arises due to the vector nature of charge intensities responsible for such bonding.

Covalent bonds are directional, meaning that atoms so bonded prefer specific orientations (directions) relative to one another. 'The orbitals which are involved covalent bonding are localized i.e.they have fixed positions. Due to this, covalent bond is directional in nature; this in turn gives to molecules a definite shape, as in the angular (bent) structure of the H_2O molecule.

Covalent bonds between identical atoms (as in H_2) are nonpolar i.e, electrical uniform-while those between unlike atoms are polar i.e, one atom is slightly negatively charged and the other is slightly positively charged. This partial ionic character of covalent bonds increases with the difference in the electro negativities of the two atoms.

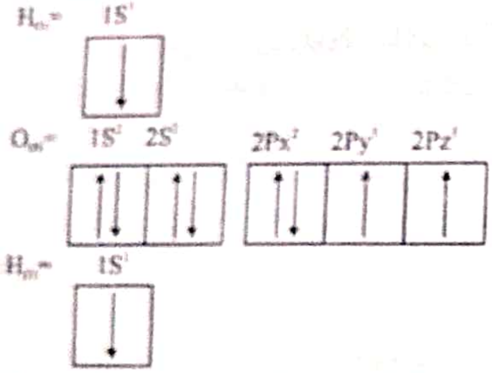
When none of the elements in a compound is a metal, no atoms in the compo have an ionization energy low enough for electron loss to be likely. In such a c covalence prevails. As a general rule, covalent bonds are formed between elements ly toward the right in the periodic table (i.e, the non-metals).

1.11 Directional Nature of Covalent Bond

Covalent bond is a directional bond. This means that, covalently bonded ato have definite relative positions in space with respect to each other. Covalent bo possesses direction when non-spherical orbitals such as p-orbitals are involved in formation, because in such orbitals electron density is concentrated in particular directio

Due to directional characteristics of covalent bond, covalent molecules posses definite geometrical shapes.

Example : Formation of H_2O molecule



Now, since 2py and 2pz orbitals of oxygen are mutually perpendicular, the tw O-H bonds formed in the H_2O are also mutually perpendicular and hence the bond an water is expected to be 90^0

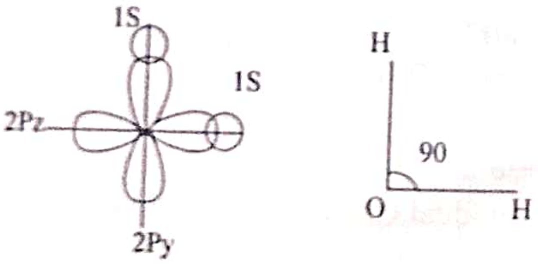


Fig. 1.4 : Structure of water molecule.

Similarly, since 2px, 2py, and 2pz, orbitals of nitrogen are mutually perpendicular the three N-H bonds formed in NH_3 molecule are also mutually perpendicular hence the bond angle in ammonia is expected to be 90^0

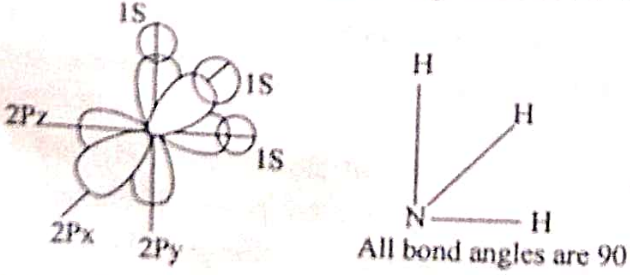


Fig. 1.5 : Structure of Ammonia Molecule

3.12 Hybridization

"Hybridization is the process of mixing and recasting of atomic orbitals of same atom of nearly same energy to produce equal number of new equivalent orbitals"

The Need of hybridization:

i) To explain the observed valence of an element

ii) To explain the equivalence of bonds (i.e. to explain equivalence of bond length, bond angle, bond energies)

iii) To explain the observed geometrical shapes of covalent molecules

Steps involved in hybridization

Following steps are involved in the process of hybridization.

1. **Formation of excited state**: Atom in ground state absorbs some energy and goes to excited state. In this process usually a pair of electrons in lower energy orbital is split up and one of the electrons from this pair is promoted to higher energy orbital in the same subshell. This step is necessary when atom has less number of unpaired electrons than the valency of central atom in a molecule.
2. **Mixing and recasting of atomic orbitals**:
   a) The atomic orbitals in excited state unite and mix up their energies giving new set of hybrid orbital of equal energy.
   b) The total number of hybrid orbitals formed is equal to the number of atomic orbitals mixed.
3. **Reorientation of hybrid orbitals**: The hybrid orbitals are arranged symmetrically in the available space around the central atom and oriented in the space in such a way that they lie as far apart as possible so that repulsive interaction between them is minimum.

Condition of hybridization

There are three main conditions for hybridization.

1. Atomic orbitals of same atom can take part in hybridization.
2. Atomic orbitals of the same atom participating in the process of hybridization should have nearly same energy.
3. Atomic orbitals whether vacant, half-filled or completely filled can take part in the process of hybridization. electrons present in them do not take part in this process.

Characteristics (or Features) of hybridization

1. The atomic orbitals of same atom with comparable energy take part in hybridization.
2. The number of hybrid orbitals formed equal to the number of atomic orbitals used for hybridization.
3. All hybrid orbitals are identical in respect of energy, directional character, shape and size.
4. The hybrid orbitals are more directly concentrated and hence they can form stronger covalent bond due to better overlapping.

5. The hybrid orbitals differ from atomic orbitals from shape, size and energy but th contain character of parent atomic orbitals.
6. The distribution of electrons inhybrid orbitals is similar to that in the original atom orbitals each hybrid orbitals contain at the most two electrons with opposite spin.

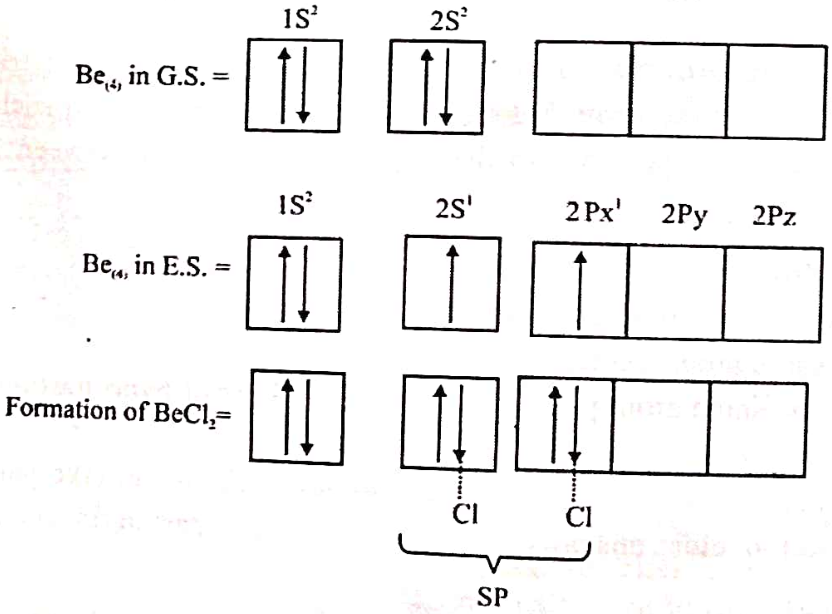
1.13 Types of hybridization

Different types of hybridization depending upon the number and type of atom orbitals involved in mixing with corresponding geometry and one example of molecu are given in following table.

S.No.	Types of hybridization	Geometry	Example of molecule
1.	SP hybridization	Diagonal or Linear	$BeCl_2$, BeH_2
2.	SP^2 hybridization	Triangular Planer	BF_3, BCl_3
3.	SP^{3}hybridization	Tetrahedral	CH_4, NH_4^+
4.	SP^{3}d hybridization	Trigonal Pyramidal	PCl_5
5.	SP^{3}d^2 hybridization	Octahedral	SF_6
6.	SP^{3}d^3 hybridization	Pentagonal bipyramidal	IF_7

1. Structure of $BeCl_2$

Electronic configuration of Beryllium in ground state is $1S^2\ 2S^2$. One of the 2S electron gets promoted to next available atomic orbitals (i.e. 2Px) and there for electroni configuration of beryllium in excited state is $1S^2\ 2S^1\ 2Px^1$.



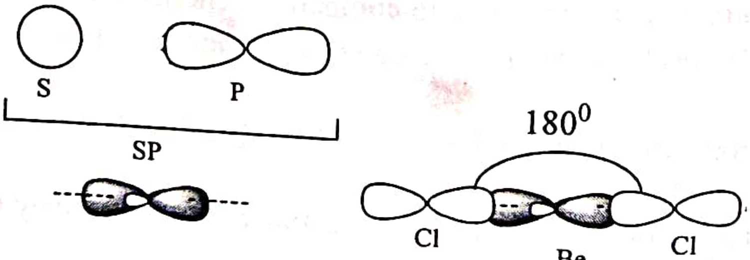
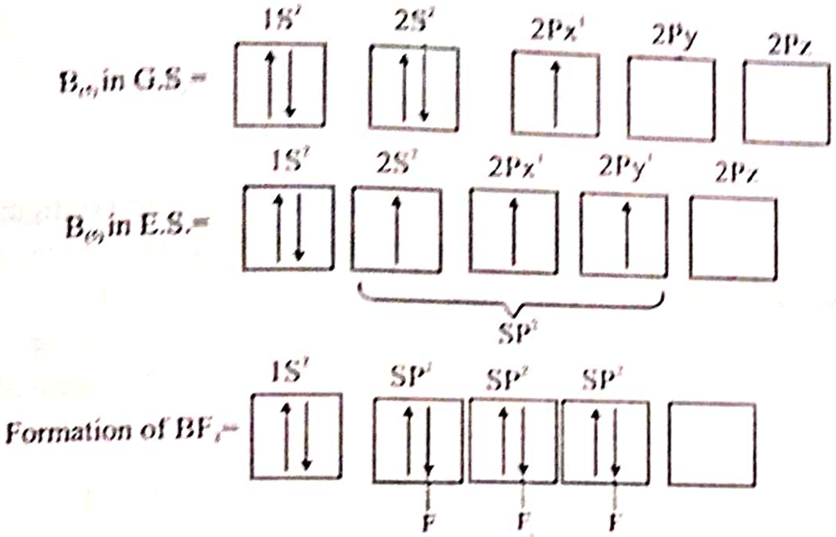


Fig. 1.6 : Liner Structure of $BeCl_2$ Molecule

2. Structure of BF_3

Electronic configuration of boron in ground state is $1S^2\ 2s^2 2Px^1$.One of the 2S electrons get promoted to the next available vacant orbitals (2Py).The electronic configuration of boron in excited state is $1S^2\ 2S^1\ 2Px^{12}\ Py^1$, One 2S and Two 2Px, 2Py undergo SP^2 hybridization give three SP^2 hybrid orbitals having single electrons overlap with 2Pz orbitals of Fluorine atoms to form three B-F bonds, bond angle between F-B-F is 120^0.



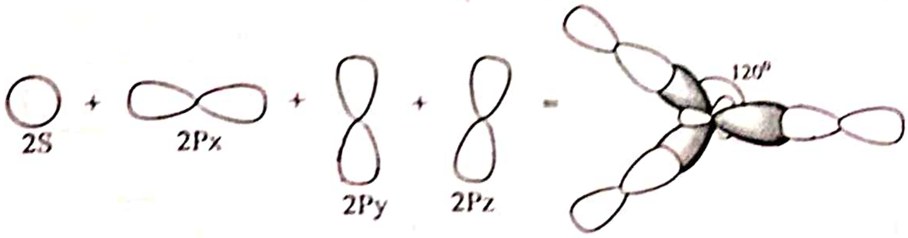
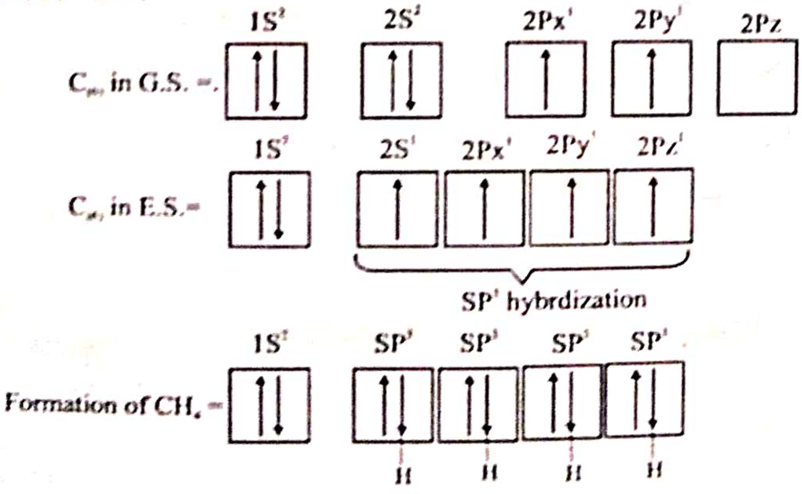


Fig. 1.7 : Trigonal Stucture of BF_3 Molecule

3. Structure of CH_4

Atomic number of carbon in ground state is $1S^2 2S^2 2Px^1\ 2Py^1\ 2Pz$, electronic configuration in excited state is $1S^2\ 2S^1\ 2Px^1\ 2Py^1 2Pz^1$. There are four atomic orbitals having unpaired electrons undergo SP^3 hybridization. All four hybridized orbitals overlap with 1S orbitals of hydrogen atoms, so four C-H sigma (σ) bonds are formed .The angle H-C-H is 109^0 28'.



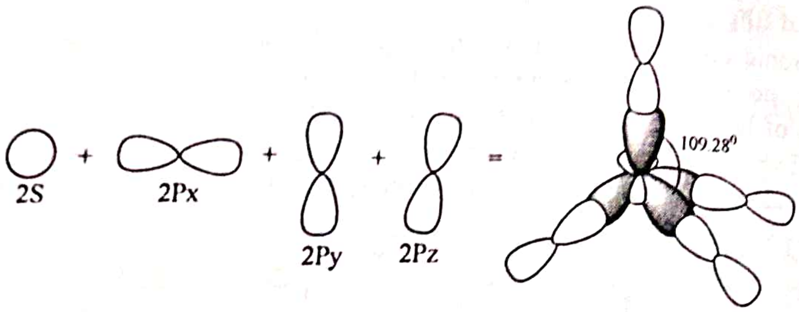
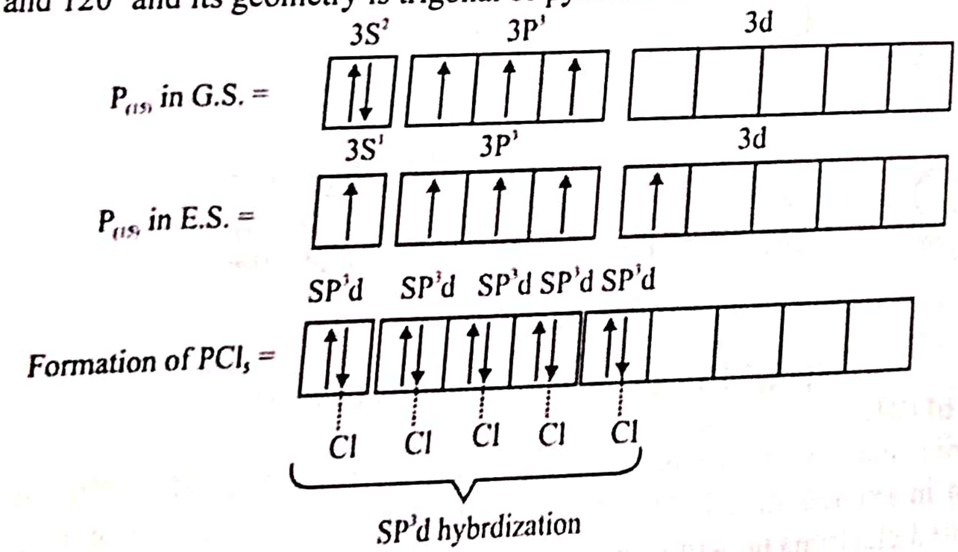


Fig. 1.8 : Tetrahedral structure of CH_4 Molecule

4. Structure of PCl_5

Atomic number of phosphorus atom is 15 its outer electronic configuration ground state is $1S^2 2S^2 2P^6 3S^2 3Px^1 3Py^1 3Pz^1$. Its electronic configuration in excited sta is $1S^2 2S^2 2P^6 3S^1 3Px^1 3Py^1 3Pz^1 3d^1$. There are four atomic orbitals having unpair electrons undergo SP^3d^1 hybridization. All five hybridized orbitals overlap with orbitals of chlorine atoms, so four P-Cl sigma (σ) bonds are formed .The angle of P-Cl 90^0 and 120^0 and its geometry is trigonal bi-pyramidal.



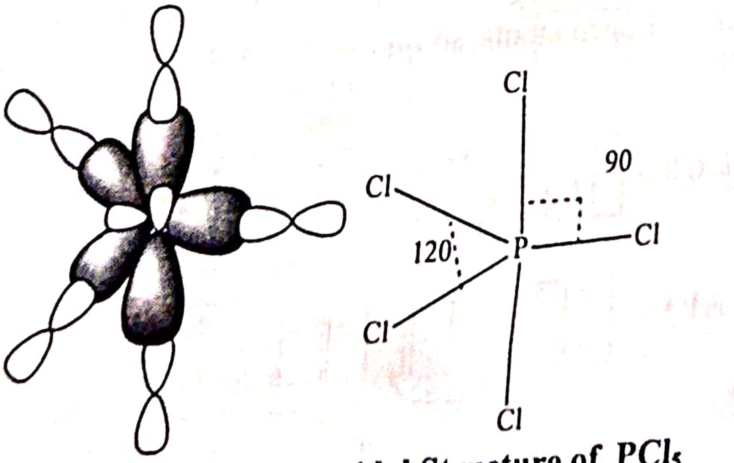
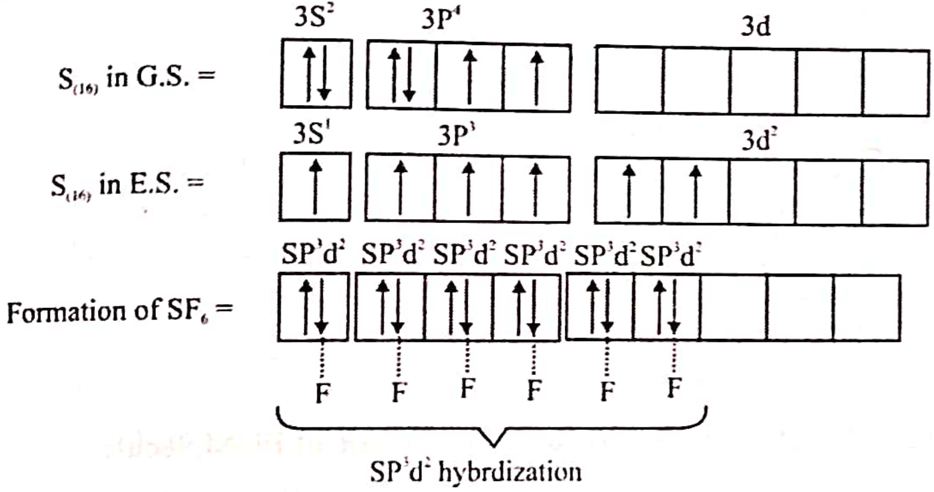


Fig. 1.9 : Trigonal bi-pyramidal Structure of PCl_5

5. Structure of SF_6

Atomic number of sulphur atom is 16 its outer electronic configuration in ground state is $1S^2 2S^2 2P^6\ 3S^2\ 3Px^2 3Py^1 3Pz^1$. Its electronic configuration in excited state is $1S^2\ 2S^2\ 2P^6\ 3S^1\ 3Px^1\ 3Py^1\ 3Pz^1\ 3d^2$. The formation of SF_6 molecule Undergo sp^3d^2 hybridization to produce six hybrid orbitals, each containing one unpaired electron. These six sp^3d^2 hybrid orbitals are oriented at the corners of regular octahedron and overlap with 2p, orbitals of fluorine to form six S-P bonds in SF_6 Since hybridization is sp^3d^2 (octahedral hybridization), shape of SF_6, molecule is octahedral four, out of six; S-F bonds lie in one plane and make an angle 90^0 while the other two are directed above and below the plane perpendicularly.



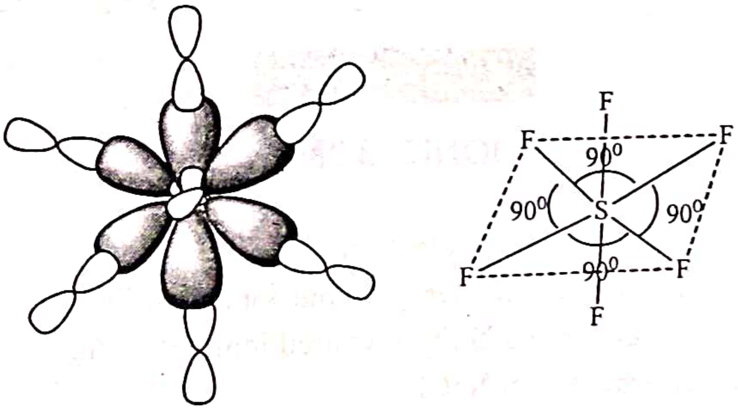
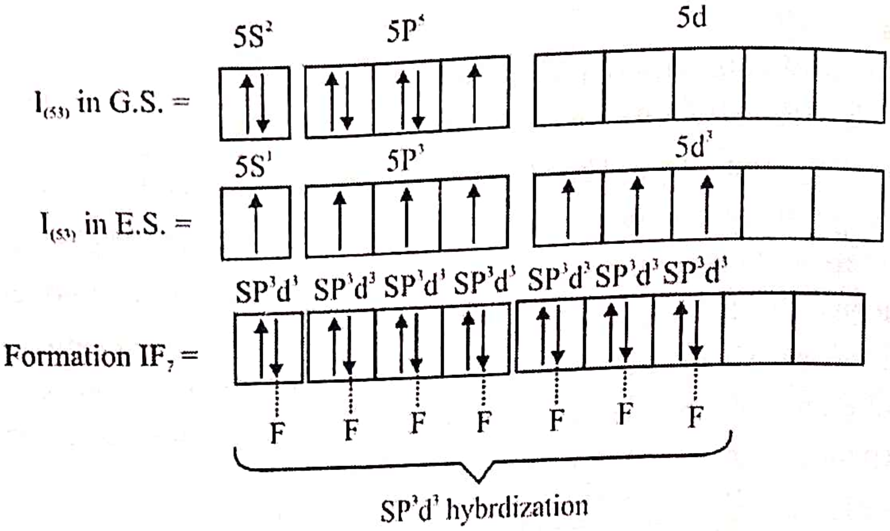


Fig. 1.10 : Octahedral structure of SF_6 molecule.

6. Structure of IF_7 molecule

In IF_7, the central iodine have atomic number 53 and its ground state electronic configuration $5s^2\ 5Px^2$, $5py^2$, $5pz^1$, in its valence shell. In the excited state of iodine have seven orbitals namely $5s^1$, $5px^1$, $5py^1$, $5pz^1$, $5dxy^1$, $5dyz^1$ and $5dxz^1$ undergo sp^3d^3 hybridization to produce seven hybrid sp^3d^3 hybrid orbitals, each containing one unpaired electron. Each of the seven sp^3d^3 hybrid orbitals overlaps axially with 2pz, orbital of fluorine atom to form IF_7 molecule. The five of these hybrid orbitals lays in one plane and point out along the corners of regular pentagon at an angle of 72^0. Two of the remaining hybrids lie axially to these five orbitals on plane. Thus, the seven sp^3d^3 hybrids of IF_7 molecule is pentagonal bipyramidal geometry.



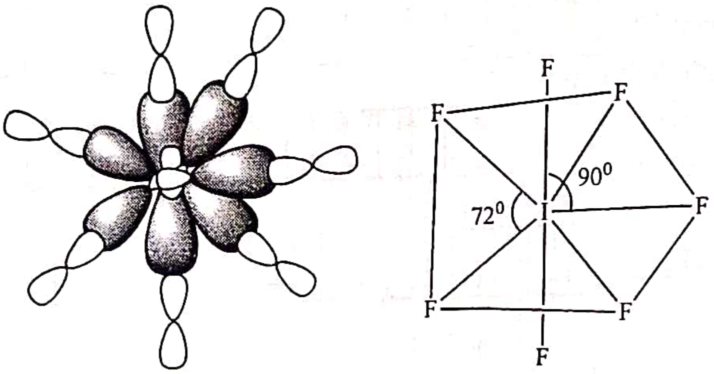


Fig. 1.11 : Pentagonal bipyramidal structure of IF_7 Molecule

****

EXERCISE

IONIC BOND

FILL IN THE BLANKS:

1. Ionic bond is formed by .... of electrons.
2. Cation having .... ionisation energy favour ionic bonding.
3. Anion having .... electron affinity favoured ionic bonding.
4. CsCl solid is .... stable than NaCl.
5. Melting point of NaCl is .... than $AlCl_3$.
6. The ions having pseudo inert gas configuration Ag^+ , Pb^{++}, Hg^{++}, etc. have .... anion polarising effect.
7. Salts (AgCI, $PbCl_2$, $HgCl_2$) have .... solubility in water
8. The interaction that takes place when a substance is introduced in a solvent and th energy change associated with this process is called ....
9. Energy change associated with this process is called ....

LONG ANSWER QUESTION:

1. What are the factors favouring ionic bond formation?
2. What are the essential conditions for the formation of ionic bond?
3. How is lattice energy is calculated by Born-Haber's cycle?

4. Draw a neat diagram showing Born-Haber's cycle for the formation of NaCl.
5. How lattice energy is calculated by using this cycle?
6. Define - Solvation and solvation energy
7. Explain which type of intermolecular interaction is involved when Cl_2 gas dissolves in water
8. What are the factors affecting solvation and solvation energy.
9. Explain the following:
   a) HF has less ionic character than HI
   b) CuCl and AgCl are insoluble in water whereas NaCl is highly soluble in water.
10. What is Born-Haber cycle? Discuss its usefulness by explaining the stability of solids.
11. The lattice energies of silver halides are almost the same as that of alkali metal halides, they are insoluble in water. Explain.
12. logic bonds are non-directional in nature.
13. Define ionic bond and factors which favour formation of ionic bond.
14. The experimental lattice energy of SnO_2 is -1159.5 kJ mol^{-1} Calculate the heat of formation of SnO_2. Given:
    S(Sn) = 291.6 kJ mol^{-1}; I (Sn) = 8991.4 kJ mol^{-1}
    D(O) = 454.3 kJ mol^{-1}, E (O) = + 635.9 kJ mol^{-1}.
15. Describe Born-Haber cycle for calculating lattice energy of an ionic solid MX.

SELECT THE PROPER ANSWER FROM GIVEN ALTERNATIVE:

1. Ionic bond formation is favoured if
   a) Metal has low ionisation energy b) Metal has high ionization energy.
   c) Metal has very high ionization energy d) None of these.
2. What is trend of m.p. NaCl and BaO
   a) $BaO > NaCl$ b) $BaO = NaCl$ c) $BaO \geq NaCl$ d) None of these
3. What is the trends of hardness in AgF, AgCl and AgBr.
   a) $AgF < AgCl < AgBr$ b) $AgF > AgCl > AgBr$
   c) $AgF = AgCl = AgBr$ d) None of these
4. According to Fajan's rule the cation and anion have
   a) Similar Charges b) Dissimilar charges
   c) Cation have greater charge than anion d) None of these.
5. Ionic bond formation is favoured if
   a) Resulting solid has low lattice energy
   b) Resulting solid has high lattice energy
   c) Resulting solid has zero lattice energy
   d) None of these.

ANSWERS OF MCQ:

1 - a	2 - c	3 - b	4 - b	5 - a

POLARIZATION

FILL IN THE BLANKS:

1. When cation penetrates the anionic electron cloud giving a ....
2. .... of cation not much and is considered as negligible.
3. Polarization leads to partial .... character in ionic compounds.
4. Small cation or large anions are ....in character.
5. Induced covalent character in ionic compounds increases with .... in s cation and or increase with charge on the cation.
6. The polarizing power of a cation is directly proportional to its .... and inv proportional to its size.
7. Higher the ionic potential of a cation, the .... would be its polarizing power
8. The molecules having cations with .... electrons valence shell configu (Cu^+, Ag^+, Au^{3+} etc) are more covalent than those having 8 electrons.
9. The concept of polarization is useful in assessing degree of .... character ionic compound.

LONG ANSWER QUESTION:

1. What is polarization? Explain with suitable example.
2. Explain the polarization of the anion by the cation.
3. Explain Fajan's Rules and their Applications How does polarization affect covalent character of a bond?
4. Discuss any two rules proposed by Fajan.
5. Give reasons that $ZnCl_2$is soluble in organic solvents while $MgCl_2$ is insoluble.
6. Describe Fajan's Rules and their Applications.
7. $AlCl_3$ anhydrous is covalent but $AlCl_3.6H_2O$ is ionic in nature? How would account for this behaviour.
8. Explain $SnCl_4$ is more covalent than $SnCl_2$.
9. Explain Mg^{2+} has greater polarising power than Na^+
10. Why Ca^{2+} has greater polarising power than Cu^{2+}.

SELECT THE PROPER ANSWER FROM GIVEN ALTERNATIVE:

1. The polarizing power of a cation is directly proportional to its charge
   a) Density b) Size c) Charge d) None of these.
2. The molecules having cations with 18 electrons valence shell configuration is
   a) Na^+ b) Li^+ c) Be^+ d) Ca^{2+}
3. Among these ionic covalent compound is
   a) NaCl b) KCl c) $FeCl_3$ d) None of these
4. Compound of cation are less ionic
   a) Cu^+ b) Ag^+ c) Au^{3+} d) Na^+

5. Concept of polarization is not useful in assessing
   a) The degree of covalent character in an ionic compound.
   b) Melting points of salts.
   c) Test of salts
   d) None of these

ANSWERS OF MCQ:

1 - a	2 - d	3 - d	4 - a	5 - c

VALENCE BOND THEORY

FILL IN THE BLANKS:

1. Hybrid orbitals are .... in shape .
2. The process of mixing and recasting of atomic orbitals are called as ....
3. Participating atomic orbitals have .... energy.
4. In $BeCl_2$ .... hybridization.
5. Bond angle in $BeCl_2$ is ....
6. All six bonds in SF_6 are .... in length.
7. Bond angle in CH_4 is ....
8. What is hybridization in IF_7 molecule is ....
9. Structure of $BeCl_2$ is trigonal Planer While BF_3 is ....
10. In IF_7 , I–F bond length are .... length.

LONG ANSWER QUESTION:

1. What is hybridization? Explain different types of hybridization.
2. Explain geometry of $BeCl_2$ on the basis of valence bond theory.
3. Explain structure of BF_3 is trigonal planer while CH_4 is tetrahedral.
4. What is hybridization? What shape associated with SP^3d and SP^3d^2 types of hybridization?
5. Explain all S-F bonds in SF_6 are equivalent While in PCl_5 are different.
6. Explain structure and bonding in IF_7.
7. What is hybridization? Gives condition of hybridization.
8. Distinguish between atomic and hybrid orbitals.
9. Explain structure and bonding in PCl_5.
10. Draw the structure of BF_3 and CH_4 by using concept of hybridization.
11. Discuss different steps of hybridization
12. Distinguish between regular and irregular geometry.

SELECT THE PROPER ANSWER FROM GIVEN ALTERNATIVE:

1. The process of mixing and recasting of atomic orbitals is called as
   a) polarisation b) polarisability c) Hybridization d) None of these
2. SP hybridization gives geometry
   a) Linear b) trigonal planer c) Tetrahedral d) Octahedral

3. Example of SP^2 hybridization
   a) $BeCl_2$ b) CH_4 c) BF_3 d) SF_6
4. PCl_5 is formed which hybridization
   a) SP^2 b) SP c) SP^3d d) SP^3d^2
5. What is hybridization in SF_6
   a) SP^3 b) SP^2 c) Sp^3d^2 d) SP^3d
6. What is the geometry IF_7
   a) Linear b) Tetrahedral
   c) Trigonal d) Pentagonal Bipyramidal
7. Which molecule has regular octahedral shape?
   a) BF_3 b) CH_4 c) SF_6 d) PCl_5
8. All bonds in PCl_5 are ....
   a) Same in Length b) Different Length
   c) Two axial same in length and another three are equatorial same in length
   d) None of these
9. Bond angle in PCl_5 are
   a) 100 and 75 b) 120 and 90 c) 100 and 90 d) 100 and 75
10. Bond angle in IF_7
   a) 110 and50 b) 72 and 90 c) 100 and 75 d) 120 and 90.

ANSWERS OF MCQ:

1 - c	2 - a	3 - c	4 - c	5 - c
6 - d	7 - c	8 - c	9 - b	10 - b

****

UNIT II

VSEPR THEORY AND MOLECULAR ORBITAL THEORY

A. VSEPR THEORY

2.1 Introduction:

The Valence Shell Electron Pair Repulsion Theory abbreviated as VSEPR theory. In 1940, Nevil Sidgwick and Herbert Powell firstly proposed Valence Shell Electron Pair Repulsion Theory and were modified by Ronald Nyholm and Ronald Gillespie in 1957. This theory is also known as the Gillespie - Nyholm theory to honour these chemists.

The VSEPR theory is used to predict the shape of the molecules from the electron pairs that surround the central atoms of the molecule. The VSEPR theory is based on the assumption that the molecule will take a shape such that electronic repulsion in the valence shell of that atom is minimized.

According to this theory, the geometry of the molecule depends upon the number of electron pairs present in the valence shell of the central atom. The electron pairs present in the valence shell of the central atom may be of two types viz.

i) Bonding Electron Pairs or bond pairs i.e. electron pairs involved in bonding

ii) Non bonding Electron Pairs or lone pairs i.e. electron pairs not involved in bonding.

These electron pairs always try to occupy such positions in space so that there is minimum repulsion amongst them and hence maximum stability. This situation can arise only if the electron pairs arrange themselves in certain fixed geometrical positions. Due to this the molecules attain a definite geometrical shape depending upon the number of electron pairs.

According to the VSEPR theory, the repulsion between two electrons is caused by the Pauli Exclusion Principle that has greater importance than electrostatic repulsion in the determination of molecular geometry.

2.2 Rules under VSEPR theory to explain molecular geometry

Rule 1 : When the central atom has only bond pairs of electrons in its valence shell the molecule has a regular geometric shape which depends upon the number of bond pairs.

Table 1: Geometrical shapes of molecules containing only bond pairs of electrons

No. of bond pairs	Molecules A- Central Atom B- Bonded atoms	Geometry	Bond Angle	Examples
2	AB_2	Linear	180°	$BeCl_2$, BeF_2
3	AB_3	Trigonal Planer	120°	BF_3
4	AB_4	Tetrahedral	109°28'	CH_4
5	AB_5	Trigonal Bipyramidal (TBP)	120°, 90°	PCl_5
6	AB_6	Octahedral	90°	SF_6
7	AB_7	Pentagonal Bipyramidal (PBP)	90°, 72°	IF_7

Rule 2: Presence of one or more lone pairs of electrons around the central a distorts or disturbs the regular geometry of the molecule and also affects the b angle.

This is due to the lone pair occupies more space than the bond pair, becaus bond pair is under the influence of two nuclei while the lone pair is under the influenc only one nucleus. Hence, it moves closer to the nucleus and exerts greater repulsive f on other electron pairs. If two lone pairs are present they repel each other as well as r the bond pairs. Actually the extent of repulsion between different electron pairs is ir order

Lone Pair- Lone Pair > Lone Pair- Bond Pair > Bond Pair- Bond Pair

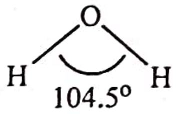
Due to these repulsions between various electron pairs, bond angles are gre affected, e.g. in CH_4, which is tetrahedral the bond angle is 109.28° and it contains bond pairs. In NH_3 (3 bond pairs & one lone pair) the bond angle is reduced to 107° w in water (2 bond pairs and 2 lone pairs) the bond angle further decreases to 104.5 *should be noted that in the Trigonal bipyramidal (TBP) geometry the lone pair (pc always occupy equatorial sites. In case of octahedral geometry when two lone pairs present they will always occupy trans positions i.e. opposite to each other.* Effec presence of one or more lone pairs on the regular geometry and bond angl summarized in following table 2.

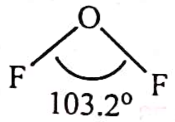
Table 2: Geometrical shapes of molecules containing lone pair of electrons.

Total No. of Electron pairs & geometry	No. of Bond pairs	No. of lone pairs	Molecules type A-Central atom B-Bonded atoms L-Lone Pairs	Actual Geometry	Bond Angle	Exampl s
3 (Trigonal planer)	2	1	AB_2L	V-shaped	95°	$SnCl_2$
4 (Tetrahedral)	3	1	AB_3L	Pyramidal	107°	NH_3
	2	2	AB_2L_2	V-shaped	104.5°	H_2O
5 (Trigonal Bipyramidal)	4	1	AB_4L	See-saw	<120°, <90°	SF_4, $TeCl_4$
	3	2	AB_3L_2	T-shaped	90°	ClF_3
	2	3	AB_2L_3	Linear	180°	ICl_2^- ion
6 (Octahedral)	5	1	AB_5L	Square pyramidal	90°	IF_5, BrF_5
	4	2	AB_4L_2	Square planer	90°	XeF_4
7 (Pentagonal Bipyramidal)	6	1	AB_6L	Distorted Octahedral	-	XeF_6

Rule 3: The bond angle depends upon the electronegativity of atoms attached t the central atom-greater is the electronegativity of the attached atoms lesser is th bond angle.

This is due to the bonding electron pairs are attracted or pulled towards the more electronegative atoms bonded to the central atom. In other words the bond pairs are shifted away from the central atom. Due to this the mutual repulsion between the bond pairs is reduced or decreased and the bond angle decreases. As Fluorine is more electronegative than hydrogen hence bond angle is more in H_2O than in F_2O.





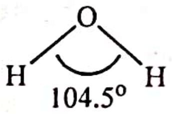
Similarly in phosphorus halides the bond angle decreases in the order-

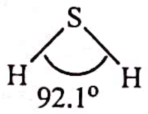
$$PI_3(102^\circ) > PBr_3(101.5^\circ) > PCl_3(100^\circ)$$

because the electro negativity of the halogen atoms attached to phosphorus atom increases in the order I<Br <Cl

Rule 4: Repulsions between electron pairs in completely filled valence shells are greater than repulsions between electron pairs in incompletely filled valence shells.

Hence in H_2O the bond angle is 105° while in H_2S it is 92°. This is because in H_2O the central atom is oxygen which has a filled valence shell and hence the extent of repulsion in electron pairs is more. This results in greater bond angle on the other hand in H_2S the central atom is Sulphur with an incompletely filled valence shell. This results in decrease in extent of repulsion amongst the electron pairs leading to lesser bond angle.





Rule 5: Bond angles in molecules involving multiple bonds are generally greater than those involving single bonds.

Multiple bonds behave like lone pairs and occupy those sites where there is minimum interaction with other electron pairs. Thus in TBP geometry, the multiple bonds will occupy equatorial sites. It should be noted that presence of multiple bonds does not affect the geometrical shape of the molecule -it only changes the bond angle.

2.3 Structures of Molecules with Regular Geometry (Molecules containing only bond pairs)

We aware of that in accordance to VSEPR theory, if the valence shell of central atom has all the bond pairs, then the molecule have a regular geometry. This is because in order to minimize the repulsion and maximize the stability the bond pairs occupy definite positions in space and impart a definite geometrical shape to the molecule.

Structures of some molecules are discussed as follows.

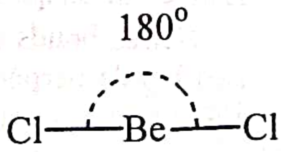
1. AB_2 type molecule

Example- $BeCl_2$

In $BeCl_2$, the central atom is Beryllium (Be)

Electronic configuration of Be- $1s^2 2s^2$

Number of valence electrons in Beryllium - 2



Numbers of electrons contributed by two chlorine atoms – 2

Total number of valence electrons - 2+2 = 4

Number of valence electron pairs = 2

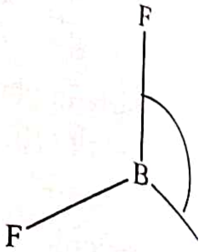
Number of bond pairs = 2

Hence, the geometrical shape of $BeCl_2$ molecule is **linear** and bond angle is 18

2. AB_3 type molecule

Example- BF_3

In BF_3, the central atom is Boron (B)



Electronic configuration of B - $1s^2 2s^2 2p^1$

Number of valence electrons in Boron- 3

Number of electrons contributed by 3 fluorine atoms - 3

Total number of valence electrons - 3+3 = 6

Number of valence electron pairs - 3

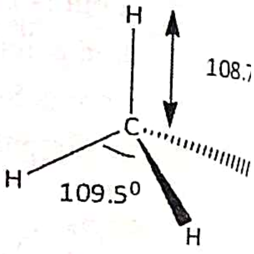
Number of bond pairs- 3

Hence, the geometrical shape of BF_3 molecule is **trigonal planar** and bond angle i

3. AB_4 type molecule

Example- CH_4

In CH_4, the central atom is Carbon (C)



Electronic configuration of Carbon - $1s^2 2s^2 2p^2$

Number of valence electrons in Carbon - 4

Number of electrons contributed by 4 hydrogens - 4

Total number of valence electrons - 4 +4 = 8

Number of valence shell electron pairs- 4

Number of bond pairs - 4

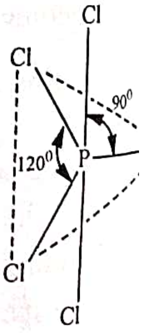
Hence, the geometrical shape of CH_4 molecule is **tetrahedral** and bond an 109.5°.

(NH_4^+ ion also has a similar structure as here also there are in all 4 electron p valence shell of nitrogen atom)

4. AB_5 type molecule

Example- PCl_5

In PCl_5, the central atom is phosphorous (P)



Trigonal bipyran

Electronic configuration of phosphorous - $1s^2 2s^2 2p^6 3s^2 3p^3$

Number of valence shell electrons in phosphorous - 5

Number of electrons contributed by five chlorine (Cl) atoms -5

Total number of valence electrons - 5+5= 10

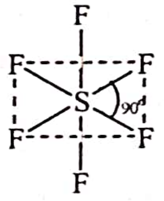
Number of valence electron pairs =5

Number of bond pairs = 5

Hence, the shape of PCl_5 molecule is **trigonal bipyradmidal (TBP).**

Three bonds present along the trigonal plane are called as equatorial bonds two bonds perpendicular to the plane are called as axial bonds. The bond ang 120° (amongst equatorial bonds) and 180° (amongst axial bonds).

5. AB_6 type molecule



Example- SF_6

In SF_6, the central atom is sulphur (S)

Electronic configuration of Sulphur - $1s^2 2s^2 2p^6 3s^2 3p^4$

Number of valence shell electrons in sulphur- 6

Number of electrons contributed by six fluorine(F) atoms - 6

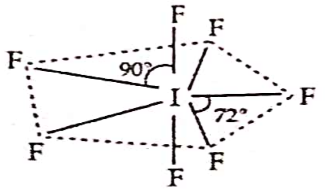
Total number of valence shell electrons - 6 +6 =12

Number of valence shell electron pairs = 6

Number of bond pairs = 6

Hence, the geometry of the molecule will be **octahedral** and the bond angle will be 90°

6. AB_7 type molecule



Example- IF_7

In IF_7, the central atom is iodine (I)

Valence shell electronic configuration of iodine -$5s^2\ 5p^5$

Number of valence electrons in iodine – 7

Number of electrons contributed by seven fluorine (F) atoms -7

Total number of valence electrons - 7+7 =14

Number of valence electron pairs = 7

Number of bond pairs = 7

Hence, the geometrical shape of molecule will be **pentagonal bipyramidal**. The bond angles between Iodine (I) and equatorial fluorine (F) atoms i.e. $F_{(e)}$-I-$F_{(e)}$ are 72° and the bond angles between equatorial fluorine (F) atom, Iodine (I) and axial fluorine (F) atom and i.e. $F_{(e)}$-I-$F_{(a)}$ are 90°

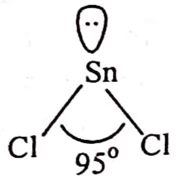
2.4 Structures of Molecules with Distorted Geometry (Molecules Containing Lone Pairs):

According to VSEPR theory, presence of one or more lone pairs in the valance shell of the central atom distorts the regular geometrical shape of the molecule and also affects the bond angle. This is due to fact that the lone pairs repel each other as well as repel the bond pairs. Actually the extent of repulsion between the various electron pairs is in the order.

LP-LP repulsion > LP-BP repulsion > BP-BP Repulsion

On the basis of this concept the structures of different molecules can be explained as follows. (In the following discussion following symbols are used. A - Central atom, B - Bonded atoms and L -Lone pairs)

1. AB_2L type molecule (2 bond pairs and 1 lone pair)



Example- $SnCl_2$

In $SnCl_2$ the central atom is tin (Sn)

The valence shell electronic configuration of tin- $5s^2 5p^2$

The number of valence electrons in tin- 4

The number of electrons contributed by two chlorine (Cl) atoms- 2

Total number of valence electrons- 4 +2= 6

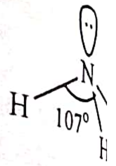
Total number of valence electron pairs- 3

The structure shows presence of two bond pairs Lone pair and one lone pair. A total number of electron pairs are three the expected electron pair geometry geometry predicted from number of electron pairs) is Trigonal planar. However to presence of one lone pair the geometry is distorted and the actual geo becomes **V-shaped or angular or bent.** The bond angle is 95° (less than 120°).

2. AB_3L type molecule (3 bond pairs and 1 lone pair)

Example- NH_3, PCl_3

i) In NH_3, the central atom is nitrogen (N)



The electronic configuration of nitrogen- $1s^2 2s^2 2p^3$

The number of valence electrons in nitrogen =5

The number of electrons contributed by three hydrogen (H) atoms- 3

Total number of valence electrons- 5 +3 = 8

Total number of valence electron pairs- 4

The structure shows presence of three bond pairs and one lone pair.

As the total number of electron pairs is four, the basic electron pair geom expected is tetrahedral. However due to presence of one lone pair of electrons geometry is distorted and it becomes **Trigonal pyramidal.** Also the bond a decreases to 107° (from expected 109° 28')

ii) In PCl_3, the central atom is phosphorous (P)

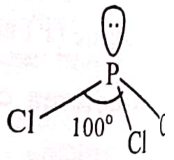
Electronic configuration of phosphorous - $1s^2 2s^2 2p^6 3s^2 3p^3$

Number of valence shell electrons in phosphorous - 5

Number of electrons contributed by three chlorine (Cl) atoms -3

Total number of valence electrons - 5+3= 8

Number of valence electron pairs- 4



The structure shows presence of three bond pairs and one lone pair.

As the total number of electron pairs is four, the basic electron pair geome expected is tetrahedral. However due to presence of one lone pair of electrons t geometry is distorted and it becomes **Trigonal pyramidal.** Also the bond ang decreases to 100° (from expected 109°28')

(PBr_3 and PI_3 will also have similar structure as here also the valence shell c phosphorous will have 3 bond pairs and one lone pair).

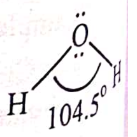
3. AB_2L_2 type molecule (2 bond pairs and 2 lone pair)

Example- H_2O

In H_2O, the central atom is oxygen (O)

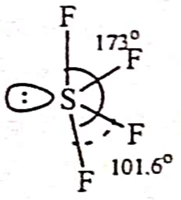
The electronic configuration of oxygen- $1s^2 2s^2 2p^4$

The number of valence electrons in oxygen – 6



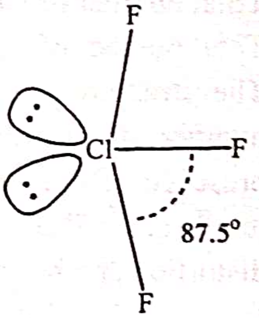
The number of electrons contributed by two hydrogen atoms- 2
Total number of valence shell electrons- 6+2 = 8
Total number of valence shell electron pairs - 4
The structure shows presence of two bond pairs and two lone pairs.
As the total number of electron pairs is four, the expected basic electron pair geometry is tetrahedral but due to presence of two lone pairs the geometry is distorted and it becomes **angular or bent or V-shaped.**

4. **AB_4L type molecule (4 bond pairs and 1 lone pair)**



Example- SF_4
In SF_4, the central atom is Sulphur (S)
Electronic configuration of Sulphur - $1s^2 2s^2 2p^6 3s^2 3p^4$
Number of valence shell electrons in sulphur- 6
The number of electrons contributed by four fluorine (F) atoms - 4
Total number of valence shell electrons - 6 +4 = 10
Total number of valence shell electron pairs- 5
The structure shows presence of four bond pairs and one lone pair. As the total numbers of electron pairs are five, the expected electron pair geometry is Trigonal bipyramidal (TBP). However due to presence of one lone pair the geometry is distorted. The loan pair occupies the equatorial position in TBP geometry. Hence the actual geometrical shape of molecule is see-saw type or distorted tetrahedral type. The bond angles also get changed. The bond angles between Sulphur (S) and equatorial Fluorine (F) atoms i.e. $F_{(e)}$-S-$F_{(e)}$ and bond angles between equatorial fluorine (F) atom, Sulphur (S) and axial Fluorine (F) atom are i.e. $F_{(e)}$-S-$F_{(a)}$ are 101.6°. The bond angles between Sulphur (S) and axial Fluorine (F) atoms i.e. $F_{(a)}$-S-$F_{(a)}$ is 173°

5. **AB_3L_2 type molecule (3 bond pairs and 2 lone pair)**



Example- ClF_3
In ClF_3, the central atom is Chlorine (Cl).
The electronic configuration of chlorine- $1s^2 2s^2 2p^6 3s^2 3p^5$
The number of valence shell electrons - 7
The number of electrons contributed by three fluorine (F) atoms - 3
Total number of valence shell electrons- 7 +3 = 10
Total number of valence shell electron pairs - 5
The structure shows presence of three bond pairs and two lone pairs. Since, the total number of electron pairs is five, the expected electron pair geometry is Trigonal bipyramidal (TBP) but presence of two lone pairs distorts the geometry. Two lone pairs occupy the equatorial position in TBP geometry. Hence the actual shape of molecule is approximately **T-shaped.** The bond angles decreases to 87.5° due to repulsions between lone pairs.

AB_4L_2 type molecule (4 bond pairs and 2 lone pair)

Example- XeF_4

In XeF_4, the central atom is Xenon (Xe).

The valence shell electronic configuration of Xenon- $5s^2\,5p^6$

The number of valence shell electrons - 8

The number of electrons contributed by four fluorine (F) atoms - 4

Total number of valence shell electrons- 8+4 = 12

Total number of valence shell electron pairs - 6

The structure shows presence of four bond pairs and two lone pairs. Since, the number of electron pairs is six, the expected electron pair geometry is octahedra presence of two lone pairs distorts the geometry. Two lone pairs occupy the position in octahedral geometry. Hence the actual shape of XeF_4 molecule becc **square planer.**

.5 Structures of molecules with multiple bonds:

The multiple bonds behave like lone pairs and their presence although does ffect the geometry of the molecule, it affects the bond angles. In TBP geomet nultiple bond will always occupy equatorial position. It should be noted that w ounting the electron pairs forming multiple bond, we should take into consideration he electron pair forming the σ-bond and not the π-bond. This is because π-bon always accompanied by a σ-bond.

Structure of XeO_3

In XeO_3, the central atom is Xenon (Xe).

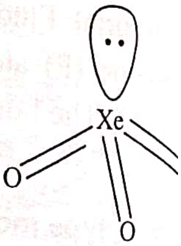
The valence shell electronic configuration of Xenon- $5s^2\,5p^6$

The number of valence shell electrons - 8

The number of electrons contributed by three oxygen (O) atoms - 6

Total number of valence shell electrons- 8+6 = 14

Total number of valence shell electron pairs - 7



The structure shows presence of six bond pairs and one lone pairs. Since, the tc number of electron pairs is seven, the expected electron pair geometry is tetrahedral l presence of one lone pairs distorts the geometry. The lone pair occupy at the corner tetrahedron. Due to presence of one lone pair of electron, the molecule undergoes sor distortion and has a **pyramidal** structure instead of being tetrahedral.

2.6 Limitations of VSEPR Theory:

1) VSEPR theory fails to explain isoelectronic species (i.e. elements having the san number of electrons). The species may vary in shapes despite having the san number of electrons.

2) The structure of several compounds of transition metals cannot be correctly describe by this theory. This is because the VSEPR theory does not take into account th associated sizes of the substituent groups and the lone pairs that are inactive.

3) Shapes of highly polar molecules cannot be explained by VSEPR theory, e.g. Li_2O should have same structure as that of H_2O (i.e. V-shaped) but actually Li_2O is linear.
4) Shapes of molecules with extensive delocalized electron system cannot be explained by VSEPR theory.
5) VSEPR theory cannot explain shapes of certain molecules having inert pairs of electrons.

****

B. MOLECULAR ORBITAL THEORY (MOT)

Molecular orbital theory (MOT theory) is another approach to explain the formation of covalent bonds in molecules or ions. This theory mainly developed by Hund and Mulliken in 1932 and latter by Lennerd Jones and Coulson. This theory is also known as Hund-Mulliken theory. This theory is based on the Linear Combination of Atomic Orbital (LCAO) of the atoms constituting the molecules or ions and hence is also called as LCAO-MO theory.

According MOT, all the electrons in given molecule or ions are considered to be present in molecular orbitals. Thus, these electrons move under the influence of all the nuclei of all the constituent atoms making the molecule or ion.

2.7 Postulates or Salient features of MO Theory

1. According to MOT, all the electrons in a molecule are considered to be under the influence of all the nuclei present in a molecule.
2. The appropriate atomic orbitals (satisfying the energy and symmetry rules) combine to give rise to a new set of orbitals called molecular orbitals (MO's).
3. The number of MO's formed is equal to the number of atomic orbitals combining. When two atomic orbitals combine, two molecular orbitals are formed. One is of lower energy called as bonding molecular orbital and other is of higher energy called as antibonding molecular orbital.
4. The combination of atomic orbitals (AO's) takes place by LCAO (Linear Combination of Atomic Orbital) approximation or LCAO method.
5. The electrons are distributed in MO's following the usual rules i.e. energy rule, Pauli Exclusion Principle and Hund's rule.
6. Possibility of covalent bond formation is decided by calculating the bond order. (If bond order is zero then no bond formation takes place).

2.8 LCAO approximation

Formation of Bonding Molecular Orbitals (BMO) and Antibonding Molecular Orbitals (ABMO):

Linear Combination of Atomic Orbital (LCAO) approximation is made to consider formation of Molecular Orbitals (MO's) by combination of Atomic Orbitals (AO's). LCAO means that a set of MO's can be obtained either by adding or by subtracting the appropriate wave functions of combining atomic orbitals.

Consider two atoms A and B combining with each other. Suppose Ψ'_A and the wave functions of electrons in them. According to the LCAO method the functions can be added or subtracted to give rise to new wave functions Ψ'_b $\Psi'_{antibonding}$ corresponding to new orbitals formed. With some approximations this mathematically expressed as:

$$\Psi'_{bonding} = N_b(\Psi'_A + \Psi_B) \text{ or } (+ + \text{overlap})$$

$$\Psi'_{antibonding} = N_a(\Psi_A - \Psi_B) \text{ or } (+ - \text{overlap})$$

Where, N_b and N_a are normalizing constants.

Addition of wave functions i.e. $(\Psi_A + \Psi_B)$ indicates increase in electron between the two nuclei. The new orbital formed is called Bonding Molecular (BMO). It has a lower energy than the corresponding atomic orbitals from whic formed. Hence it represents a situation favorable for bond formation between two The energy of bonding molecular orbital (BMO) is given as

$$E_{BMO} = E_o - \beta$$

Where, E_o is the energy of atomic orbitals and β is a constant.

In case of hydrogen molecule where 1s orbitals of two hydrogen atom involved in bonding, the formation of BMO can be graphically shown in fig. 1

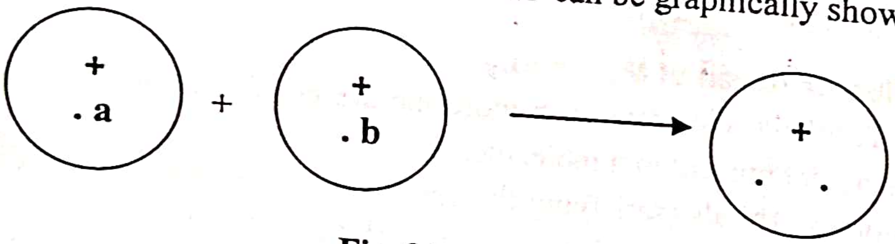


Fig. 2.1 : Formation of BMO

Similarly subtraction of wave functions i.e. $(\Psi_A - \Psi_B)$ indicates decreas electron density between two nuclei. The molecular orbital formed is termed a Antibonding Molecular Orbital (ABMO). It has a higher energy than the correspon atomic orbitals from which it is formed. Hence it represents a situation unfavorabl bond formation. The energy of Antibonding Molecular Orbital (ABMO) is given as -

$$E_{ABMO} = E_o + \beta$$

Where, E_o is the energy of atomic orbitals and β is a constant.

In case of hydrogen molecule, the formation of ABMO can be graphically represen shown in fig. 2

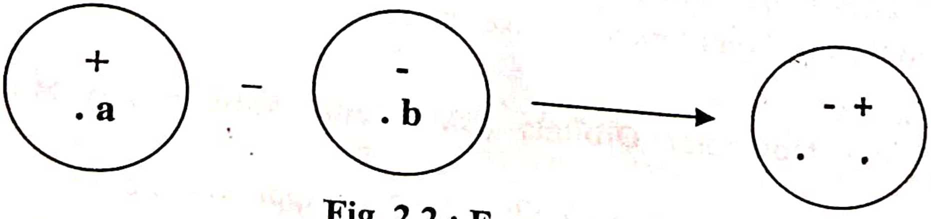


Fig. 2.2 : Formation of ABMO

In short, when two atomic orbitals combine, two molecular orbitals are form having one BMO and one ABMO.

Comparison of Atomic Orbital and Molecular Orbital

Similarities

1. Just as atomic orbitals, molecular orbitals (in a molecule) too also have definite size, shape and energy.
2. Distribution of electrons in molecular orbitals takes place in the same manner as in case of atomic orbitals i.e. by same rules namely, Aufbau principle, Pauli exclusion principle and Hund's rule.
3. Like atomic orbitals, molecular orbitals are represented by definite wave functions.
4. Like atomic orbitals, molecular orbitals are also associated with a set of quantum numbers which govern the size, shape and energy of molecular orbitals.

Differences between Atomic Orbital and Molecular Orbital

Atomic Orbital	Molecular Orbital
1) Atomic orbital is the region in space around the nucleus of atom where there is maximum probability of finding the electron.	1) Molecular orbital is the region in space around two or more nuclei where there is maximum probability of finding the electron.
2) Atomic orbital is associated with atom.	2) Molecular Orbital is associated with molecule and it is formed by combination of atomic orbitals.
3) Atomic orbital is monocentric.	3) Molecular orbital is polycentric.

Difference between Bonding Molecular Orbitals and Antibonding Molecular Orbitals

Bonding Molecular Orbital (BMO)	Antibonding Molecular Orbital (ABMO)
1) BMO is formed by LCAO method by addition of wave function i.e. $(\Psi_A + \Psi_B)$	1) ABMO is formed by LCAO method by subtraction of wave functions i.e. $(\Psi_A - \Psi_B)$
2) BMO has a lower energy than corresponding atomic orbitals and hence represents stabilization.	2) ABMO has a higher energy than corresponding atomic orbitals and represents destabilization.
3) BMO favours the bonding process.	3) ABMO opposes the bonding process.
4) BMO represents increase in electron density between two nuclei.	4) ABMO represents decrease in electron density between two nuclei.

2.3 Rules for Linear Combination of Atomic Orbitals (LCAO)

The molecular orbitals are formed by linear combination of atomic orbitals. However, it should be noted that all the atomic orbitals do not undergo linear combination. Only those atomic orbitals which fulfill the following rules undergo linear combination.

1. **Energy Rule**: The atomic orbitals which undergo linear combination must have comparable energy (i.e. these orbitals must have same or nearly same energy).

2. **Symmetry Rule**: The atomic orbitals which undergo linear combination mu same symmetry with respect to internuclear axis.

The 's' orbitals which are spherically symmetrical have sigma (σ) sym Similarly, if we choose X-axis as the internuclear axis, the p_x orbital has a sig symmetry while p_y and p_z orbitals (which are perpendicular to internuclear axi pi (π) symmetry.

3. **Extent of overlapping**: The orbitals which undergo linear combination must to a maximum extent.

2.11 Homonuclear Diatomic Molecules - Formation of MO's from 1s, 2s a AO's.

Homonuclear diatomic molecule means a molecule containing two atoms o type i.e. of same element e.g. H_2, N_2, O_2, F_2 etc.

In the homonuclear diatomic molecules of 1st and 2nd period elements (H the atomic orbitals involved are 1s, 2s, $2p_x$, $2p_y$ and $2p_z$. On the basis of vario these atomic orbitals combine to form various molecular orbitals as given in table

Table 3 : Various MO's formed by combination of 1s, 2s & 2p AO's.

Atomic Orbitals (AO's) combining		Molecular Orbitals (MO's) formed
Atom 1	Atom 2	
1s	1s	σ*1s (ABMO) σ 1s (BMO)
2s	2s	σ*2s (ABMO) σ 2s (BMO)
$2p_x$	$2p_x$	σ*$2p_x$ (ABMO) σ $2p_x$ (BMO)
$2p_y$	$2p_y$	π*$2p_y$ (ABMO) π $2p_y$ (BMO)
$2p_z$	$2p_z$	π*$2p_z$ (ABMO) π $2p_z$ (BMO)

Here, x-axis is considered as internuclear axis and hence $2p_x$ is a σ-symm orbital while $2p_y$ and $2p_z$ are π -symmetry orbitals.

The molecular orbitals formed by combination of σ -symmetry AO's (such a 2s, $2p_x$) are labeled as sigma (σ) molecular orbitals. Similarly the MO's forme combination of π-symmetry orbitals (such as $2p_y$ and $2p_z$) are labeled as pi (π) mole orbitals. Antibonding molecular orbitals (ABMO's) are indicated with an asterik (star

e.g. σ*1s, π*$2p_y$, σ*$2p_x$ etc.

Formation of various MO's has been diagrammatically represented in fig. 3

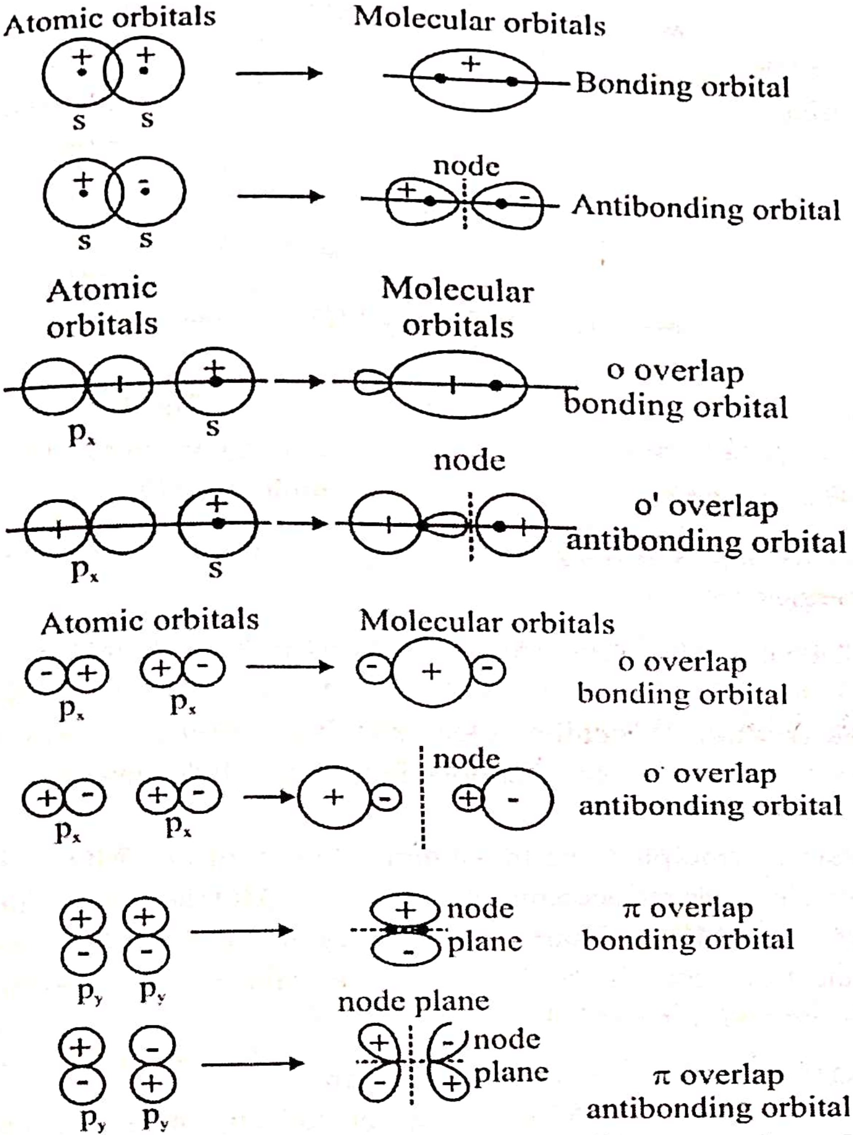


Fig. 2.3 : Formation of various MO's by combination of s and p AOs.

[It should be noted that in some molecules like B_2, C_2 and N_2 there may be combination of even 2s and $2p_x$ orbitals as these orbitals have less energy difference. Due to this, the energy sequence of various MO's is slightly changed.]

2.11 Energy Sequence of MO's in Homonuclear Diatomic Molecules:

In case of homonuclear diatomic molecules of type H_2, N_2, O_2 etc. the atomic orbitals involved in linear combination are 1s, 2s, $2p_x$, $2p_y$ and $2p_z$. The energy sequence of various MO's formed by combination of these AO's is given in figure 4 (a). In case of molecules like B_2, C_2 and N_2 the energy sequence is slightly different and is given in figure 4(b). The difference arises due to the fact that in these molecules there is combination of even 2s and $2p_x$ orbitals.

E ↑

σ^*2p_x

$\pi^*2p_y = \pi^*2p_z$

$\pi2p_y = \pi2p_z$

$\sigma2p_x$

σ^*2s

$\sigma2s$

σ^*1s

$\sigma1s$

← Highest Energy MO →

E ↑

← Lowest Energy MO →

σ^*2p_x

$\pi^*2p_y = \pi^*2p_z$

$\pi2p_y = \pi2p_z$

$\sigma2p_x$

σ^*2s

$\sigma2s$

σ^*1s

$\sigma1s$

Fig. 2.4 (a)

Energy sequence of MO's for molecules like H_2, O_2 and F_2

Fig. 2.4 (b)

Energy sequence of MO's for molecules like B_2, C_2 and N_2

The orbitals $\pi2p_y$ and $\pi2p_z$ as well as π^*2p_y and π^*2p_z are called as deger MO's as their energies are same.

2.12 Rules for Distribution of Electrons in Molecular Orbitals (MO's)

The electrons are distributed in various MO's according to following rules.

1. **Energy Rule (Aufbau Principle):** Electrons always prefer lowest energy mole orbitals. Hence while filling the electrons in various MO's the energy sequence g in figure 4 should be followed.
2. **Pauli Exclusion Principle:** The maximum capacity of any MO is of two elec and when two electrons are accommodated in same MO their spins must be oppo
3. **Hund's Rule:** The MO's of same energy (degenerate MO's) are available va orbital the electrons are singly fill with their spins are parallel and after si occupation is over pairing will take place.

2.13 Molecular Orbital (MO) Energy Level Diagram:

The various aspects of MO description of any molecule can be suit conveniently represented by energy level diagram. Such diagrams are called as Energy Level diagrams.

Following are the important aspects of MO energy level diagrams. They represent

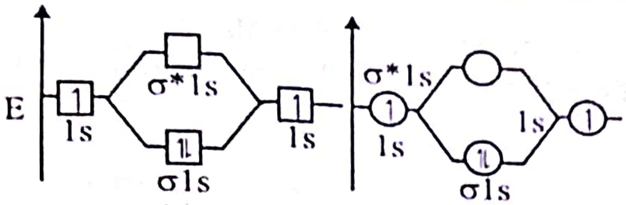
a) Atomic orbitals involved in linear combination.

b) Various MO's formed.

c) Energy sequence of the MO's.

d) Distribution of electrons in MO's.

In these MO energy level diagrams, the AO's and MO's can be represented circles, square boxes or thick lines. Fig. 2.5 shows the various ways of representing M energy level diagram for H_2 molecule.



(a) (b)

Fig. 2.5 : MO energy level diagram for H_2 molecule.

2.14 Bond Order:

Bond order actually represents the number of covalent bonds between two atoms. In terms of MO theory, bond order is nothing but half the difference in number of electrons present in BMO and ABMO and is calculated as

$$\text{Bond order} = \frac{\text{No. of electrons in BMO} - \text{No. of electrons in ABMO}}{2}$$

When bond order is 1 it represents a single bond, when it is 2 -a double bond and when it is 3- a triple bond. When the bond order is zero it indicates that no covalent bond is formed between two atoms.

2.15 Molecular Orbital (MO) structures of Various Molecules:

In general, to discuss the MO structure of any molecule we have to go by following steps.

a) Finding which AO's are involved in linear combination.
b) Finding which MO's are formed.
c) Finding how the electrons are distributed in various MO's.
d) Drawing the MO energy level diagram.
e) Calculating the bond order.
f) Symbolically representing the MO structure.
g) Discussion on important properties of the molecule on the basis of MO structure.

On the basis of this concept the MO structures of some homonuclear diatomic molecules are discussed below.

1. Structure of Hydrogen (H_2) Molecule

In a hydrogen molecule we have two hydrogen atoms each with $1s^1$ configuration. The near combination of 1s orbitals of each of the two hydrogen atoms will produce two molecular orbitals namely $\sigma 1s$ and $\sigma^* 1s$.

$$\begin{array}{l} H = 1s^1 \\ 1s + 1s \\ H = 1s^1 \end{array} \left\{ \text{——} \quad \begin{array}{l} \sigma 1s \text{ BMO} \\ \\ \sigma^* 1s \text{ ABMO} \end{array} \right.$$

Now the total number of electrons in H_2 molecules is two. These two electrons will be placed in lower energy $\sigma 1s$ bonding molecular orbital. The MO energy level diagram for H_2 molecule is shown in figure 5.

Symbolically the MO structure can be represented as-

$H(1s^1) + H(1s^1) = H_2[(\sigma 1s)^2]$

Now, the bond order is calculated using the formula

Bond order = ½ [No. of electrons in BMO - No. of electrons in ABMO]

Hence for H_2, we have

Bond order = ½[2-0]

= 1

As the bond order is 1, it indicates that there is a single covalent bond betwe hydrogen atoms.

2. Structure of He_2 Molecule.

Noble gas molecules are monoatomic because covalent bond formation possible in them and hence they cannot form diatomic molecules. This can be exp with the example of formation of He_2 molecule on the basis of MO theory. In th molecule there are two helium atoms each with electronic configuration $1s^2$. The combination of 1s orbitals of each of the two helium atoms will give rise t molecular orbitals namely $\sigma 1s$ and $\sigma^* 1s$. There are all four electrons (two from helium atom) to be distributed in MO's. $\sigma 1s$ will have two electrons and $\sigma^* 1s$ wil two electrons. The MO energy level diagram for He_2 molecule is shown in fig. 2.6

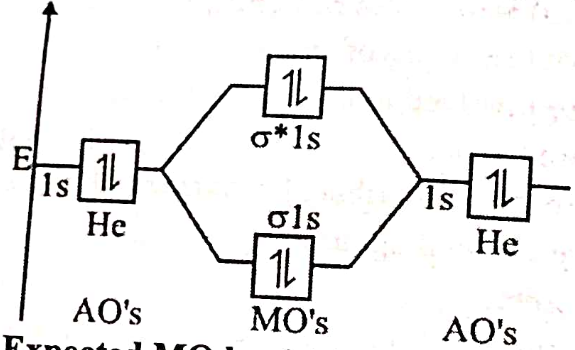


Fig. 2.6 : Expected MO level diagram of He_2 molecule

Symbolically the MO structure can be represented as

$$He(1s^2) + He(1s^2) = He_2[(\sigma 1s)^2 (\sigma^* 1s)^2]$$

Now, the bond order is calculated using the formula

Bond order = ½ [No. of electrons in BMO - No. of electrons in ABMO]

Hence for He_2, we have

Bond order = ½[2-2]

= 0

As the bond order is 0 (zero), it indicates that there is no covalent bond format between two Helium atoms or in other words formation of He_2, types of molecule is possible. Hence in general we can say that noble gas molecules are monoatomic.

3) Structure of Nitrogen (N_2) Molecule.

In nitrogen (N_2) molecule we have two nitrogen atoms, each with the followin lectronic configuration.

N_7	=	$1s^2$	$2s^2$ $2p_x^1\,2p_y^1\,2p_z^1$
N_7	=	$1s^2$	$2s^2$ $2p_x^1\,2p_y^1\,2p_z^1$
Closed shells			Orbitals involved in linear combination

Thus, in nitrogen molecule 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals will be involved in bondin. However, for the sake of simplicity it is assumed that 1s orbitals being inner shell orbitals do not take part in bonding and remain as closed shells. Thus, only the valence shell orbitals namely 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals are involved in linear combination to form different MO's. The total numbers of electrons involved in bonding are ten (five electrons from each nitrogen atom). The distribution of electrons in various MOs is shown in figure 7 which depicts the MO energy level diagram for nitrogen (N_2) molecule.

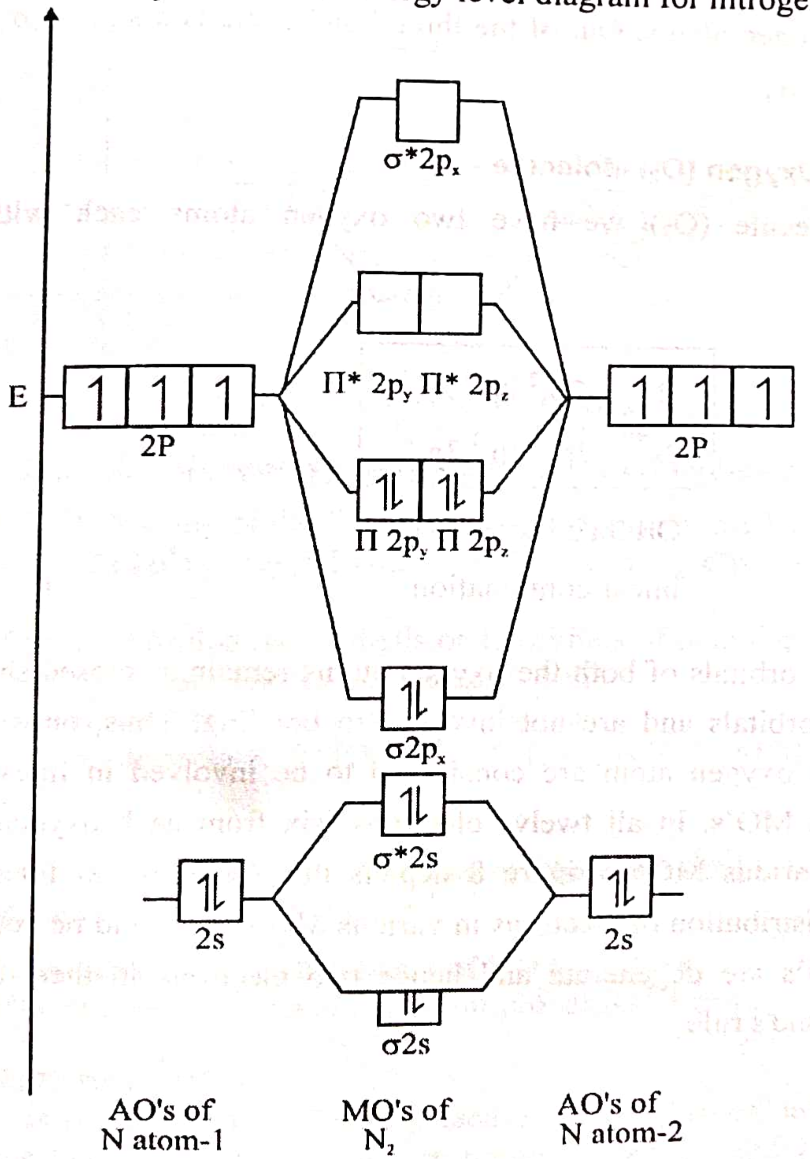


Fig. 2.7 : MO energy level diagram for N_2 molecule.

Symbolically, the MO structure of the N_2 molecule can be represented as follows.

$N(1s^2 2s^2 2p^3) + N(1s^2 2s^2 2p^3) = N_2[KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 (\pi 2p_z)^2]$

Here, KK represents that the K-shells or 1s orbitals of both the nitrogen at as closed shells and are not involved in bonding.

Now, the bond order in nitrogen (N_2) molecule is given as -

Bond order = ½ [No. of electrons in BMO - No. of electrons in ABMO]

Bond order = ½[8-2]

= 3

Thus in N_2, molecule the bond order is three which indicates that there is a triple between two nitrogen atoms. Out of the three bonds, one is a sigma (σ) bond and two are pi (π) bonds.

4. Structure of Oxygen (O_2) Molecule -

In oxygen molecule (O_2) we have two oxygen atoms each with an elect configuration.

O_8	=	$1s^2$	$2s^2$ $2p_x^2 2p_y^1 2p_z^1$
O_8	=	$1s^2$	$2s^2$ $2p_x^2 2p_y^1 2p_z^1$
		Closed shells	Orbitals involved in linear combination

Now, 1s orbitals of both the oxygen atoms remain as closed shells because t are inner shell orbitals and are not involved in bonding. Thus, only the valence s orbitals of each oxygen atom are considered to be involved in linear combinatio produce various MO's. In all twelve electrons (six from each oxygen atom) are to distributed in various MO's. Figure 8 depicts the MO diagram for oxygen molec indicating the distribution of electrons in various MO's. It should be noted that the π* and $\pi^* 2p_z$ MO's are degenerate and hence two electrons in them are placed sing according to Hund's rule.

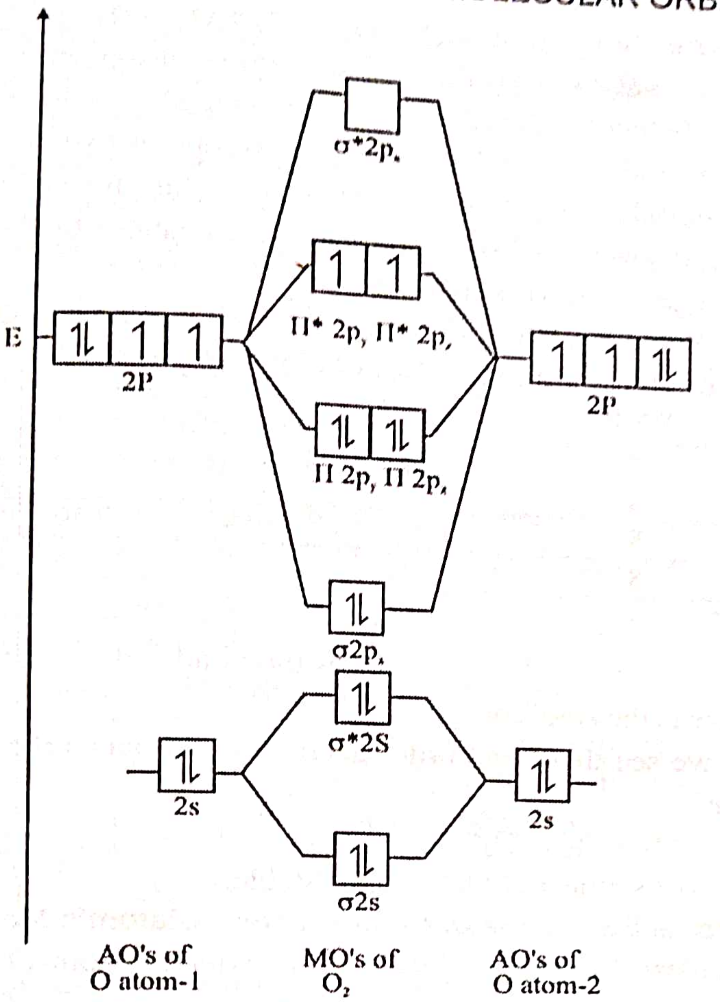


Fig. 2.8 : MO energy level diagram for O_2 molecule

Symbolically, the MO structure of the O_2 molecule can be represented as follows.
$O(1s^2 2s^2 2p^4) + O(1s^2 2s^2 2p^4) = O_2 [KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 = (\pi 2p_z)^2, (\pi^* 2p_y)^1 = (\pi^* 2p_z)^1]$

Here, KK represents that the K-shells or 1s orbitals of both the oxygen atoms are not involved in bonding and are remaining as closed shells.

Now, the bond order in nitrogen (O_2) molecule is given as -
Bond order = ½ [No. of electrons in BMO - No. of electrons in ABMO]
Bond order = ½[8-4]
= 2

As the bond order is 2 it indicates that in O_2 molecule there is a double bond in which one is a sigma (σ) bond and other is a pi (π) bond.

2.16 Important Properties of O_2 on the basis of MO Structure

On the basis of MO structure of oxygen important properties of oxygen can be explained as follows.

a) Paramagnetic Nature of Oxygen

A substance is paramagnetic due to presence of one or more unpaired electrons. In O_2 molecule two unpaired electrons are present in π*2py and π*2pz molecular orbitals in accordance with Hund's rule. The presence of these two unpaired electrons is responsible for paramagnetic nature of O_2.

b) Stability Sequence in oxygen- $O_2^{2+} > O_2^{+} > O_2 > O_2^{-} > O_2^{2-}$

It is observed that amongst the various species of oxygen molecule, O_2^{2+} i stable while O_2^{2-} is least stable. This can be explained as follows.

Positive ions (O_2^{+} and O_2^{2+})are formed by loss of one or two electrons from A π^*2p_y and π^*2p_z, while negative ions (O_2^{-} and O_2^{2-})are formed by addition of two electrons to the same ABMO's. Due to these changes the bond order in d species will change as shown in table 2

Table 4 : Bond orders in various species of O_2

Species	No. of electrons in BMO	No. of electrons in ABMO	Bond Ord
O_2^{2+}	8	2	3
O_2^{+}	8	3	2.5
O_2	8	4	2
O_2^{-}	8	5	1.5
O_2^{2-}	8	6	1

Now, it should be noted that, higher is the bond order greater is the bond e and therefore greater is the stability.

In case of oxygen we see that bond order decreases and hence the stability decreas the following order.

$$O_2^{2+} > O_2^{+} > O_2 > O_2^{-} > O_2^{2-}$$

Therefore, O_2^{2+} is most stable and O_2^{2-} is least stable.

2.17 Molecular Orbital Structures of Heteronuclear Diatomic Molecules:

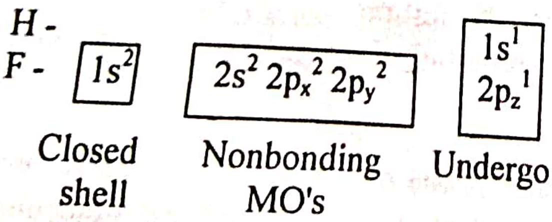
A heteronuclear diatomic molecule is one which contains two atoms of diff elements. e.g. HF, NO, CO etc.

Nonbonding Molecular Orbitals (NBMOs):

The molecular orbitals which neither favor nor oppose the bonding process known as nonbonding molecular orbitals (NBMOs).

In the case of heteronuclear diatomic molecules two atoms of different type involved. In this case the atomic orbitals of one atom may not have the same en and/or same symmetry as the atomic orbitals of other atoms. Due to this one or m atomic orbitals of any particular atom may not take part in linear combination to f molecular orbitals. Such orbitals then remain as nonbonding molecular orbitals

e.g. in HF molecule 2s, $2p_x$ and $2p_y$ orbitals of Fluorine atom remain as non bonding M because orbitals of comparable energy or symmetry are not available in hydrogen atom



It should be noted that the energy of NBMO remains unchanged (i.e. it remai ame as the energy of AO's)

2.18 MO structures of some heteronuclear diatomic molecules

1. MO Structure of Carbon Monoxide (CO)- Coulson's Structure.

The MO structure of carbon monoxide as explained by Coulson could satisfactorily explain the various properties of CO.

In Coulson's structure it is assumed that both carbon and oxygen atoms are in sp hybrid state. The ground state electronic configurations of carbon and oxygen are given as

$C_{(ground)}$	=	$1s^2$	$2s^2 \quad 2p_x^1$	$2p_y^1 2p_z^0$
$O_{(ground)}$	=	$1s^2$	$2s^2 \quad 2p_x^2$	$2p_y^1 2p_z^1$
		Closed shells	Undergo 'sp' hybridization	

Now, 1s orbitals of both carbon and oxygen atoms, being inner shell orbitals do not take part in bonding and remain as closed shells. In both carbon and oxygen atoms, 2s and $2p_x$ orbitals undergo 'sp' hybridazation. Out of two hybrid orbitals one sp hybrid orbital of each atom remains as nonbonding MO. Hence the orbitals undergoing linear combination of both the atoms will be sp, 2py and 2pz orbitals,

$C_{(hybrid)}$	=	$1s^2$	$(sp)^2$	$(sp)^1$	$2p_y^1 2p_z^0$
$O_{(hybrid)}$	=	$1s^2$	$(sp)^2$	$(sp)^1$	$2p_y^1 2p_z^2$
		Closed shells	NBMOs	Undergo linear combination	

Thus six atomic orbitals (3 from carbon and 3 from oxygen) will undergo linear combination to produce six molecular orbitals as given in Table 3

Table 5 : MO's formed in Carbon Monoxide

Atomic orbitals combining		Molecular orbitals formed
Carbon atom	**Oxygen atom**	
$(sp)^1$	$(sp)^1$	σ and σ^*
$2p_y^1$	$2p_y^1$	Π_1 and Π_1^*
$2p_z^0$	$2p_z^2$	Π_2 and Π_2^*
-	$(sp)^2$	Nb_1
$(sp)^2$		Nb_2

Now the total number of electrons to be accommodated in MOs is ten (4 from carbon atom and 6 from oxygen atom). The distribution of these electrons is represented in the MO energy level diagram as shown in figure 9

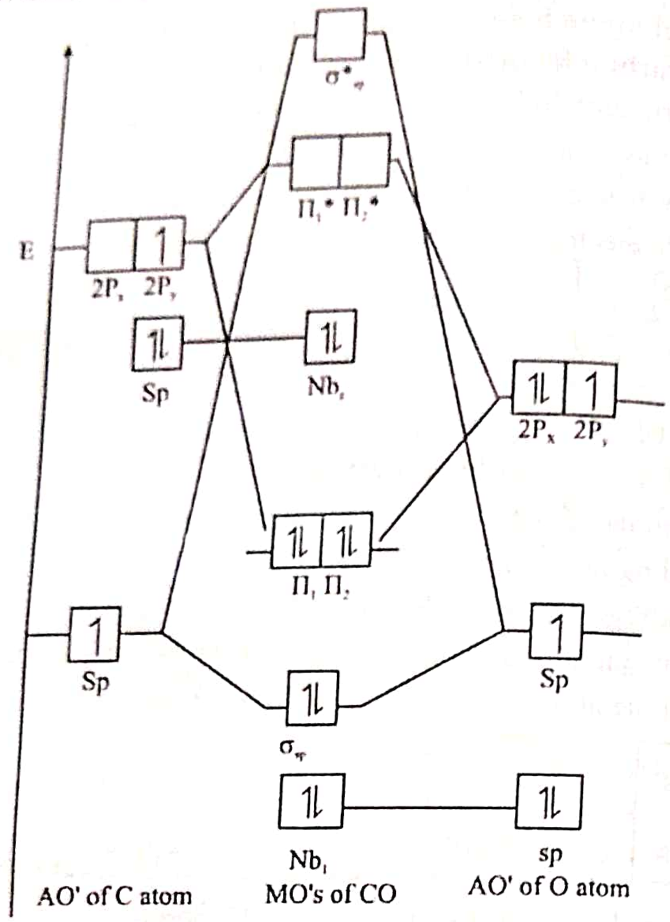


Fig. 2.9 : MO energy level diagram for CO molecule.

Symbolically, the MO structure of the CO molecule can be represented as follows.

$$C(1s^2 2s^2 2p^2) + O(1s^2 2s^2 2p^4) = CO\,[KK(Nb_1)^2 (\sigma)^2 (\pi_1)^2 (\pi_2)^2 (Nb_2)^2]$$

Now the bond order is given as

Bond order = ½ [No. of electrons in BMO - No. of electrons in ABMO]

Bond order = ½[6-0]

= 3

On the basis of MO structure of CO various properties can be explained as follows

a) Presence of a triple bond:

As the bond order is three (3) it explains the presence of a triple bond in CO which one is a σ bond and two are π bonds.

b) Almost nonpolar nature:

Due to presence bonding electrons more nearer to oxygen atom, the excess nu charge on oxygen is partly neutralized. Hence the CO molecule is almost nonpo nature which is indicated by its low dipole moment i.e. 0.1 Debye.

c) Electron donor behavior:

Carbon monoxide is a good electron donor due to presence of an electron pa higher energy nonbonding MO -Nb_2. Hence it can form compounds like n carbonyls where CO donates a pair of electron to a metal atom like that of trans metal.

d) Electron acceptor behavior:

Due to presence of vacant antibonding MO's particularly π_1^* and π_2^*, carbon monoxide can accept electron pair and act as a good electron pair acceptor. This is helpful in the process of back bonding in metal carbonyls which strengthens the metal carbon bond.

2. MO Structure of Hydrogen Fluoride (HF).

In HF we have one hydrogen atom and one fluorine atom and their electronic configurations are -

H -			$1s^1$
F -	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2$	$2p_z^1$
	Closed shell	Nonbonding MO's	Undergo linear combination

Now, 1s orbital of fluorine being inner shell orbital does not take part in bonding and remains as a closed shell. Similarly 2s, $2p_x$ and $2p_y$ orbitals of fluorine atom remain as nonbonding MO's, because orbitals of comparable energy and symmetry are not available for linear combination in hydrogen atom.

Therefore in HF only 1s orbital of hydrogen atom and $2p_z$ orbital of fluorine atom undergo linear combination to produce two MOs namely σ and σ*. It should be noted that here z-axis is considered as internuclear axis.

$$1s\,(H) + 2p_z\,(F) \longrightarrow \begin{cases} \sigma^* \text{ ABMO} \\ \sigma \text{ BMO} \end{cases}$$

Now, in all two electrons are to be distributed in σ and σ* MO's. These two electrons will go to σ MO. The MO energy level diagram for HF is shown in figure 10

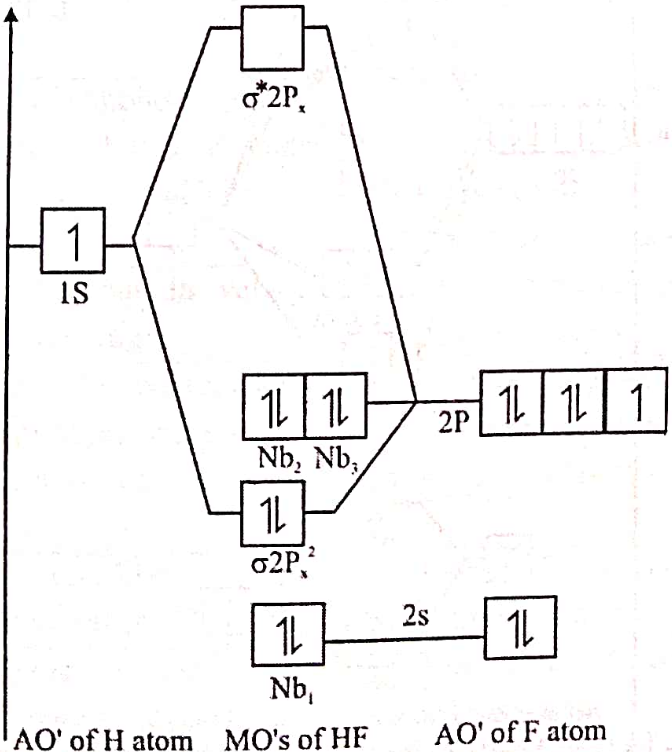


Fig. 2.10 : MO energy level diagram for HF molecule.

Symbolically, the MO structure of HF can be represented as -

$$H(1s^1) + F(1s^2 2s^2 2p^5) = HF\ [KK(F)\ (Nb_1)^2\ (\sigma 2P_x)^2\ (Nb_2)^2\ (Nb_3)^2]$$

The bond order is given as-

Bond order = ½ [No. of electrons in BMO - No. of electrons in ABMO]

Bond order = ½[2-0]

= 1

As the bond order is one it indicates that a single covalent bond is present in HF.

3. MO Structure of Nitric Oxide (NO).

In nitric oxide (NO) there is one nitrogen atom and one oxygen ato electronic configurations of these atoms are-

N = $1s^2$ | $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

O = $1s^2$ | $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

Closed shells — Orbitals involved in linear combination

Out of the various orbitals, Is orbitals of both nitrogen and oxygen atoms inner shell orbitals do not take part in bonding and remain as closed shells. Thus o $2p_x$, $2p_y$ and $2p_z$ orbitals of both the atoms undergo linear combination to produce v MOs. Now, in all eleven (11) electrons (six from oxygen atom and five from nit atom) are to be accommodated in various MOs. Figure 11 depicts the MO energy diagram for Nitric Oxide (NO) molecule.

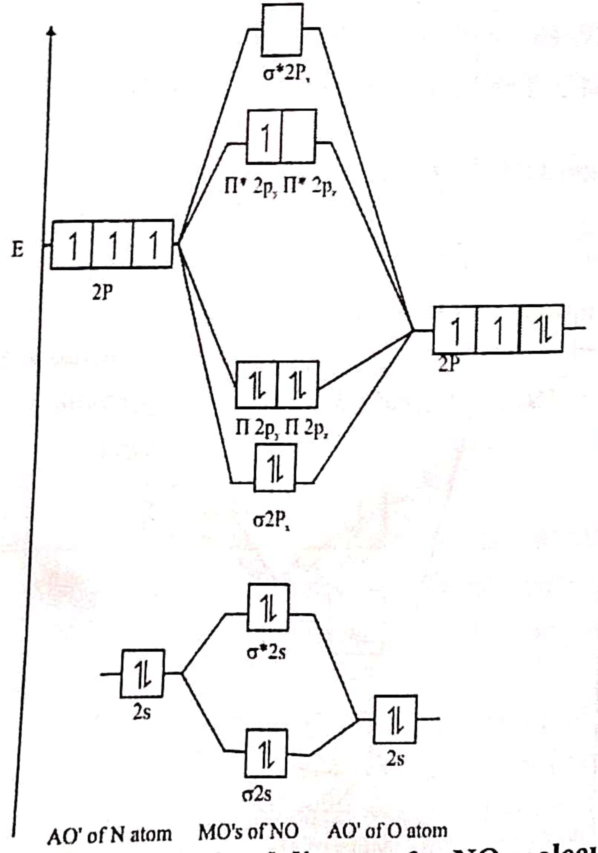


Fig. 2.11 : MO energy level diagram for NO molecule.

Symbolically, the MO structure of the NO molecule can be represented as follows.
$N(1s^2 2s^2 2p^3) + O(1s^2 2s^2 2p^4) = NO\,[KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 = (\pi 2p_z)^2 (\pi^* 2p_y)^1 = (\pi^* 2p_z)^0]$

The bond order is given as -

Bond order = ½ [No. of electrons in BMO - No. of electrons in ABMO]

Bond order = ½[8-3]

= 2.5

The MO structure of NO shows presence of one unpaired electron in $\pi^* 2p_y$ MO. Hence, NO is paramagnetic in nature. Similarly the molecule is relatively less stable than N_2 molecule as it has lower bond order (2.5) than that of N_2 (3.0).

2.19 Comparison of Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT).

Similarities:

1. Both the theories explain the nature of covalent bond and hence both take into consideration the sharing of electrons and pairing of electrons spins.
2. Both the theories take into consideration the overlapping of atomic orbitals of comparable energy and same symmetry.
3. Both the theories give an explanation for the directional nature of covalent bond.
4. Both the theories consider increase in electron density as the criterion for bond formation.

Differences:

VB Theory	MO Theory
1. Atomic orbitals are involved in bond formation and their identity is retained even after the molecule is formed.	1. Molecular orbitals are involved in bond formation and as soon as the MOs are formed, atomic orbitals lose their identity.
2. Atomic orbitals are monocentric i.e. electrons in atomic orbitals are under the influence of only one nucleus.	2. Molecular orbitals are polycentric i.e. electrons in MOs are under the influence of more than one nucleus.
3. Only unpaired electrons in valence shell take part in bonding.	3. All the electrons in valence shell take part in bonding.
4. It cannot explain the paramagnetic nature of O_2 molecule, properties of CO and spectra of molecules satisfactorily.	4. It can explain satisfactorily the paramagnetic nature of O_2 properties of CO and spectra of molecules.
5. It takes into consideration the phenomenon of resonance.	5. It does not take into consideration the phenomenon of resonance.
6. Bond order means the number of electron pairs shared between two atoms.	6. Bond order is calculated as half the difference in number of electrons present in BMO and ABMO.

EXERCISE

FILL IN THE BLANKS:

1. VSEPR theory was proposed by .... and was modified by.........
2. The geometry of the $SnCl_2$ molecule is ....
3. Shape of the XeF_4 molecule is ....
4. There are .... bond pairs and .... lone pair present in SF_4.
5. In AB_5 type , the shape of the molecule is ....
6. In AB_3L_2 type , the shape of the molecule is ....
7. Bond angles in IF_7 are .... and ....
8. In the Trigonal bipyramidal (TBP) geometry the lone pair (pairs) always occupi .... sites.
9. In octahedral geometry when two lone pairs are present they will always occupy .... positions.
10. In TBP, three bonds present along the trigonal plane are called as .... bonds two bonds perpendicular to the plane are called as .... bonds.
11. The atomic orbital's combine to give rise to a new set of orbitals is called as .....
12. The combination of atomic orbitals takes place by .... method.
13. Atomic orbital is .... centric.
14. Molecular orbital is .... centric.
15. BMO has .... energy than the corresponding AO's.
16. ABMO has .... energy than the corresponding AO's.
17. When two 1s atomic orbitals combine together then .... BMO and .... ABMO are formed.
18. The bond order of O_2 is ....
19. The MO structure of carbon monoxide explained by ....
20. In N_2, ... sigma bond and .... pi bonds are present.

SHORT ANSWER QUESTIONS:

1. Define bond pair and lone pair.
2. Predict shapes of $BeCl_2$, BF_3 , CH_4 and NH_3.
3. Identify geometry of PCl_5 and SF_6.
4. Write order of extent of repulsion between different electron pairs.
5. State why the bond angle of H_2O is greater than H_2S.
6. Interpret the bond angles of $SnCl_2$, ClF_3 , XeF_4 and SF_6.
7. Write limitations of VSEPR theory.
8. Enlist postulates of MOT theory.
9. Give the similarities between VBT and MOT.
10. Differentiate between VBT and MOT.
11. How does molecular orbital form?
12. Define BMO
13. Define ABMO
14. What is bond order?
15. How is bond order calculated?
16. Give the characteristics of BMOs and ABMOs.
17. State why does the He_2 molecule not exist?
18. Show stability sequence of O_2. .
19. Calculate bond order of CO.
20. Determine bond order of HF.

LONG ANSWER QUESTIONS:

1. Write any three rules of VSEPR theory.
2. With the help of VSEPR theory explain the structure of $BeCl_2$ and BF_3.
3. Explain VSEPR theory with suitable examples.
4. How will you compare atomic orbitals with molecular orbitals ?
5. Explain geometrical shapes of $SnCl_2$ and H_2O.
6. Discuss shapes of ClF_3 and XeF_4.
7. Describe the structure of the SF_6 molecule on the basis of VSEPR theory.
8. Explain the structure of IF_7 molecule on the basis of VSEPR theory.
9. With the help of VSEPR theory explain the structure of PCl_5 molecule.
10. Define molecular orbital ? What is the maximum number of electrons that can occupy a molecular orbital?
11. Differentiate MOs from AOs.
12. How many molecular orbitals of H_2 originate from the hydrogen atomic orbitals?
13. Explain bond order with suitable examples.
14. What do you understand about BMO and ABMO? Draw the MOs obtained by the combination of two 1s AOs.
15. Write energy sequence of MO's in homonuclear diatomic molecules.
16. Draw molecular orbital energy level diagram of O_2 molecule. Calculate its bond order.
17. Explain paramagnetic character of oxygen molecule with the help of MO diagram.
18. Briefly discuss the concept of linear combination of atomic orbitals to produce MOs.
19. Explain the formation of N_2 molecule on the basis of MOT. Calculate its bond order.
20. Draw MO diagram of NO molecule and calculate its bond order.
21. Draw Coulson's MO diagram of CO molecule.
22. Explain following properties of CO i) Bond order ii) non- polar nature ii) acceptor properties iv) donor properties.
23. How does MO theory differ from VBT?
24. Predict electron pair and molecular geometries of HF molecule.
25. Give molecular orbital configuration of O_2 and CO.
26. Draw MO diagram for He_2

SELECT THE PROPER ANSWER FROM GIVEN ALTERNATIVE:

VSEPR THEORY

1. Which of the following species has 120° bond angles?
   a) PCl_3 b) PI_3 c) ClF_2 d) BF_3
2. Which of the following species has a Trigonal planar shape?
   a) BF_3 b) CH_4 c) PCl_5 d) IF_7
3. Which of the following has a linear shape?
   a) $SnCl_2$ b) $BeCl_2$ c) H_2O d) SF_6
4. The geometry of $SnCl_2$ is
   a) Linear b) Trigonal planer c) TBP d) Angular
5. Find the molecule in which the central atom is having one lone pair of electrons
   a) NH_3 b) PCl_5 c) H_2O d) CH_4
6. In ClF_3, lone pairs are present at the equatorial positions. This is to minimize
   a) bp-bp repulsion only b) lp-lp repulsion only c) lp-bp repulsion only d) both (b) and (c)
7. Find the species with a maximum bond angle

a) CH_4 b) $SnCl_2$ c) NH_3 d) PCl_3

XeF$_4$ is

a) Square planer b) Tetrahedral c) Octahedral d) TBP

9. Number of bond pair and lone pair electrons present on Cl atom in ClF_3 are

a) 3, 1 b) 3, 2 c) 3, 3 d) 2, 3

10. The geometry of SF_6 molecule is

a) Tetrahedral b) Octahedral c) Trigonal Bipyramidal d) Linear

MOLECULAR ORBITAL THEORY

11. MOT is firstly proposed by

a) Hund and Mulliken b) Jones and Coulson
c) Sidgwick and Powell d) Gillespie and Nyholm

12. LCAO method used in

a) VBT b) MOT c) VSEPR d) CFT

13. Lower energy atomic orbital is known as

a) BMO b) ABMO c) Both a and b d) only orbital

14. Higher energy atomic orbital is known as

a) BMO b) ABMO c) Both a and b d) only orbital

15. When two atomic orbitals combine then

a) One molecular orbital is formed b) Two molecular orbital is formed
c) Three molecular orbital is formed d) No molecular orbital is formed

16. Bond order is

a) ½ [No. of electrons in BMO + No. of electrons in ABMO]
b) ½ [No. of electrons in BMO - No. of electrons in ABMO]
c) [No. of electrons in BMO + No. of electrons in ABMO]
d) [No. of electrons in BMO - No. of electrons in ABMO]

17. Find the molecule having least bond order

a) HF b) CO c) NO d) O_2

18. Find the molecule having the highest bond order

a) H_2 b) N_2 c) He_2 d) O_2

19. Which of the following is paramagnetic?

a) H_2 b) N_2 c) He_2 d) O_2

20. Find the molecule having the highest bond order

a) O_2^+ b) O_2^- c) O_2^{2-} d) O_2

21. Find the molecule having the highest no. of electrons in ABMO

a) O_2^+ b) O_2^- c) O_2^{2-} d) O_2

22. Identify most stable species

a) O_2^+ b) O_2^- c) O_2^{2-} d) O_2

23. Identify least stable species

a) O_2^+ b) O_2^- c) O_2^{2-} d) O_2

24. Bond order in case of CO molecule is

a) 2 b) 3 c) 4 d) 1

Answer key

1 - d	2 - a	3 - b	4 - d	5 - a	6 - b	7 - a	8 - a	9 - b	10 -b
11 - a	12 - b	13 - a	14 - b	15 - b	16 - b	17 - a	18 -b	19 - d	20 - a
21 - c	22 - a	23 - c	24 - b						

****

UNIT III

HALOALKANES, HALOARENES AND POLYHYDRIC ALCOHOLS

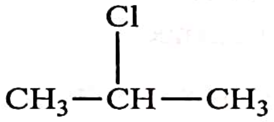
A. HALOALKANES

An organic compound containing carbon—halogen (C—X) bond is called as Haloalkane (Alkyl halide). In Haloalkanes a halogen atom (Cl, Br, F or I) is bonded to an alkyl group.Haloalkane has the general representation as R—X, where, R is any alkyl group and X represents a halogen atom. Haloalkane compound shows wide variety of chemical reactions and is considered one of the important intermediates in organic syntheses.

Haloalkanes are named by either common or IUPAC names. In common name system they are simply called Alkyl halide, the name of alkyl group followed by name of halogen. In IUPAC nomenclature system, they are considered as a halogen derivative of hydrocarbons, and named as haloalkane.

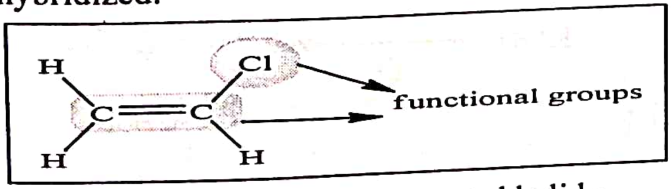
Alkyl halides may be classified as saturated or unsaturated based on the presence or absence of π - bond. In unsaturated alkyl halides all σ- bonds are present whereas in unsaturated alkyl halides one or more π - bonds are present. Unsaturated alkyl halides are generally known by their common names.

In this part we will focus on unsaturated alkyl halides.

$CH_3—Cl$	$CH_3—CH_2—Br$	 $CH_3—CH(Cl)—CH_3$
Methyl chloride	Ethyl bromide	iso-propyl chloride
	Saturated Alkyl halides	
$CH_2{=}CH—Cl$	$CH_2{=}CH—CH_2—Cl$	$CH_2{=}CH—CH_2—Br$
Vinyl chloride	Allyl chloride	Allyl bromide
	Unsaturated Alkyl halides	

3.1 Vinyl Chloride:

Vinyl chloride, also known as chloroethene, is the derivative of ethylene obtained by substituting any one of the hydrogen atoms with a chlorine atom. In vinyl chloride carbon atoms are sp^2 hybridized.



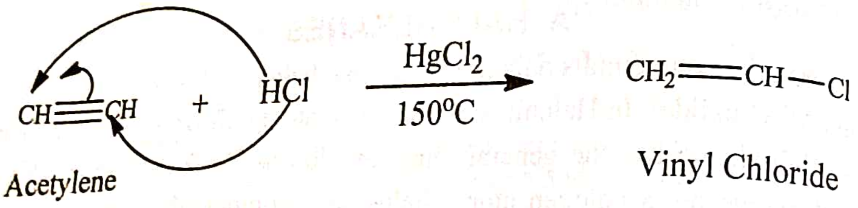
Vinyl chloride is the most important unsaturated halide.

Preparations of vinyl chloride

Vinyl chloride may be prepared in the laboratory by the following methods.

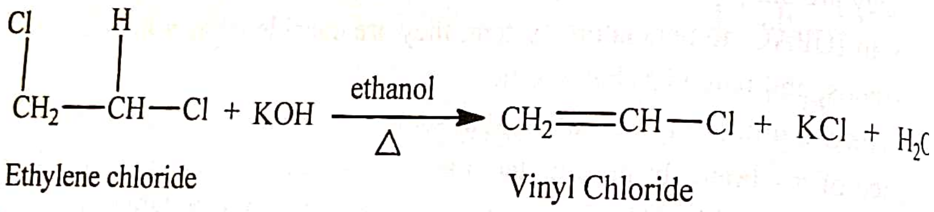
1. From Acetylene:

Hydrogen chloride is added on acetylene in controlled conditions in presen mercuric chloride ($HgCl_2$) as a catalyst to form vinyl chloride.



2. From Ethylene chloride:

Ethylene chloride when heated with alcoholic KOH gives vinyl chloride. (*In reaction elimination of hydrogen and chlorine atoms takes place with the formation o bond between the carbon atoms.)*



$$CH_2(Cl)-CH(H)-Cl + KOH \xrightarrow[\Delta]{\text{ethanol}} CH_2=CH-Cl + KCl + H_2O$$

Ethylene chloride — Vinyl Chloride

Chemical reactions:

Vinyl chloride contains carbon-carbon double bond and a chlorine atom functional groups. The chlorine atom of vinyl chloride is quite inert and it does involve in nucleophilic substitution reaction as easily as the other alkyl halides do.

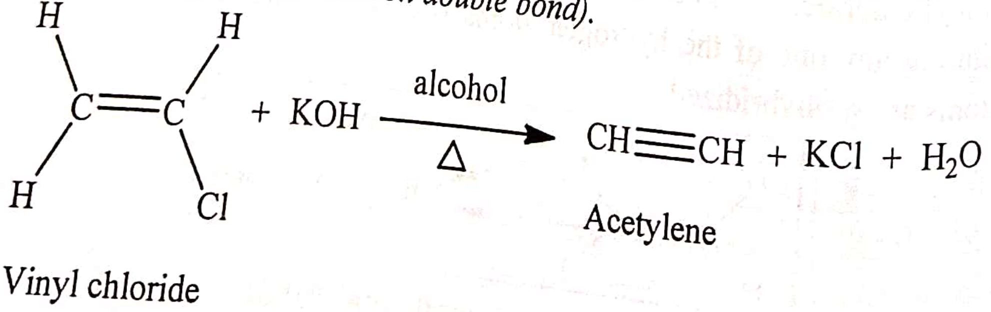
1. Reaction with aqueous KOH:

Vinyl chloride cannot be hydrolyzed by aqueous sodium hydroxide, this unusu reactivity of vinyl chloride with aqueous sodium hydroxide is due to the strong carbo chlorine bond.

$$\underset{\text{Vinyl chloride}}{CH_2=CH-Cl} + NaOH \xrightarrow{\text{Water}} \text{No reaction}$$

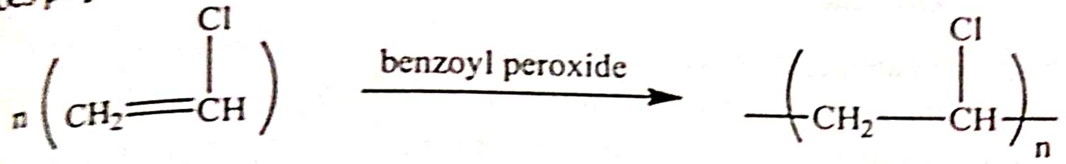
2. Reaction with alcoholic KOH:

When vinyl chloride is treated with alcoholic KOH it gives acetylen *Elimination of hydrogen and chlorine atoms from adjacent carbon atoms takes plac ith the formation of carbon- carbon double bond).*



3. Polymerization reaction:

Vinyl chloride in presence of benzoyl peroxide ($C_6H_5CO—O—COC_6H_5$) undergoes polymerization reaction to form polyvinyl chloride polymer.



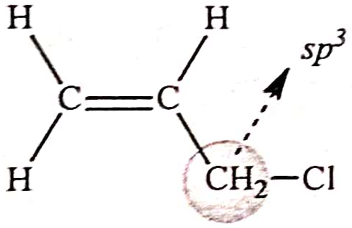
$$n\,(CH_2=CH\text{-}Cl) \xrightarrow{\text{benzoyl peroxide}} -(CH_2-CH(Cl))_n-$$

Vinyl Chloride Polyvinyl Chloride (PVC)

PVC is a very important compound which is used in the manufacturing of synthetic leather goods, plastic pipes and packaging materials.

3.2 Allyl Chloride

Allyl chloride is also known as 3-chloropropene, which is the derivative of propene, obtained by replacing hydrogen atom of $-CH_3$ group of propene. In allyl chloride chlorine atom is attached to *sp3* hybridized carbon atom.



Allyl chloride

Preparation of Allyl chloride:

1. From Propylene:

When propylene is treated with chlorine at high temperature (500°C), it gives allyl chloride. (*Although propylene (alkene) typically reacts with chlorine by addition reaction at room temperature and below, but at higher temperature substitution competes with addition, when the concentration of chlorine is low).*

$$CH_2=CH-CH_2-H + Cl-Cl \xrightarrow{500^\circ C} CH_2=CH-CH_2-Cl + HCl$$

Propylene Allyl chloride

Reactions of Allyl chloride

Allyl chloride shows reactions of both an alkyl halide at chlorine and an alkene at carbon-carbon double bond. Allyl chloride is in fact more reactive than vinyl chloride as well as corresponding alkyl chloride in nucleophilic substitution reaction. The extra reactivity of allyl chloride is due to formation of stable allyl carbocation.

1. Reaction with aqueous KOH

Ally chloride on reaction with aqueous potassium hydroxide (KOH) at room temperature, undergoes substitution reaction to form allyl alcohol.

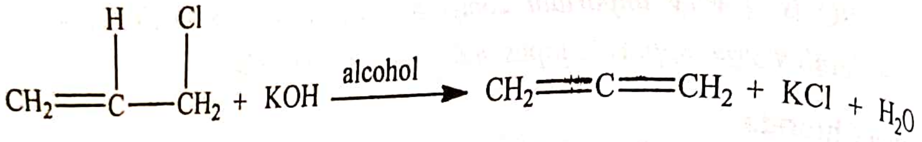
$$CH_2{=}CH{-}CH_2{-}Cl + KOH \xrightarrow{water} CH_2{=}CH{-}CH_2{-}OH +$$

Allyl chloride

Allyl alcohol

2. Reaction with alcoholic KOH

Allyl chloride on reaction with alcoholic potassium hydroxide(KOH) at temperature undergoes elimination reaction with the loss of hydrogen and chlorine f adjacent carbons to form allene.



$$CH_2{=}\overset{H}{C}{-}\overset{Cl}{CH_2} + KOH \xrightarrow{alcohol} CH_2{=}C{=}CH_2 + KCl + H_2O$$

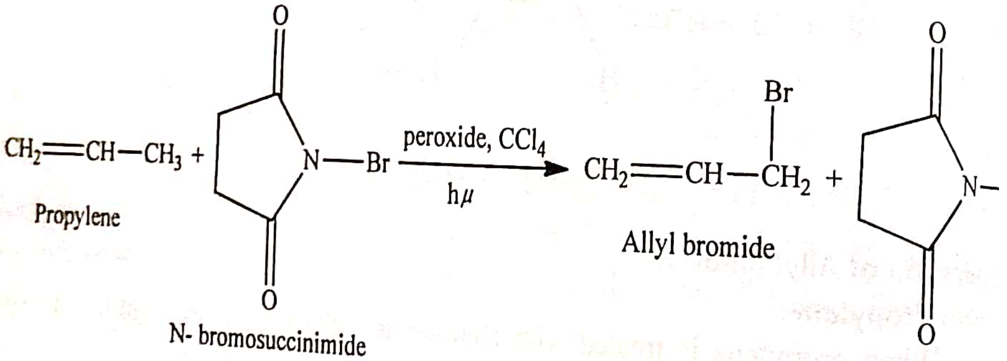
Allyl chloride

1,2-propadiene

3.3 Allyl bromide

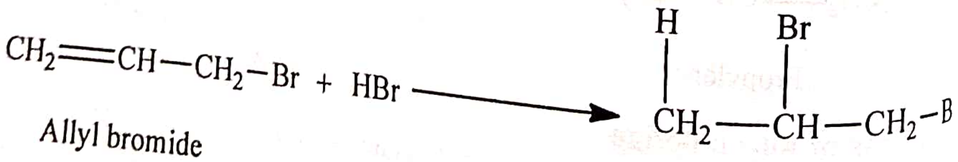
Preparation from Propylene

Propylene when refluxed with N-Bromosuccinimide in presence of benz peroxide, heat or light, gives allyl bromide.



Reaction with HBr

Allyl bromide on reaction with hydrogen bromide(HBr), gives 1, dibromopropane. *The carbon-carbon double bond of allyl bromide shows usual additi reaction in accordance with Markovnikov's rule.*



$$CH_2{=}CH{-}CH_2{-}Br + HBr \longrightarrow \overset{H}{CH_2}{-}\overset{Br}{CH}{-}CH_2{-}B$$

Allyl bromide

1,2-dibromopropane

3.4 Comparative reactivity of vinyl chloride and allyl chloride in nucleophili substitution reaction:

The chlorine atom of vinyl chloride is relatively inert and does not show the usua nucleophilic substitution reactions of alkyl halides. For example, vinyl chloride cannot be hydrolyzed by sodium hydroxide under normal conditions.

$$CH_2{=}CH{-}Cl + NaOH \xrightarrow{\text{Water}} \text{No reaction}$$

Vinyl chloride

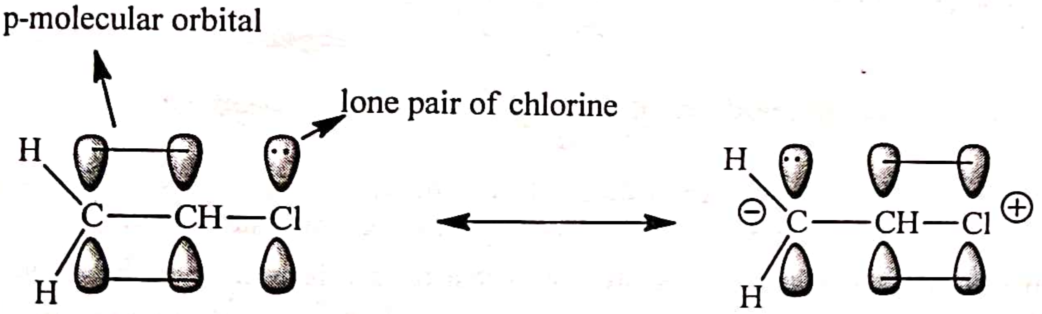
The unusual reactivity of vinyl as compared to allyl chloride in nucleophilic substitution reaction can be explained on the basis of strength of carbon- chlorine bond. This can be explained as follows-

1. Hybridization of carbon bearing chlorine:

In vinyl chloride, chlorine atom is attached to *sp*^{2}hybridized carbon atom whereas in allyl chloride it is attached to *sp*^{3}hybridized carbon atom. The *s*-character in *sp*^{2} hybrid orbital (*s*-character = 33.33%) is larger than in *sp*^{3} hybrid orbital (*s*-character = 25%), and hence *sp*^{2}-orbital is smaller in size which holds bonding electrons strongly than *sp*^{3} - orbital and hence C—Cl bond of vinyl chloride is shorter and stronger than the C—Cl bond of allyl chloride.

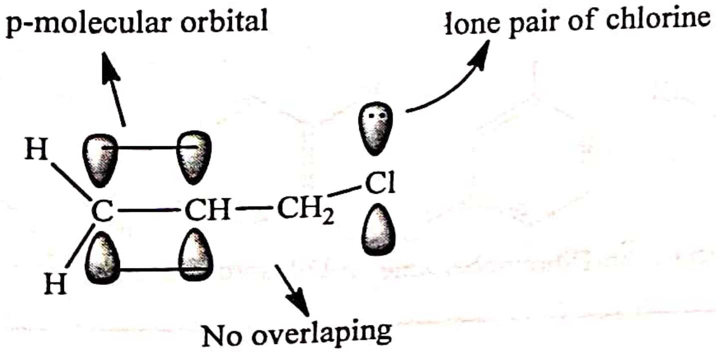
2. Partial double bond character of carbon-chlorine bond:

In vinyl chloride, one *p* orbital of chlorine having lone pair of electrons is parallel to the *p*-orbitals of carbon that are involved in π- bond formation. This *p*-orbital of chlorine overlaps with the *p*- orbitals of carbons, which results in giving carbon-chlorine bond a partial double bond character.



$$CH_2{=}CH{-}\ddot{C}l: \longleftrightarrow \overset{\ominus}{C}H_2{-}CH{=}\overset{\oplus}{C}l:$$

In allyl chloride, *p*orbital of chlorine and *p*-orbitals of carbons forming π- bond are separated by tetrahedral (*sp*^{3}hybridized) carbon atom. Hence overlapping of these *p* orbitals is not possible and carbon-chlorine bond in allyl chloride does not acquire any partial double bond character.



Due to the partial double bond character of carbon-chlorine bond of v chloride, the carbon chlorine bond becomes stronger than carbon chlorine bond of a chloride and this results in less reactivity of vinyl chloride in nucleophilic substitu reaction than allyl chloride. The higher reactivity of allyl chloride in nucleoph substitution reaction is due to the extra stability of allyl carbocation by the resonance.

Resonance stabilization of allyl carbocation

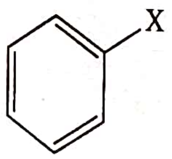
****

B. HALOARENES OR ARYL HALIDES

The halogen derivatives of aromatic hydrocarbons are called aromatic halo compounds. The aromatic halogen compounds may be divided into two grou haloarenes or aryl halides (Ar—X) and arylalkyl halides or aralkyl halides (Ar—CH X).

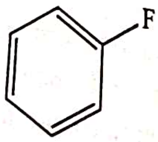
3.5 Haloarenes

Aryl halides are compounds in which halogen atom (X= F, Cl, Br,I) is attacl directlyto the sp^2 hybridized carbon atom of an aromatic ring.

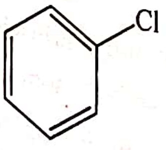


Aryl halide or haloarene
(halogen is attached to sp^2 hybridized carbon of benene ring)

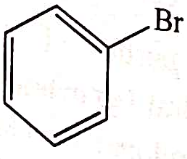
Haloarenes are named by IUPAC system as substitution derivative of benzene. They a named by prefixing the halo word to the word benzene (Halobenzene). They a represented by Ar—X, where, Ar is aryl group.



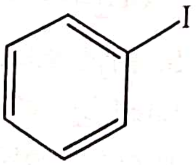
Fluorobenzene



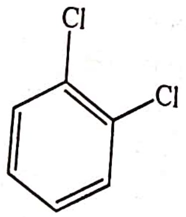
Chlorobenzene



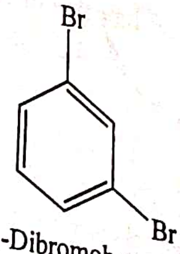
Bromobenzene



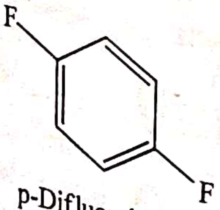
Iodobenzene



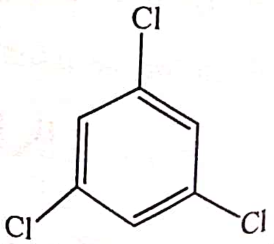
o-Dichlorobenzene



m-Dibromobenzene



p-Difluorobenzene



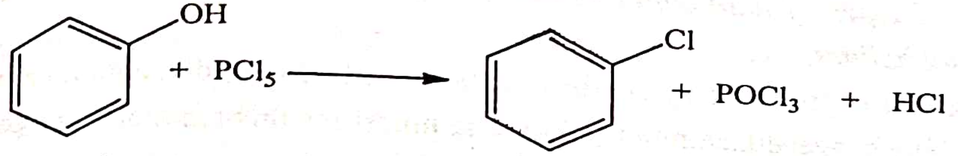
1,3,5-Trichlorobenzene

3.5.1 Chlorobenzene / phenyl chloride (C_6H_5Cl)

Chlorobenzene is a compound in which chlorine atom is attached directly to sp^2hybridized carbon of benzene ring.

Preparation of Chlorobenzene from phenol:

Phenol on heating with PCl_5 gives chlorobenzene.

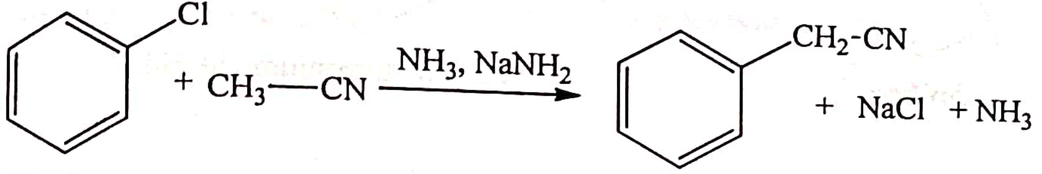


Phenol

Chlorobenzene

Reaction with acetonitrile:

Chlorobenzene on reaction with acetonitrile in the presence of ammonia and sodium amide forms benzyl nitrile (Benzyl cyanide).



Chlorobenzene

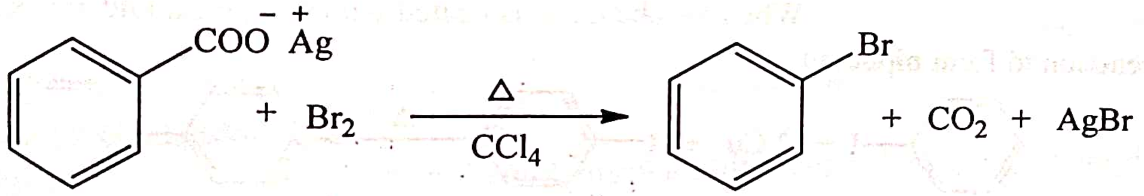
Benzyl nitrile

Bromobenzene /Phenyl bromide (C_6H_5Br)

Bromobenzene is a compound in which bromine atom is attached directly to sp^2hybridized carbon of benzene ring.

Preparation of Bromobenzene from Silver salt of benzoic acid- (Hunsdiecker reaction)

The reaction in which, silver salt of benzoic acidreacts with brominetogive bromobenzene is known as Hunsdiecker reaction.



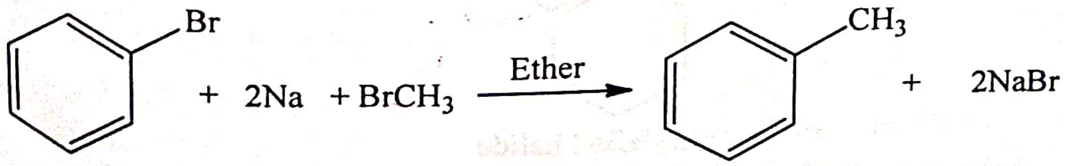
Chlorobenzene

Bromobenzene

Reaction of Bromobenzene- Wurtz-Fittig Reaction

When aryl halide is heated with alkyl halide in presence of sodium in dry etherformsalkylaryl hydrocarbon. This reaction is the Wurtz-Fittig Reaction.

Bromobenzene on heating with methyl bromide in presence of sodium in dry ether forms methyl benzene (toluene).



Bromobenzene

Toluene

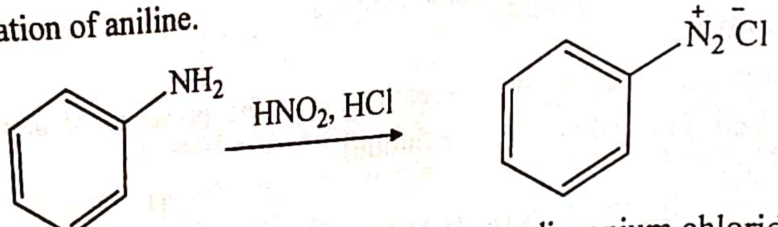
5.2 Iodobenzene /Phenyl iodide (C_6H_5I)

Iodobenzeneis a compound in which iodine atom is attached direct sp^2hybridized carbon of benzene ring.

Preparation of Iodobenzene from Benzene diazonium chloride salt-

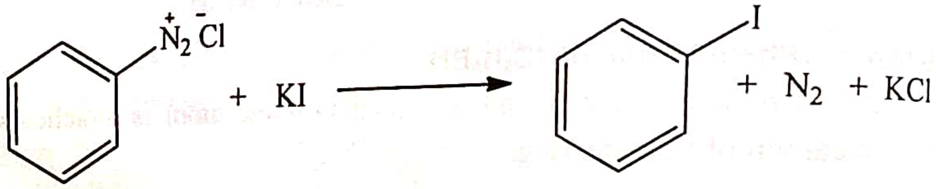
Almost all types of haloarenes are prepared from benzene diazonium sal appropriate metal halides.

Iodobenzene is prepared by the decomposition of benzenediazonium chlori presence of KI. The benzenediazonium chloride required for this reaction is prepare the diazotization of aniline.



Aniline

Benzenediazonium chloride



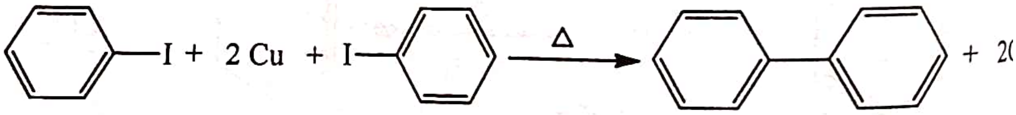
Benzenediazonium chloride

Iodobenzene

Reaction of Iodobenzene

Ullmann Reaction:

When iodobenzene is heated with Copper, it undergoes coupl reaction to form biphenyl.

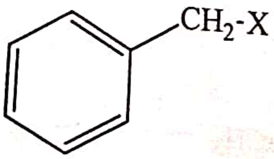


Iodobenzene

Biphenyl

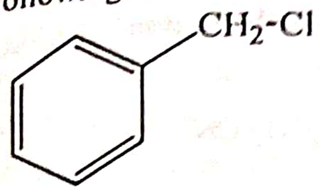
3.6 Arylalkyl halide or Aralkyl halide (Ar—CH_2—X):

Aralkyl halides are compounds in which halogen atom is attached to a carb (sp^3 hybridized) of the side chain of aromatic ring. Arylalkyl halides are exactly similar alkyl halide and shows considerably different chemical properties from aryl halides.

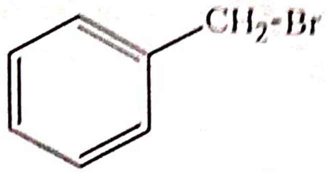


Arylalkyl halide
(halogen is attached to sp^3 hybridized carbon of side chain of benene ring)

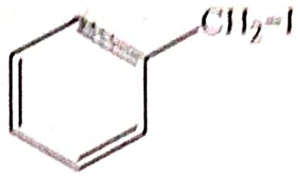
Following are some simple aralkyl halides derived from toluene.



Benzyl chloride



Benzyl bromide



Benzyl iodide

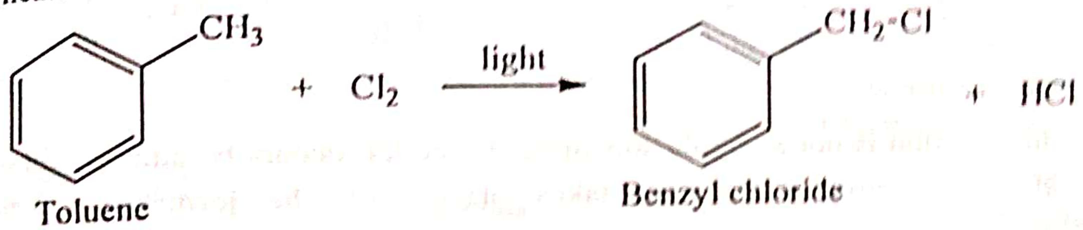
3.6.1 Benzyl chloride ($C_6H_5CH_2Cl$):

Benzyl chloride is a compound in which chlorine atom is attached to side chain (sp^3 hybridized carbon) of benzene ring.

Synthesis of Benzyl chloride:

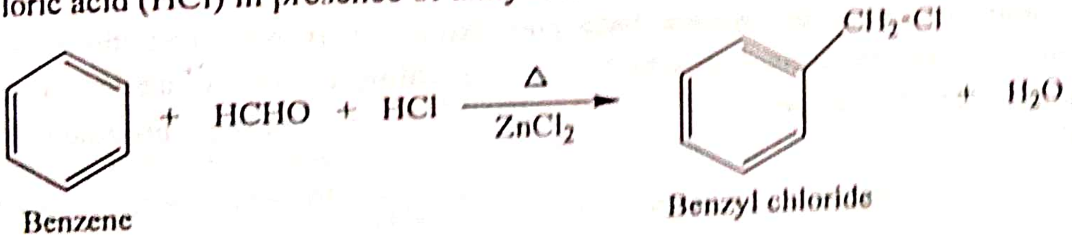
1. From Toluene

Benzyl chloride is prepared by reaction of toluene with chlorine in presence of light or heat.



2. From Benzene

Benzyl chloride is prepared by heating benzene with formaldehyde and hydrochloric acid (HCl) in presence of anhydrous Zinc chloride ($ZnCl_2$).

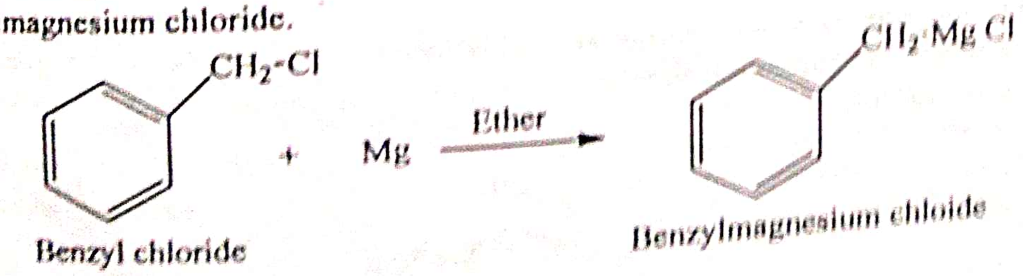


Reactions of Benzyl chloride:

Benzyl chloride shows structural similarity with allyl chloride and thus benzyl chloride undergoes nucleophilic substitution reactions at chlorine atom as readily as allylchloride.

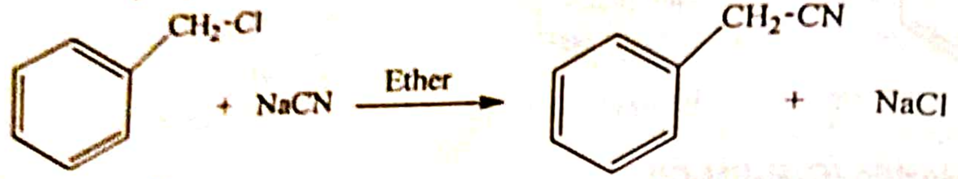
1. Reaction with Magnesium metal (Mg), (Formation of Grignard Reagent)

Benzyl chloride when reacted with magnesium metal in ether, it gives benzylmagnesium chloride.



2. Reaction with NaCN

Benzyl chloride when reacted with aq. NaCN, undergoes substitution reaction with formation of benzyl cyanide.

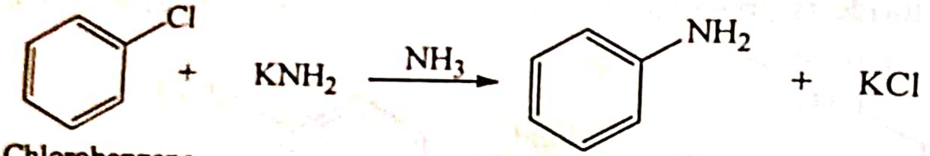


Benzyl chloride

Benzyl cyanide

3.6.2 Benzyne Intermediate Mechanism

In the nucleophilic substitution reaction of chlorobenzene, it does not unde direct displacement of chlorine atom by nucleophile. When chlorobenzene is treated w strong base like potassium amide (KNH_2) it gives aniline.



Chlorobenzene

Aniline

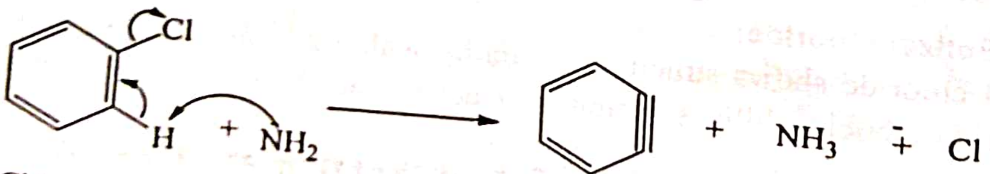
This reaction is not a simple substitution reaction occurs by addition-eliminati but an elimination-addition reaction takes place with the formation of benzyn intermediate.

Mechanism of this reaction involves following steps-

1. Elimination step:

Amide ion is a very strong base and extracts a proton from the o-carbon o chlorobenzene forming carbanion, which loses the chlorine atom as leaving group. Thi brings about dehydrohalogenation with the formation of unstable intermediate calle benzyne.

$$KNH_2 \rightleftharpoons \overset{+}{K} + \overset{-}{N}H_2$$

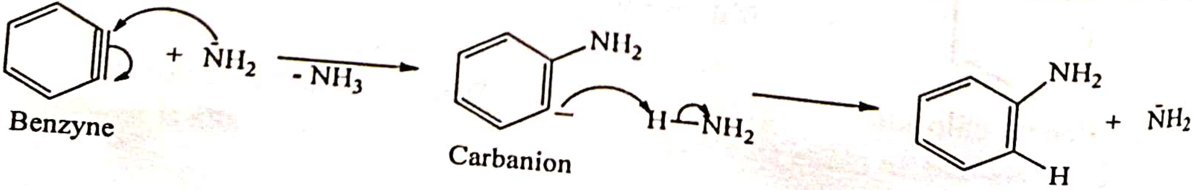


Chlorobenzene

Benzyne

2. Addition step:

Amide ion acts as a nucleophile and adds to one of the carbons of triple bond forming carbanion. This carbanion then extract proton from the ammonia which is used as a solvent, gives aniline.

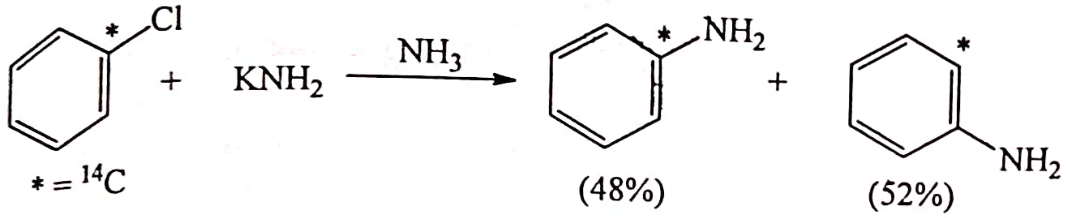


Benzyne

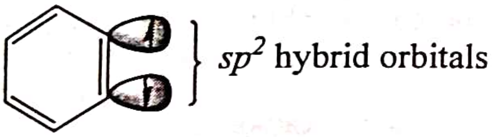
Carbanion

Aniline

This reaction, that involves the formation of benzyne intermediate, was explained by John D. Roberts in 1953 on the basis of isotope labeling experiment. He prepared a chlorobenzene in which chlorine bearing carbon is the ^{14}C isotope of carbon. Reaction of this chlorobenzene with KNH_2 in ammonia gives aniline containing almost exactly half of ^{14}C label at C-1 and half at C-2.



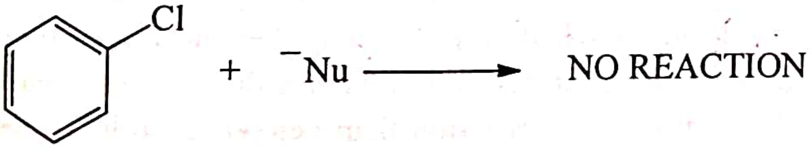
The triple bond of benzyne is different than the triple bond of alkyne. One π-bond of the triple bond of benzyne is a part of delocalized π-electron system, where *p*-atomic orbitals of carbon are involved. The second π-bond is formed by the overlapping of sp^2 hybrid orbitals of carbons externally and not by *p-p* overlapping. This π-bond is relatively weak because the involved sp^2 orbitals are not in proper orientation for effective overlapping. Also ring restricts linearity of C—C≡C—C unit and that results in the formation of weak π-bond. Benzyne is strained and highly reactive intermediate.



Benzyne

3.6.3 Comparative reactivity of chlorobenzene and benzyl chloride in nucleophilic substitution reaction:

The chlorine atom of chlorobenzene is relatively inert and it does not show the usual nucleophilic substitution reactions.However benzyl chloride shows nucleophilic substitution reactions as readily as allyl chloride.



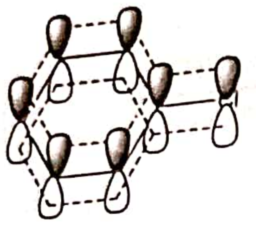
The unusual reactivity of vinyl as compare to allyl chloride in nucleophilic substitution reaction can be explained on the basis of strength of carbon- chlorine bond. This can be explained as follows-

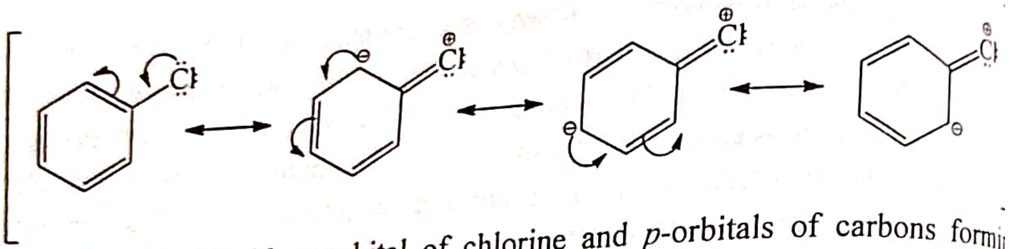
1. Hybridization of carbon bearing chlorine-

In chlorobenzene chlorine atom is attached to sp^2 hybridized carbon atom whereas in benzyl chloride to sp^3hybridized carbon atom. The*s*-character in sp^2 hybrid orbital (*s*-character = 33.33%) is larger than in sp^3 hybrid orbital (*s*- character = 25%), and hence sp^2-orbital is smaller in size than sp^3 orbital and therefore, C—Cl bond of chlorobenzene is shorter and stronger than the C—Cl bond of benzyl chloride.

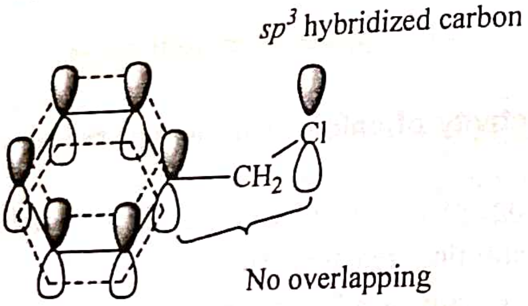
2. Partial double bond character of carbon-chlorine bond-

In chlorobenzene one *p* orbital of chlorine having lone pair of electrons is p
to *p*- orbitals of carbons forming π- bond of the ring. This *p*-orbital of chlorine o
with *p*- orbitals of carbons which results in giving carbon-chlorine bond a partial
bond character.

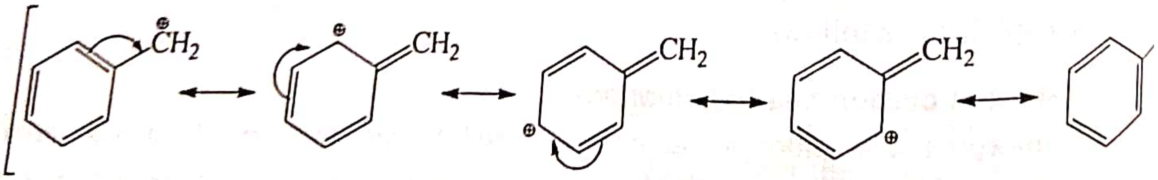




In benzyl chloride *p*-orbital of chlorine and *p*-orbitals of carbons formi electron systemare separated by tetrahedral (sp^3hybridized) carbon atom. I overlapping of these *p*orbitals is not possible and carbon-chlorine bond in allyl chl does not acquire partial double bond character.



Due to the partial double bond character of carbon-chlorine bond chlorobenzene, the carbon-chlorine bond of chlorobenzene becomes more stronger carbon-chlorine bond of benzyl chloride and this results in less reactivity chlorobenzene in nucleophilic substitution reaction than benzyl chloride. Further hi reactivity of benzyl chloride in nucleophilic substitution reaction is due to the e stability of benzyl carbocation by the resonance.



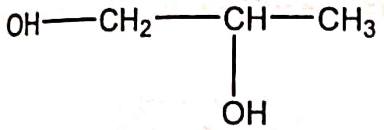
* * * *

C. POLYHYDRIC ALCOHOLS

The hydroxy compounds in which more than one hydroxyl groups per molecule are present are called *polyhydric alcohols.* Polyhydric alcohols are classified on the basis of number of –OH groups present in the molecule. The compound containing two –OH groups are ***Dihydric alcohols*** or ***Diols***. Those containing three –OH groups are called ***Trihydric alcohols*** or ***Triols.***

3.7 Dihydric Alcohols or Diols

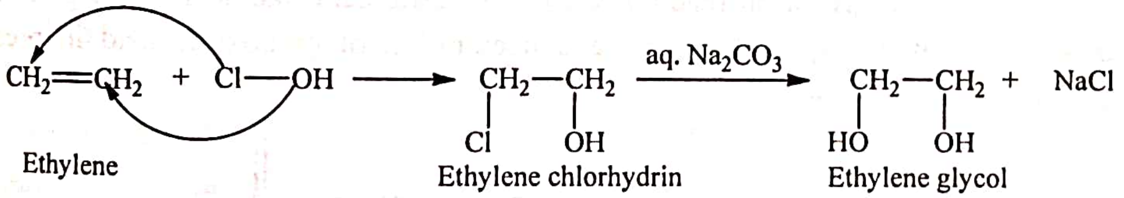
Dihydric alcohol is the compound containing two –OH groups. The dihydric alcohol is named as **Diol** according to IUPAC system and glycol in common name system. They are classified in accordance with the relative position of the two –OH groups. *For example,* 1, 2-glycols, 1,3-glycols and so on.

Formula	Common Name	IUPAC Name
$OH-CH_2-CH_2-OH$	*Ethylene glycol*	*1,2-ethanediol*
 $OH-CH_2-CH(OH)-CH_3$	*Propylene glycol*	*1,2-proanediol*
$OH-CH_2-CH_2-CH_2-OH$	*Trimethylene glycol*	*1,3-propanediol*

Synthesis of Ethylene Glycol (Diol)

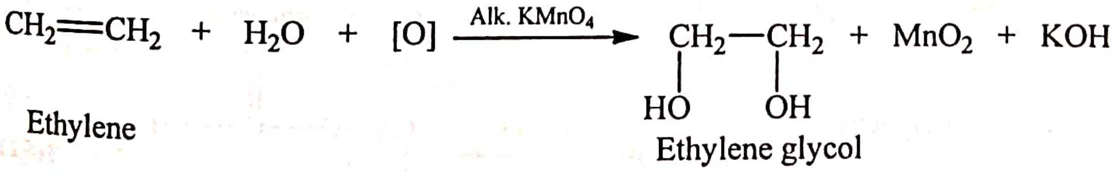
1. From Ethylene

i) Ethylene on action with hypochlorous acid results in formation of chlorohydrin which on further hydrolysis gives ethylene glycol.



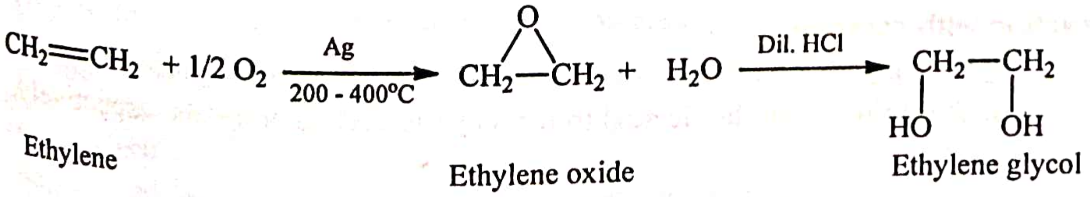
$$CH_2{=}CH_2 + Cl-OH \longrightarrow CH_2(Cl)-CH_2(OH) \xrightarrow{aq.\ Na_2CO_3} CH_2(HO)-CH_2(OH) + NaCl$$

ii) Ethylene on hydroxylation with potassium permanganate ($KMnO_4$) or osmium tetra oxide (OsO_4) at room temperature forms ethylene glycol.



$$CH_2{=}CH_2 + H_2O + [O] \xrightarrow{Alk.\ KMnO_4} CH_2(HO)-CH_2(OH) + MnO_2 + KOH$$

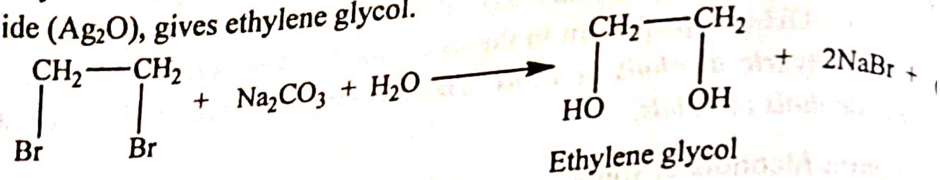
iii) Ethylene is first converted into ethylene oxide by passing ethylene and air over heated silver under pressure. Ethylene oxide is then hydrolysed by dilute HCl to give ethylene glycol.



$$CH_2{=}CH_2 + 1/2\,O_2 \xrightarrow[200-400^\circ C]{Ag} CH_2-CH_2\ (O) + H_2O \xrightarrow{Dil.\ HCl} CH_2(HO)-CH_2(OH)$$

2. From Ethylene bromide

Ethylene bromide on heating with aqueous sodium carbonate (Na_2CO_3) or m silver oxide (Ag_2O), gives ethylene glycol.



Ethylene bromide

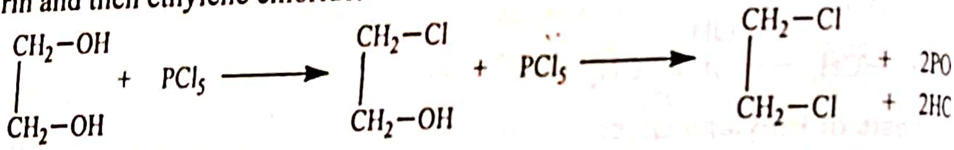
Ethylene glycol

Reactions of Ethylene glycol

Ethylene glycol contains two primary alcoholic groups. Hence it shows gen chemical reactions of primary alcohol twice over. Generally, second –OH group is involved in the reaction until the first –OH group is completely reacted. Some impor reactions of ethylene glycol are given below.

1. Reaction with Phosphorous pentachloride (PCl_5)

Ethylene glycol on reaction with phosphorous pentachloride (PCl_5) for chlorohydrin and then ethylene chloride.



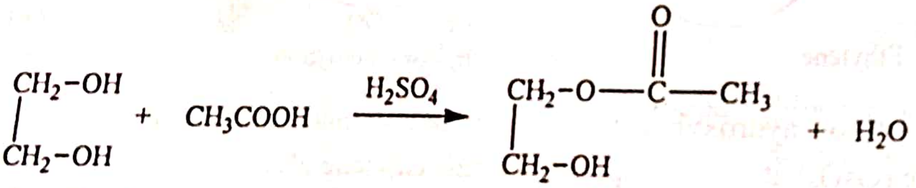
Ethylene glycol

Chlorohydrin

Ethylene chloride

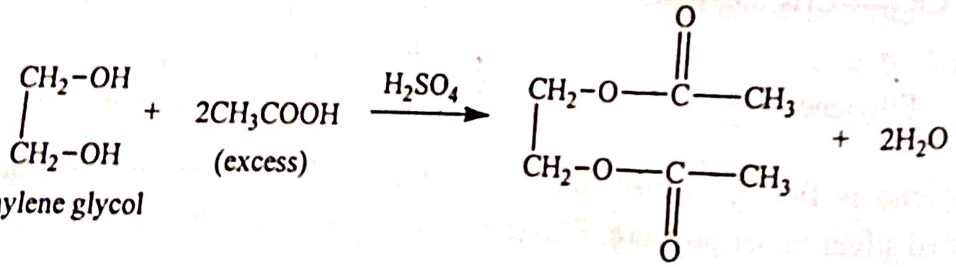
2. Reaction with carboxylic acid

Ethylene glycol on reaction with carboxylic acid like acetic acid gives mono diesters depending upon the relative concentration of carboxylic acid in presence catalytic sulphuric acid.



Ethylene glycol

Glycol monoacetate

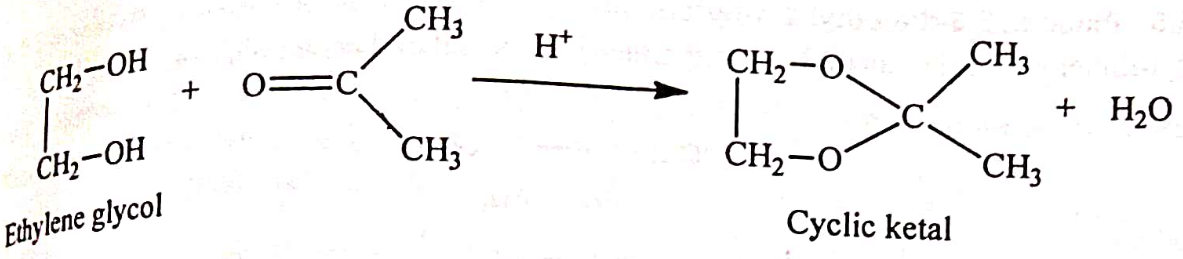


Ethylene glycol

Glycol diacetate

Reaction with acetone

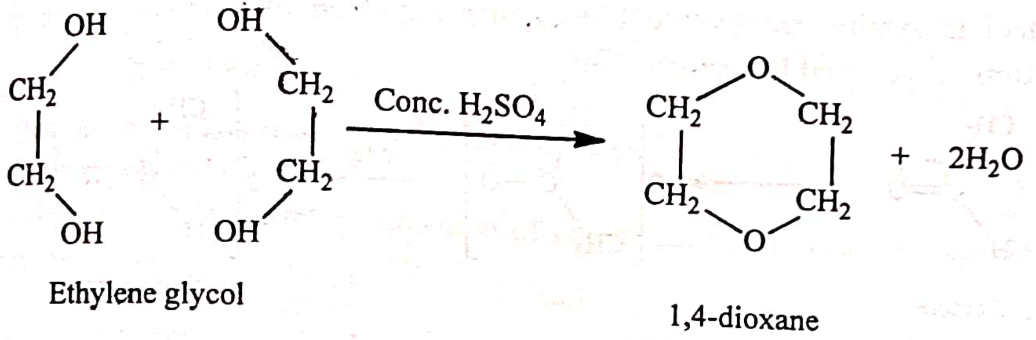
Ethylene glycol condenses with aldehydes or ketones in presence of catalyst. neral acid or p-toluene sulphonic acid to form cyclic acetals or ketals respectively.


Ethylene glycol

Cyclic ketal

4. Dehydration reaction

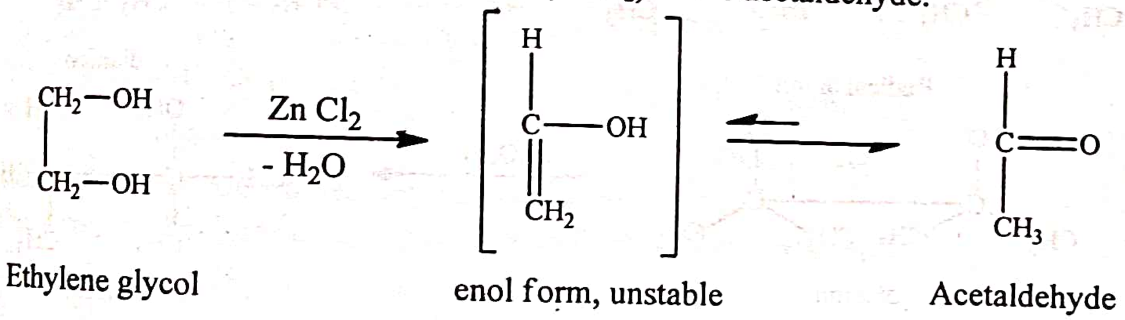
Ethylene glycol undergoes dehydration in presence of concentrated sulphuric acid to form dioxane which is used as an industrial solvent.


Ethylene glycol

1,4-dioxane

ii) By Zinc chloride ($ZnCl_2$)

Ethylene glycol when heated with Zinc chloride ($ZnCl_2$) forms acetaldehyde.


Ethylene glycol

enol form, unstable

Acetaldehyde

iii) By phosphoric acid

When ethylene glycol is heated with phosphoric acid it gives diethylene glycol with the elimination of water molecule.

$$HO-CH_2-CH_2-OH + HO-CH_2-CH_2-OH \xrightarrow{H_3PO_4} HO-CH_2-CH_2-O-CH_2-CH_2-OH + H_2O$$

Ethylene glycol

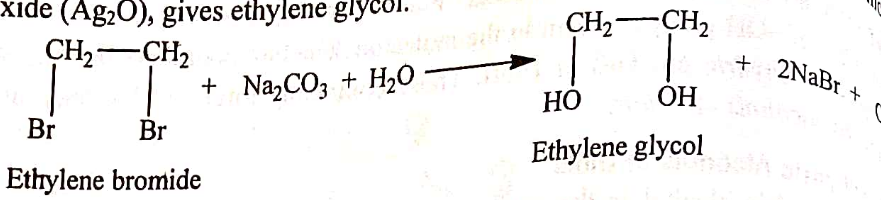
Diethylene glycol

Uses of ethylene glycol

1. Under the name of *Pristone* it is used as anti-freeze in automobile radiators because it forms low freezing mixture with water.
2. To prevent deposition and formation of ice on aeroplane wings.
3. In the manufacturing of low freezing dynamite
4. As a solvent and preservative
5. As a dielectric in electrical condenser
6. As a starting material for number of important compounds.

2. From Ethylene bromide

Ethylene bromide on heating with aqueous sodium carbonate (Na_2CO_3) or m silver oxide (Ag_2O), gives ethylene glycol.



$$\begin{array}{c}CH_2-CH_2\\ |\qquad\quad |\\ Br\qquad Br\end{array} + Na_2CO_3 + H_2O \longrightarrow \begin{array}{c}CH_2-CH_2\\ |\qquad\quad |\\ HO\qquad OH\end{array} + 2NaBr +$$

Ethylene bromide

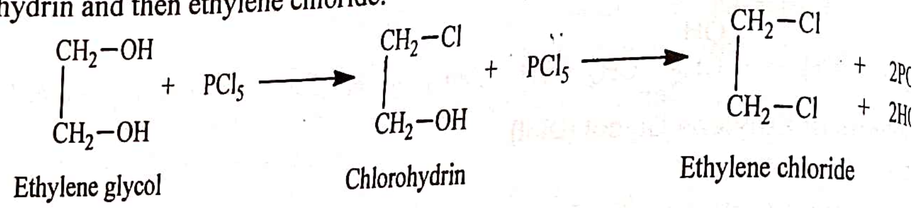
Ethylene glycol

Reactions of Ethylene glycol

Ethylene glycol contains two primary alcoholic groups. Hence it shows gene chemical reactions of primary alcohol twice over. Generally, second –OH group is involved in the reaction until the first –OH group is completely reacted. Some import reactions of ethylene glycol are given below.

1. Reaction with Phosphorous pentachloride (PCl_5)

Ethylene glycol on reaction with phosphorous pentachloride (PCl_5) for chlorohydrin and then ethylene chloride.



$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + PCl_5 \longrightarrow \begin{array}{l}CH_2-Cl\\ |\\ CH_2-OH\end{array} + PCl_5 \longrightarrow \begin{array}{l}CH_2-Cl\\ |\\ CH_2-Cl\end{array} \begin{array}{l}+\ 2P\\ \\ +\ 2H\end{array}$$

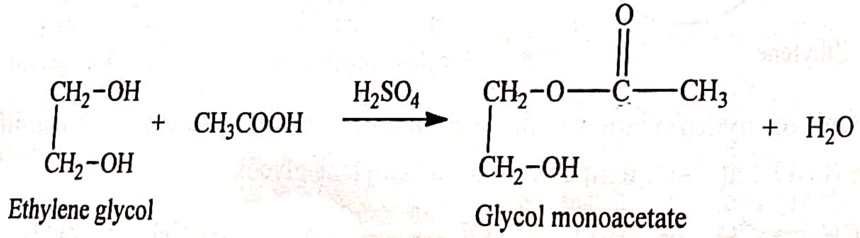
Ethylene glycol

Chlorohydrin

Ethylene chloride

2. Reaction with carboxylic acid

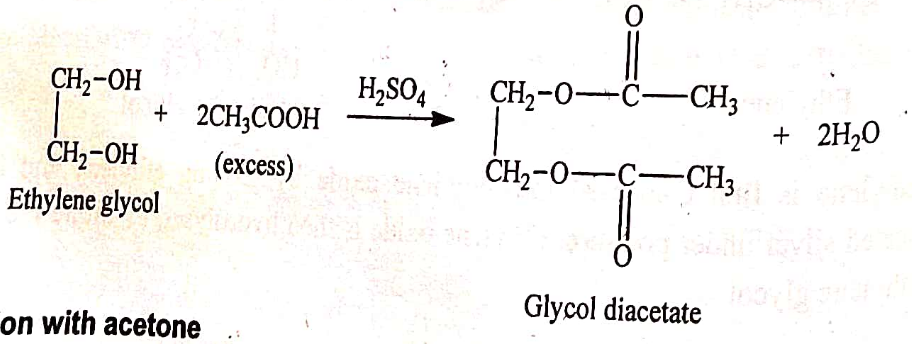
Ethylene glycol on reaction with carboxylic acid like acetic acid gives mono diesters depending upon the relative concentration of carboxylic acid in presence catalytic sulphuric acid.



$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + CH_3COOH \xrightarrow{H_2SO_4} \begin{array}{l}CH_2-O-\overset{\overset{\large O}{\|}}{C}-CH_3\\ |\\ CH_2-OH\end{array} + H_2O$$

Ethylene glycol

Glycol monoacetate



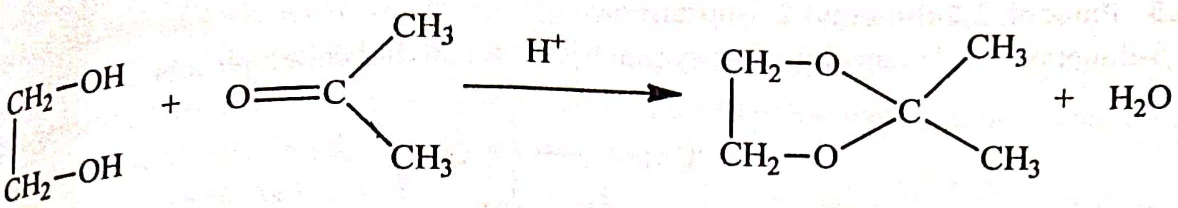
$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + \begin{array}{c}2CH_3COOH\\ \text{(excess)}\end{array} \xrightarrow{H_2SO_4} \begin{array}{l}CH_2-O-\overset{\overset{\large O}{\|}}{C}-CH_3\\ |\\ CH_2-O-\underset{\underset{\large O}{\|}}{C}-CH_3\end{array} + 2H_2O$$

Ethylene glycol

Glycol diacetate

3. Reaction with acetone

Ethylene glycol condenses with aldehydes or ketones in presence of catalys mineral acid or p-toluene sulphonic acid to form cyclic acetals or ketals respectively.

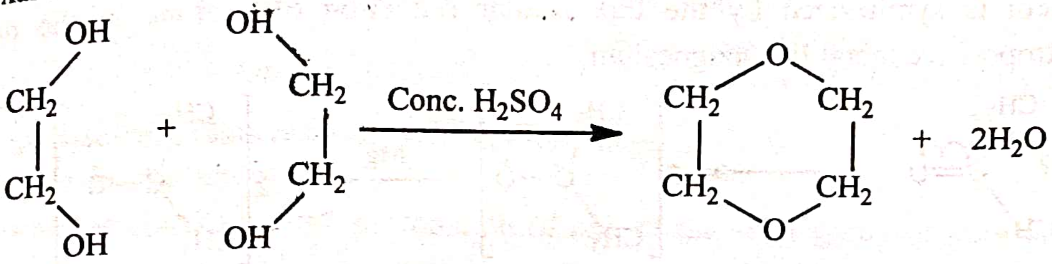


Ethylene glycol

Cyclic ketal

4. Dehydration reaction

Ethylene glycol undergoes dehydration in presence of concentrated sulphuric acid to form dioxane which is used as an industrial solvent.

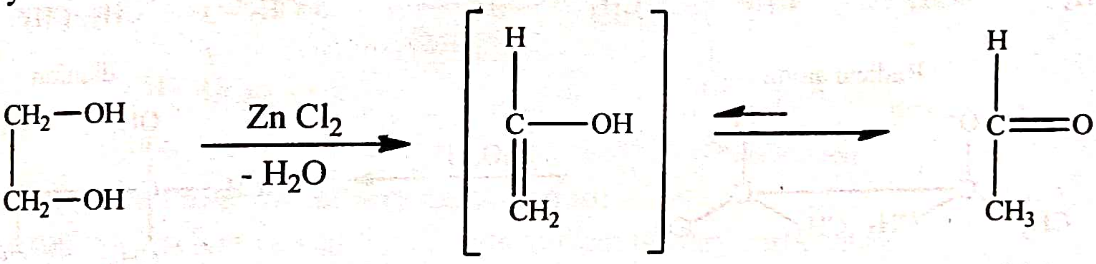


Ethylene glycol

1,4-dioxane

ii) By Zinc chloride ($ZnCl_2$)

Ethylene glycol when heated with Zinc chloride ($ZnCl_2$) forms acetaldehyde.



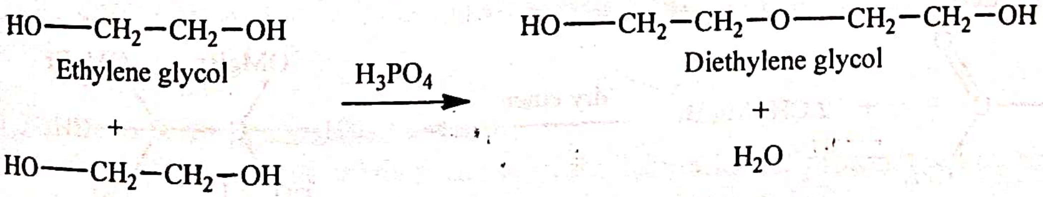
Ethylene glycol

enol form, unstable

Acetaldehyde

iii) By phosphoric acid

When ethylene glycol is heated with phosphoric acid it gives diethylene glycol with the elimination of water molecule.



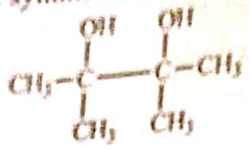
$$\underset{\text{Ethylene glycol}}{HO-CH_2-CH_2-OH} + HO-CH_2-CH_2-OH \xrightarrow{H_3PO_4} \underset{\text{Diethylene glycol}}{HO-CH_2-CH_2-O-CH_2-CH_2-OH} + H_2O$$

Uses of ethylene glycol

1. Under the name of *Pristone* it is used as anti-freeze in automobile radiators because it forms low freezing mixture with water.
2. To prevent deposition and formation of ice on aeroplane wings.
3. In the manufacturing of low freezing dynamite
4. As a solvent and preservative
5. As a dielectric in electrical condenser
6. As a starting material for number of important compounds.

3.8 Pinacol, 2,3-dimethyl-2,3-butanediol

2,3-dimethyl-2,3-butanediol is the symmetrical vicinal diol called pinacol.

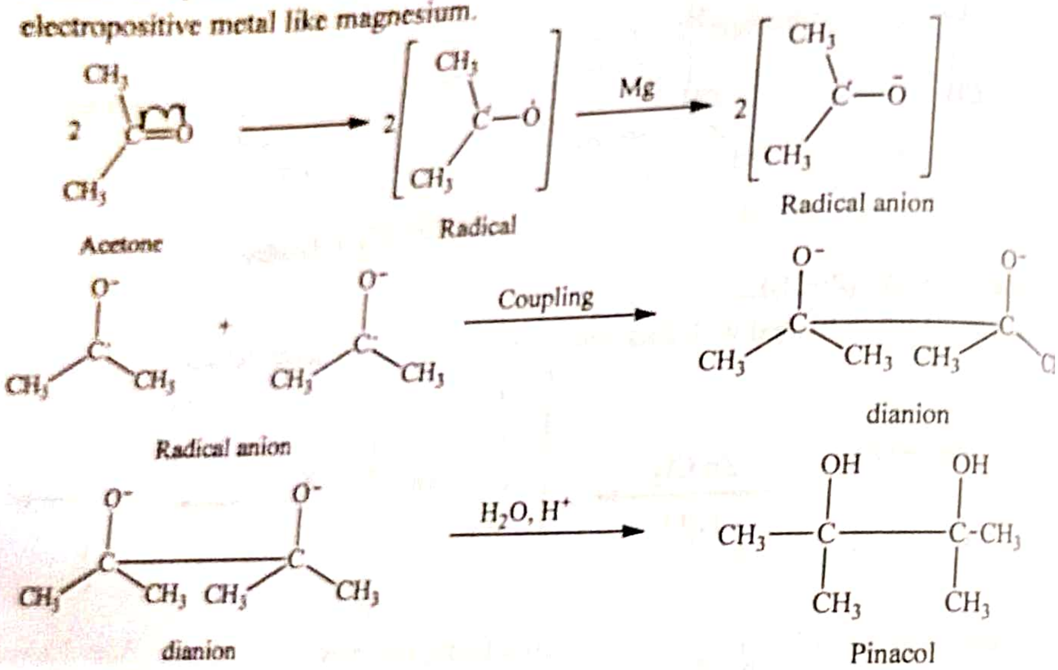


Pinacol

Synthesis of pinacol

1. From Acetone

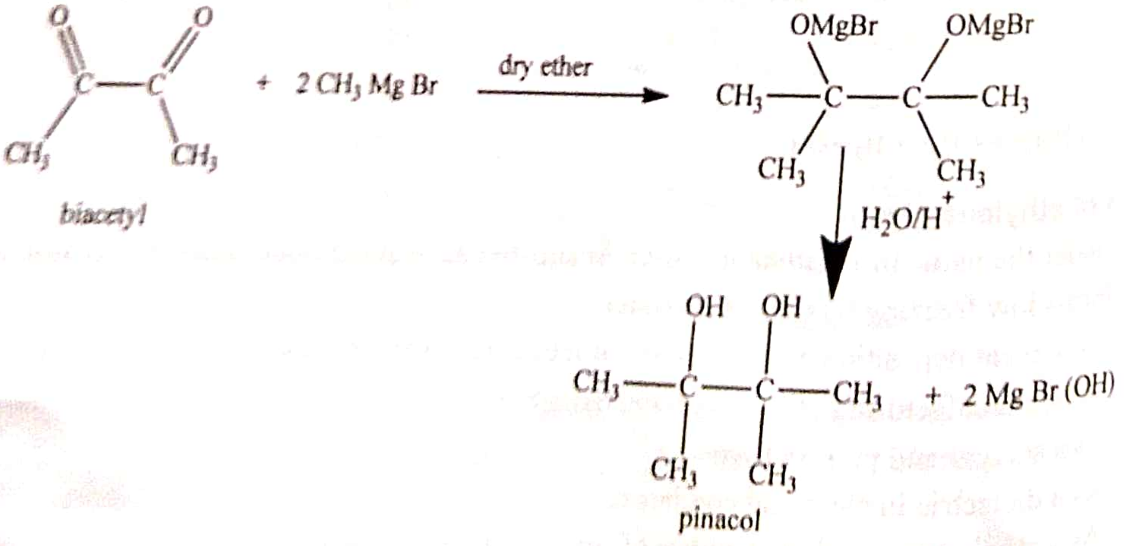
Pinacol is synthesized by the bimolecular reduction of acetone in the presenc electropositive metal like magnesium.



2. From α-diketone

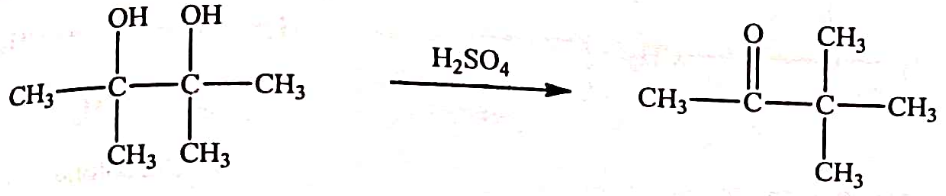
Pinacol is synthesized by the action of Grignard reagent on α-diketone.

When methyl magnesium bromide is treated with biacetyl followed by hydrolysi *it gives pinacol.*



3.9 Pinacol- Pinacolone Rearrangement Reaction:

Pinacol as well as other 1,2-diols on treatment with an acid undergo 1,2-rearrangement of an alkyl group to give methyl t-butyl ketone called pinacolone. This reaction is called as pinacol-pinacolone rearrangement.



$$CH_3-C(OH)(CH_3)-C(OH)(CH_3)-CH_3 \xrightarrow{H_2SO_4} CH_3-C(=O)-C(CH_3)(CH_3)-CH_3$$

2,3-dimethyl-2,3-butandiol
(Pinacol)

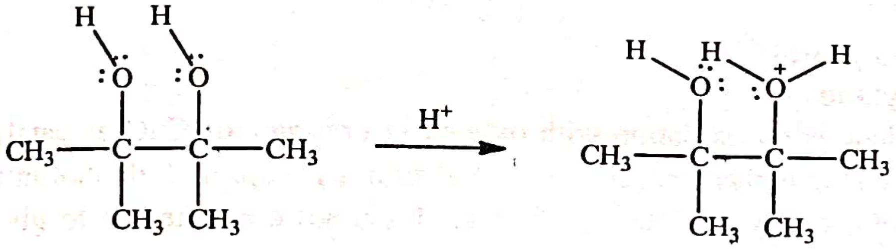
3,3-dimethyl-2-butanone
(Pinacolone)

Mechanism:

The mechanism of this reaction involves four steps-

Step 1: Protonation of pinacol:

The reaction starts with the protonation of one of the –OH group of pinacol to from oxonium ion.



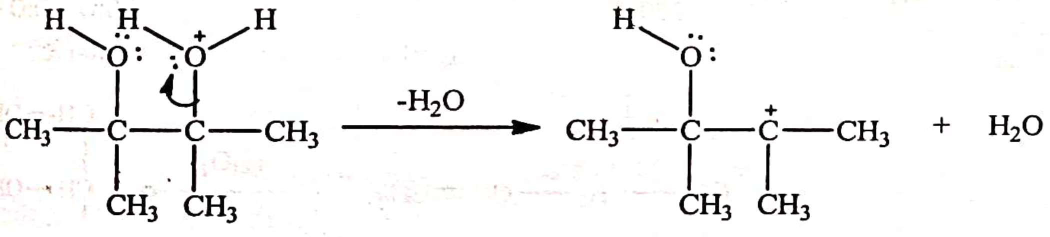
$$CH_3-C(OH)(CH_3)-C(OH)(CH_3)-CH_3 \xrightarrow{H^+} CH_3-C(OH)(CH_3)-C(\overset{+}{O}H_2)(CH_3)-CH_3$$

Pinacol

Oxonium ion

Step 2 : Loss of proton to form tertiary carbocation:

The oxonium ion loses a water molecule to form tertiary carbocation.



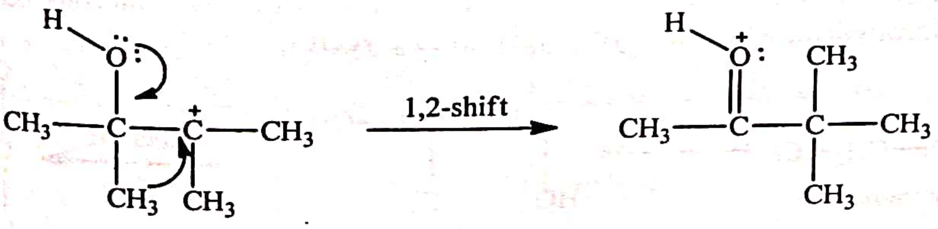
$$CH_3-C(OH)(CH_3)-C(\overset{+}{O}H_2)(CH_3)-CH_3 \xrightarrow{-H_2O} CH_3-C(OH)(CH_3)-\overset{+}{C}(CH_3)-CH_3 + H_2O$$

Oxonium ion

tertiary carbocation

Step 3 : 1,2-shift to form protonated ketone:

1,2-shift of methyl group takes place with the formation of protonated ketone, the driving force for the shift is the formation of more stable oxonium ion.



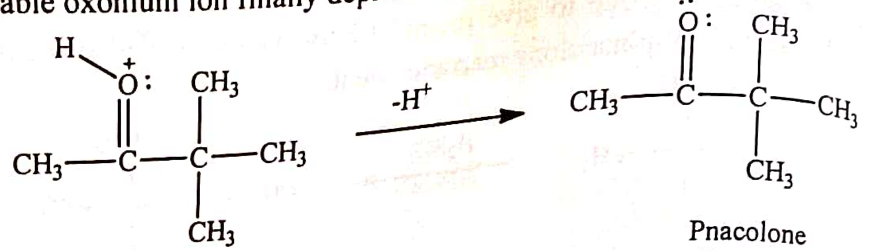
$$CH_3-C(OH)(CH_3)-\overset{+}{C}(CH_3)-CH_3 \xrightarrow{\text{1,2-shift}} CH_3-C(=\overset{+}{O}H)-C(CH_3)(CH_3)-CH_3$$

tertiary carbocation

stable oxonium ion
(protonated ketone)

Step 4: formation of pinacolone:

Stable oxonium ion finally deprotonates to form pinacolone.

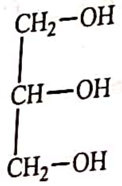


stable oxonium ion

Pnacolone (ketone)

3.10 Glycerol / Glycerine/ 1, 2,3-propanetriol

Glycerol is the important member of trihydric alcohol, in which three groups are present on adjacent carbon.

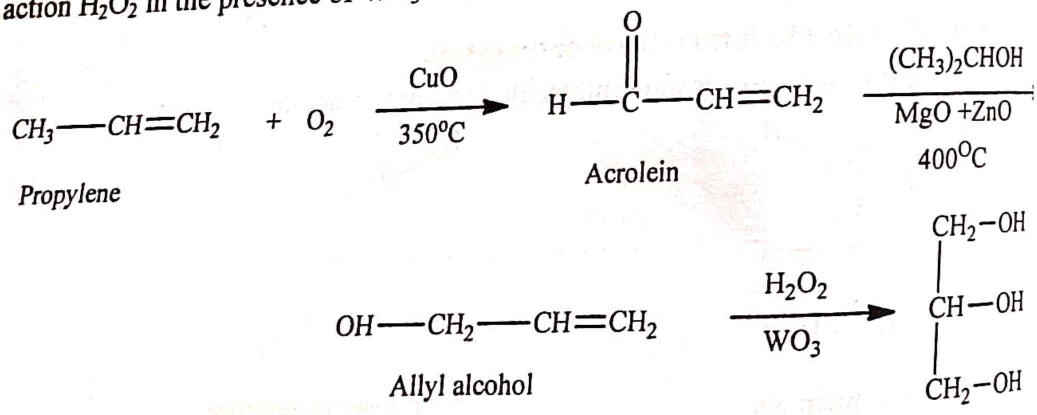


$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Synthesis of Glycerol

1. From Propylene

Propylene is on oxidation with oxygen in presence of CuO as catalyst at 3 forms acrolein. This is then reduced to allyl alcohol by isopropyl alcohol in the pres of (MgO + ZnO) catalyst at 400°C. Then allyl alcohol converted in to glycerol b action H_2O_2 in the presence of WO_3 as a catalyst.



Propylene

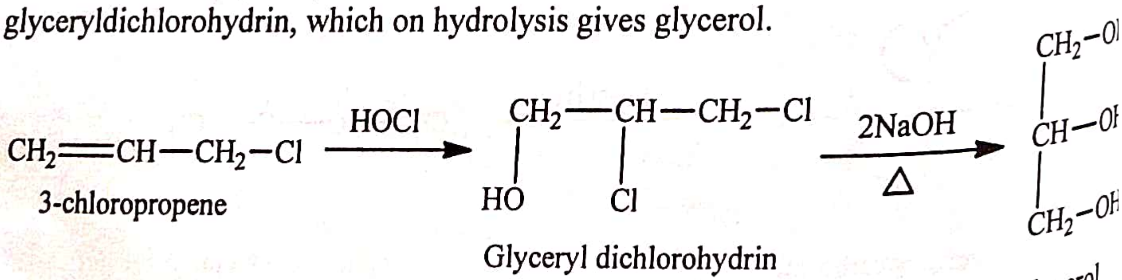
Acrolein

Allyl alcohol

Glycerol

2. From 3-chloropropene

3-chloroprpene (allyl chloride), which is treated with hypochlorous acid to fo glyceryldichlorohydrin, which on hydrolysis gives glycerol.



3-chloropropene

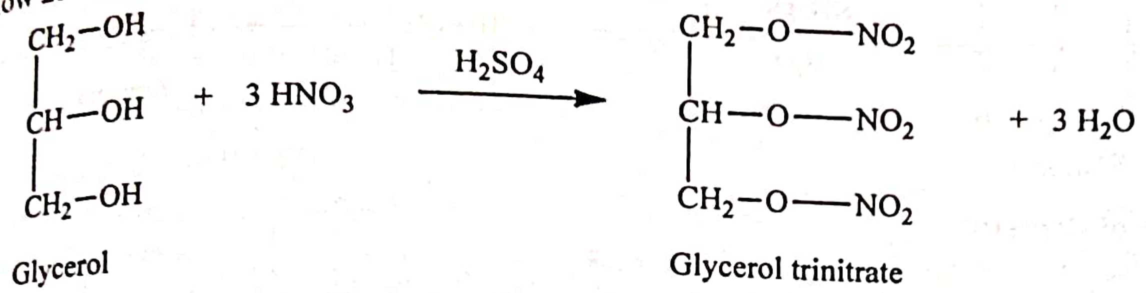
Glyceryl dichlorohydrin

Glycerol

Reactions of Glycerol

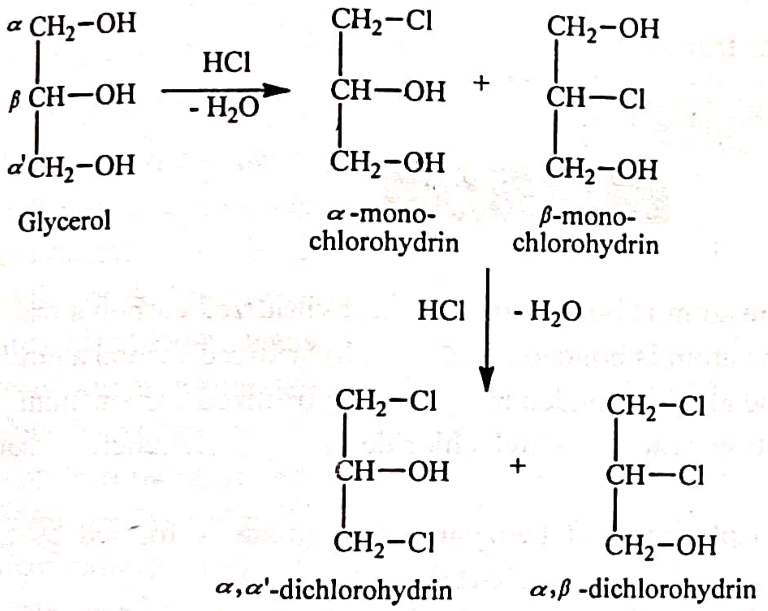
1. Reaction with Nitric acid (HNO_3)

Glycerol on reaction with nitric acid in presence of sulphuric acid at temperature below 25°C gives glycerol trinitrate (nitroglycerine).



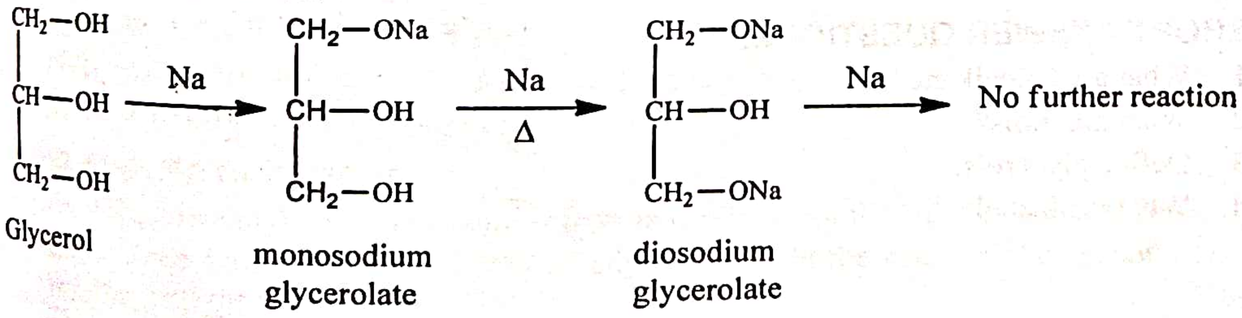
2. Reaction with Hydrochloric acid (HCl)

Hydrogen chloride when passed into glycerol at 110°C, a mixture of α- and β-mono chlorohydrin is obtained. On further action of hydrogen chloride, glycerol α, α'-dichlorohydrin and glycerol α, β-dichlorohydrin are obtained.



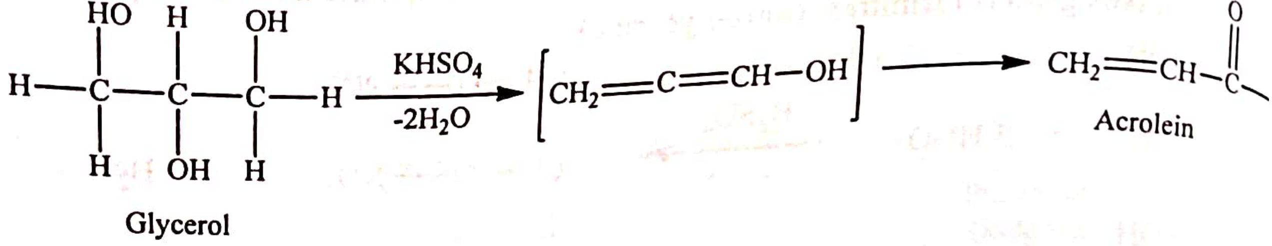
3. Reaction with Sodium metal (Na)

When glycerol is treated with sodium at room temperature, one primary hydroxyl group is reacted to form monosodium glycerolate. At higher temperature the second primary hydroxyl group reacts to from disodium glycerolate. Secondary hydroxyl group, however never reacts at all.



4. Dehydration using potassium hydrogen sulphate ($KHSO_4$)

When glycerol is heated alone or with potassium hydrogen sulphate it for acrolein (acrylic aldehyde).



Uses of Glycerol:

1. Used as a sweetening agent in beverages
2. Used in the preparation of high-class toilet soaps and cosmetics
3. Used for preparation of dynamite in the form of trinitroglycerin
4. Used in resin industry
5. Used in shoe polish and stamp colour
6. Used as antifreeze in automobile radiators
7. Used as a preservative for fruits

****

EXERCISE

FILL IN THE BLANKS:

1. In vinyl chloride, chlorine atom is bonded to .... hybridized carbon atom.
2. In alkyl chloride, chlorine atom is bonded to .... hybridized carbon atom.
3. In vinyl chloride, chlorine atom is bonded to .... hybridized carbon atom.
4. In nucleophilic substitution reaction vinyl chloride is .... reactive than alkyl chloride.
5. One of the π-bond of triple bond of benzyne intermediate is formed by .... overlap, while other is formed by .... overlap.
6. Alcohols containing two hydroxyl groups are commonly called as ....
7. Glycerol is the polyhydric alcohol containing .... hydroxyl groups.
8. Glycol is the polyhydric alcohol containing .... hydroxyl groups.
9. In chlorobenzene carbon-chlorine bond acquires the partial .... bond character.
10. 2,3-dimethyl-2,3-buatandiol is called as ....

SHORT ANSWER QUESTIONS:

1. What are haloalkane?
2. What are diols?
3. Define glycerols.
4. What is pinacol?

HOW WILL YOU PREPARE?

1. vinyl chloride from acetylene
2. acetaldehyde from vinyl chloride
3. acetylene from vinyl chloride
4. allyl chloride from propane
5. ethylene glycol from ethane
6. ethylene glycol from ethylene oxide

WHAT HAPPENS? WHEN-

1. vinyl chloride on polymerization in presence of peroxide
2. propylene treated with chlorine at high temperature
3. propylene on reaction with N-Bromo succinimide in presence of light
4. chlorobenzene on reaction with acetonitrile
5. benzene diazonium chloride treated with KI

EXPLAIN THE FOLLOWING REACTIONS WITH SUITABLE EXAMPLES

1. Hunsdiecker reaction
2. Wurtz- fittig reaction
3. Ullmann reaction

HOW WILL YOU PREPARE?

1. benzyl cyanide from benzyl chloride
2. benzyl magnesium chloride from benzyl chloride
3. benzyl chloride from benzene
4. biphenyl from iodobenzene
5. toluene from bromobenzene
6. acrolein from glycerol
7. glycerol trinitrate from glycerol
8. acetaldehyde from glycol
9. ethylene chloride from glycol
10. ethylene glycol from ethylene bromide

CONVERT THE FOLLOWING

1. ethylene to ethylene glycol
2. ethylene glycol to glycol diacetate
3. ethylene glycol to dioxane
4. ethylene glycol to diethylene glycol
5. propylene to glycerol
6. glycerol to glycerol trinitrate

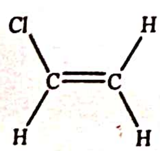
LONG ANSWER QUESTIONS

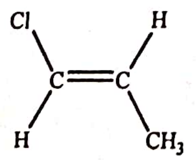
1. Explain, why vinyl chloride is almost inert in the nucleophilic substitution reaction?
2. Explain the extraordinary reactivity of allyl chloride in the nucleophilic substitution reaction.

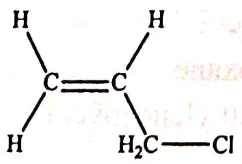
3. Explain, why allyl chloride is more reactive than vinyl chloride in nucleop substitution reaction?
4. Explain the pinacol-pinacolone rearrangement reaction with mechanism
5. Discuss the nucleophilic substitution reaction of chlorobenzene with KNH_2 mechanism.
6. Give explanation for the followings-
   i) Extraordinary reactivity of benzyl chloride in nucleophilic substitution reactio
   ii) Inertness of chlorobenzene in S_N1 reaction
   iii) Chlorobenzene is less reactive than allyl chloride in nucleophilic substitu reaction.

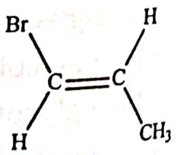
SELECT THE PROPER ANSWER FROM GIVEN ALTERNATIVE:

1. In vinyl chloride carbon bearing chlorine is .... hybridized
   a) sp b) sp^2 c) sp^3 d) d^2sp^3
2. In allyl chloride carbon bearing chlorine is .... hybridized
   a) sp b) sp^2 c) sp^3 d) d^2sp^3
3. In which of the following carbon-chorine bond is stronger
   a) vinyl chloride b) allyl chloride c) ethyl chloride d) benzyl chloride
4. Which of the following does not show S_N1 reaction?
   a) chlorobenzene b) benzal chloride c) allyl bromide d) benzyl chloride
5. Nucleophilic substitution reactions of chlorobenzene takes place by the formation .... intermediate
   a) nitrene b) benzyne c) carbon free radical d) none of the abo
6. glycerol is also called as
   a) glycol b) diol c) glycerine d) none of the abo
7. Among the following compounds, which one is has the highest reactivity nucleophilic substitution reaction?
   a) Allyl Chloride b) Vinyl Chloride c) Ethyl Chloride d) Chlorobenzene
8. Among the following compounds, which one is the most inert in nucleophi substitution reaction?
   a) Allyl Chloride b) Benzyl Chloride c) Ethyl Chloride d) Chlorobenzene
9. Which of the following compounds will react readily in S_N1 reaction?

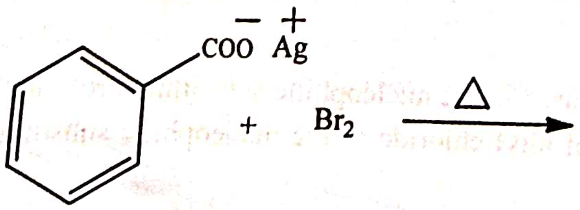
a) 

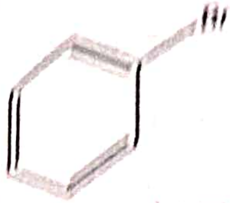
b) 

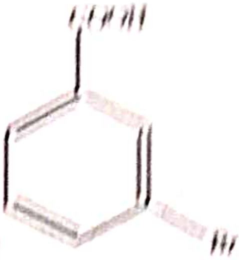
c) 

d) 

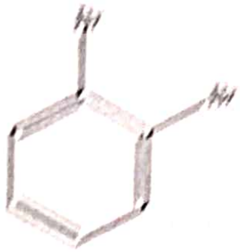
10. Which is the major product obtained in the following reaction?




a)


b)


c)


d)

11. What will be the product of following reaction?

$$CH_2{=}CH{-}CH_3 \xrightarrow[\text{peroxide}\ CCl_4\ \text{or}\ h\nu]{\text{NBS}} ?$$


a) $\overset{Br}{C}H{=}CH{-}\overset{Br}{C}H_2$


b) $CH_2{=}CH{-}\overset{Br}{C}H_2$


c) $\overset{Br}{C}H{=}CH{-}CH_3$

d) $CH_2{=}C{=}CH_2$

12. Allyl chloride on reaction with alcoholic KOH, gives ....
a) allene b) allyl alcohol c) No reaction d) none of the above

13. Chlorine atom of .... is most inert in the nucleophilic substitution reaction.
a) allyl chloride b) ethyl chloride c) chlorobenzene d) benzyl chloride

14. The reaction of silver salt of benzoic acid and bromine to give bromobenzene is ......
a) Ullmann reaction
b) Wurtz- Fittig reaction
c) Hunsdiecker reaction
d) Pinacol reaction

15. The reaction chlorobenzene with sodium amide in liq. ammonia with the formation of aniline is occurs by ....
a) addition- addition reaction
b) addition- elimination reaction
c) elimination – elimination reaction
d) elimination- addition reaction

16. The outer π-bond of triple bond of benzyne intermediate is formed by .... overlapping.
a) $sp^3 - sp^3$ b) $sp^2 - sp^2$ c) $p - p$ d) $s^2 - sp^2$

17. Ethylene on reaction with .... gives glycol.
a) hypochlorous acid followed by hydrolysis
b) $KMnO_4$
c) air and heated silver under pressure
d) All of above

18. Glycol on dehydration by .... gives dioxane
a) heated $ZnCl_2$ b) phosphoric acid c) conc. H_2SO_4 d) dil. H_2SO_4

19. Which of the following is used in automobile as an antifreeze?
a) ethyl alcohol b) nitromethane c) glycol d) phenol

20. Pinacol is the ....
a) 2,2-dimethyl-2,3-butandiol
b) 3,3-dimethyl-2,3-butandiol
c) 3,2-dimethyl-2,3-butandiol
d) 2,3-dimethyl-2,3-butandiol

21. Pinacol is prepared by the bimolecular reduction of .... in presenc electropositive metal.
a) acetaldehyde b) propionaldehyde c) acetone d) acetophenone

22. Glycerol is the member of .... alcohol
a) dihydric b) polyhydric c) trihydric d) monohydric

23. Glycerol on reaction with Na at room temperature to form-
a) monosodium glycerolate b) disodium glycerolate
c) trisodium glycerolate d) none of the above

24. Vinyl chloride on polymerization in presence of benzoyl peroxide gives-
a) polyhydric alcohol b) polyvinyl chloride
c) divinyl chloride d) polyvinyl alcohol

25. Allyl chloride is also known as-
a) 3-chloropropane b) 2-chloropropane
c) 3-chloropropene d) 2-chloropropene

26. When vinyl chloride is treated with alcoholic KOH it gives-
a) Ethylene b) Propylene c) acetylene d) 2-butene

27. Propylene on reaction with .... in presence of benzoyl peroxide and heat g allyl bromide.
a) N-bromoacetamide b) N-bromosuccinimide
c) N-chlorosuccininmide d) N-bromoacetamide

28. Benzyl chloride is prepared by heating benzene with .... and HCl in presenc anhydrous $ZnCl_2$
a) formaldehyde b) acetaldehyde c) formic acid d) acetic acid

29. Ethylene glycol on reaction with acetic acid gives ....
a) glycol monoacetate b) glycol diacetate
c) both a and b d) none of the above

30. Which of the following is the dehydration product of ethylene glycol in presence ZnCl2?
a) dioxane b) acetaldehyde c) diethyl glycol d) none of the abov

ANSWERS OF MCQ:

1 - b	11 - b	21 - c
2 - c	12 - a	22 - c
3 - a	13 - c	23 - a
4 - a	14 - c	24 - b
5 - b	15 - d	25 - c
6 - c	16 - b	26 - c
7 - a	17 - d	27 - b
8 - d	18 - c	28 - a
9 - c	19 - c	29 - c
10 - a	20 - b	30 - b

****

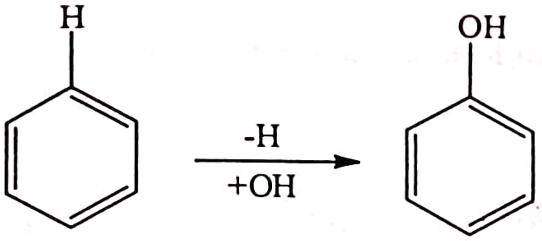
UNIT IV

PHENOLS, ETHERS AND EPOXIDES, THIOLS AND THIOETHERS

A. PHENOLS

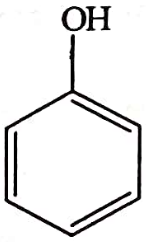
Introduction:

The hydroxyl derivative of benzene is known as Phenol. It is one of the synthetically important classes of organic compounds. The molecular formula of phenol is C_6H_5OH. In benzene ring one of the hydrogen is replaced by hydroxyl functional group (-OH) the compounds form is phenol.

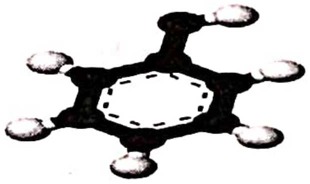


Benzene **Phenol**

Due to mild acidic nature of phenol it is also known as carbolic acid. Phenol is the important precursor in the synthesis of wide variety of organic compounds. The structural formula can be represented as follow.



Simple Structure of Phenol



Ball and Stick Model of Phenol

In nature the compounds occur in coal tar, it was first discovered by Friedlieb Ferdinand Runge in 1834. Along with the coal tar is also found in some fruits and vegetables such as olive oil, coffee, pomegranates, popcorn, wine and vinegar etc. the phenols are used in the synthesis of various drugs, dyes and polymer including plastics. It is used in the manufacture of some adhesives, rubbers, paints, resins and nylons. Phenols are also used as antiseptic and disinfectant.

4.1 Classification of Phenols

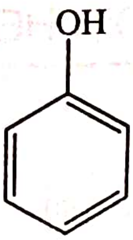
On the basis of number of hydrogens replaced by –OH groups on the benzene ring it can be classified as.

1. Monohydric phenols
2. Dihydric Phenols
3. Trihydric Phenols

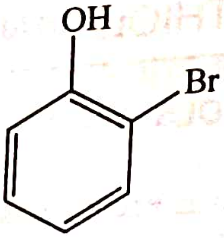
1. Monohydric Phenols

If only one hydrogen replaced by one –OH groups the phenols is kn
Monohydric Phenol

e.g.

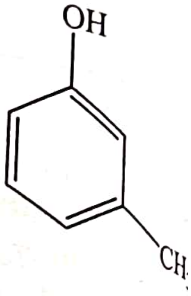


Phenol



o-bromophenol

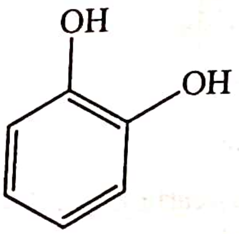
p-aminophenol



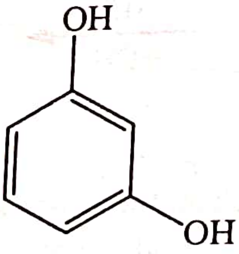
m-cresol

2. Dihydric Phenol

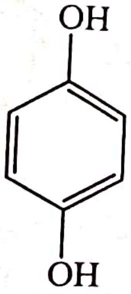
In benzene ring if two hydrogen atoms replaced by two –OH groups are ko
dihydric phenol eg.



1,2-Dihydroxy Benzene (Catechol)



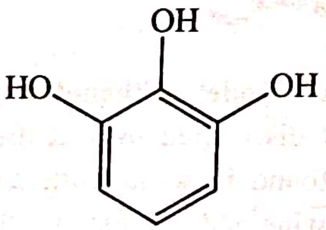
1,3-Dihydroxy Benzene (Resorcinol)



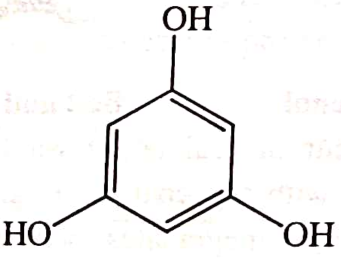
1,4-Dihydroxy Benzene (Hydroquinol)

3. Trihydric Phenols:

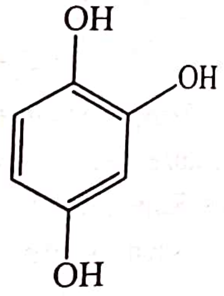
In these compounds of benzene three hydrogen replaced by three –OH group called as Trihydric Phenols.



1,2,3 Trihydroxy Benzene (Pyrogallol)



1,3,5 Trihydroxy Benzene (Phloroglucinol)



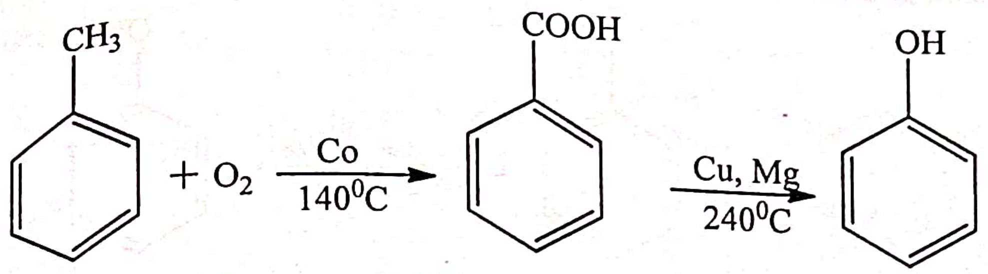
1,2,4 Trihydroxy Benzei (Hydroquinol)

4.2 Synthesis of Phenols

Phenols can be synthesized by different methods some of the important method synthesis are briefly discussed below.

1. From Toluene

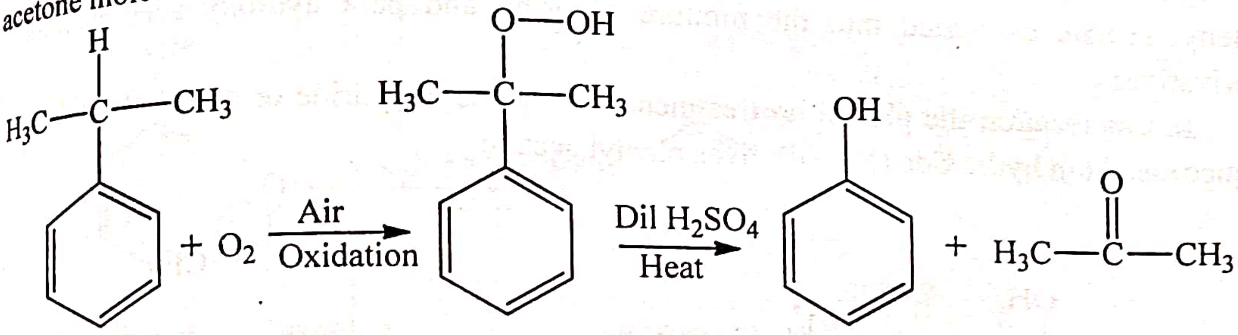
On air oxidation of phenol by heating at 140°C using cobalt as a catal produces first the Benzoic acid. The benzoic acid obtained on further treatment at 240 in presence of copper and Magnesium as a catalyst produces Phenol.



Toluene **Benzoic Acid** **Phenol**

2. **From Cumene or isopropyl benzene**

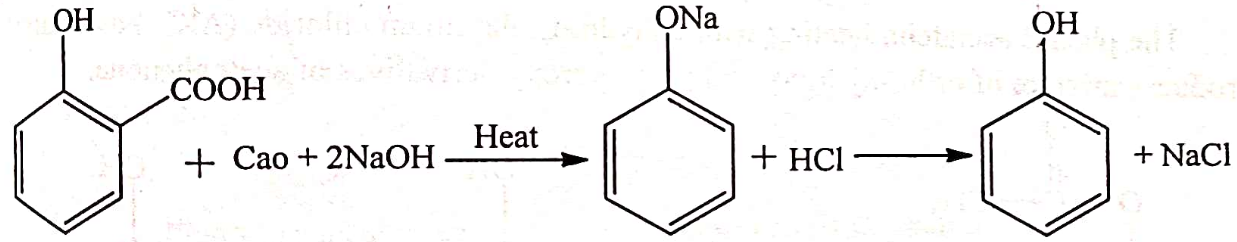
Cumene on oxidation with air first gives the cumene hydroperoxide it is on treatment with the dilute sulphuric acid yields the phenol along with the elimination of acetone molecule



Cumene **Cumene Hydroperoxide** **Phenol** **Acetone**

3. **From Salicylic acid**

Salicylic acid is decarboxylated by treatment with the soda lime it forms sodium phenoxide. Sodium phenoxide by acidification with dilute hydrochloric acid produces the phenol along with the elimination of sodium chloride molecule.



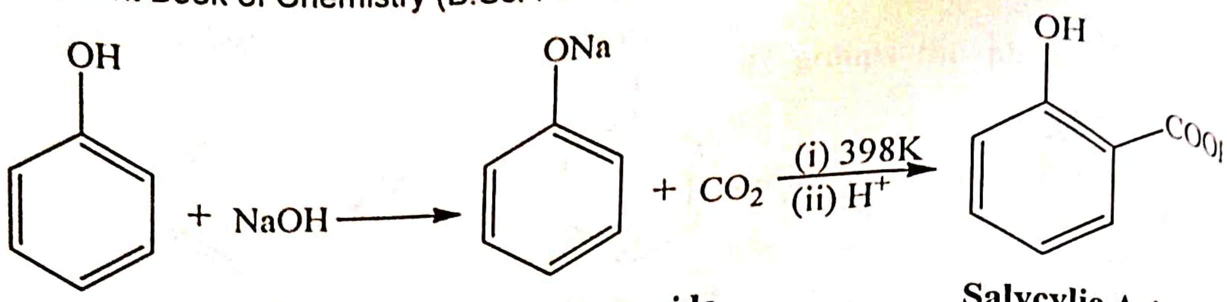
Salicylic Acid **Sodium Phenoxide** **Phenol**

4.3 Chemical Reactions of Phenols

Phenol undergoes the electrophilic substitution reaction. The hydroxyl functional group is the ortho para directing groups due to high electron density at these positions therefore the phenol produces the mixture of ortho and para substituted products. Some of the chemical reactions shown by the phenols are discussed below.

Kolbe's Carboxylation reaction

Phenol on treatment with sodium hydroxide it gives the sodium phenoxide. The sodium phenoxide on heating with carbon dioxide at 398K followed by acidification with dilute hydrochloric acid gives Salicylic acid.

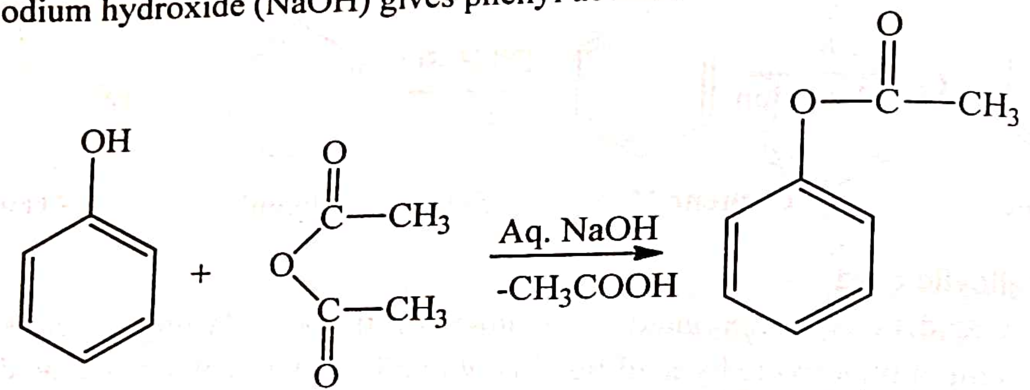


Phenol **Sodium Phenoxide** **Salycylic Acid**

Fries rearrangement

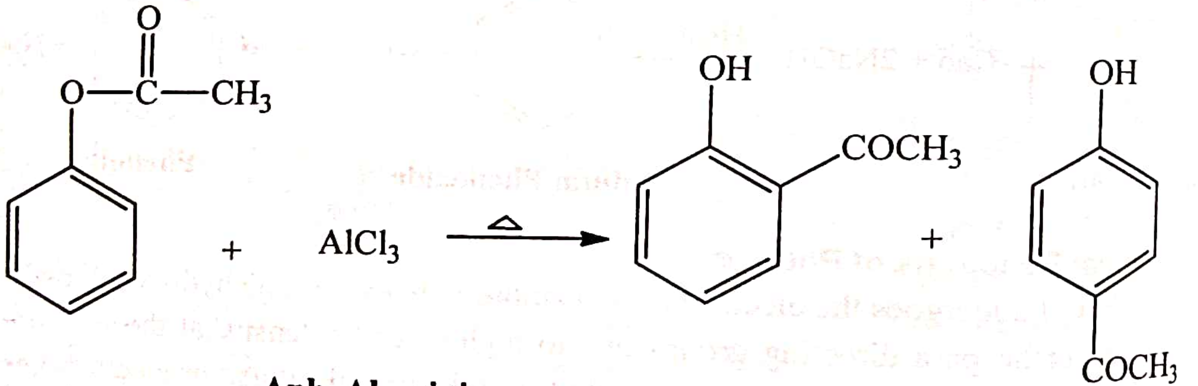
It is one of the most important reactions in organic synthesis because it is utilizin the synthesis of valuable chemicals. It is the rearrangement type of reaction in wh phenyl acetate converted into the mixture of ortho and para hydroxy acetophen derivatives.

In this reaction the phenol on treatment with acetic anhydride or acetyl chloride aqueoussodium hydroxide (NaOH) gives phenyl acetate.



Phenol **Acetic Anhydride** **Phenyl Acetate**

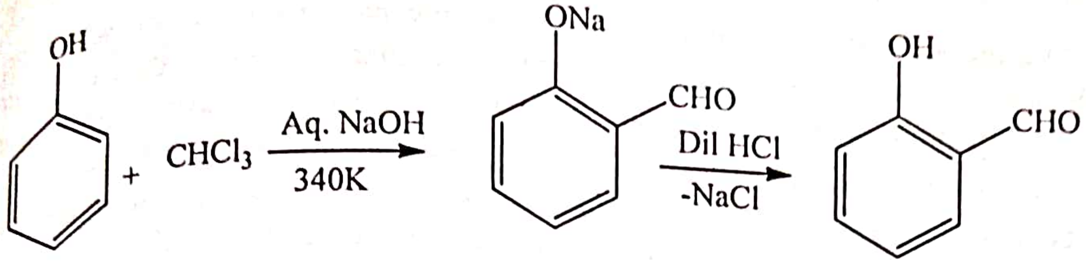
The phenyl acetateon heating with anhydrous aluminum chloride ($AlCl_3$) as cataly produces mixture of ortho-hydroxy and para hydroxy derivatives of acetophenone.



Phenyl Acetate **Anh. Aluminium Chloride** **o-hydroxy acetophenone** **p-aydroxy acetophenone**

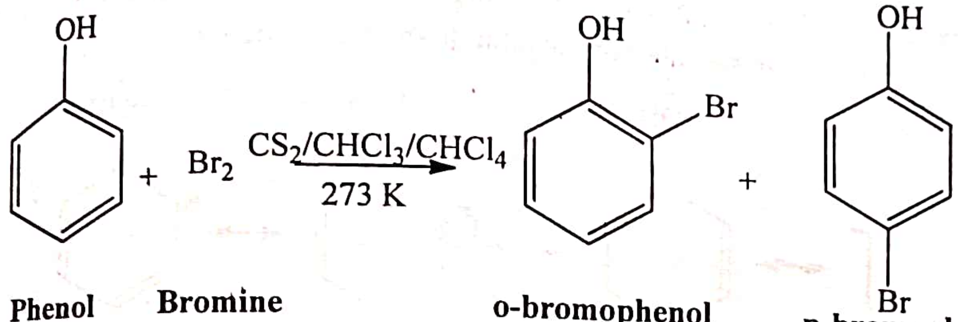
Reimer-Tiemann reaction

In this reaction the phenol and chloroform react together in presence of aqueous Sodium Hydroxide (NaOH) at 340K followed by hydrolysis gives o-hydroxy benzaldehyde this product is also known as salicylaldehyde.This reaction is called Reimer-Tiemann reaction.

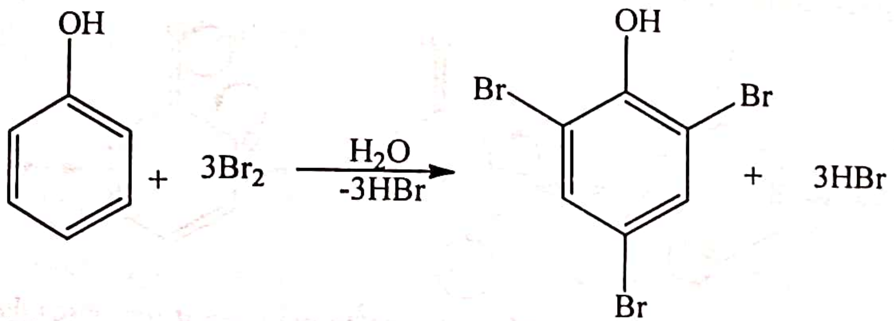


Bromination

In this reaction when phenol is treated with bromine in presence of carbon disulphide or Chloroform or Carbon tetrachloride as these are less polar solvent and at low temperature produces mixture of o-bromophenol and p-bromophenol

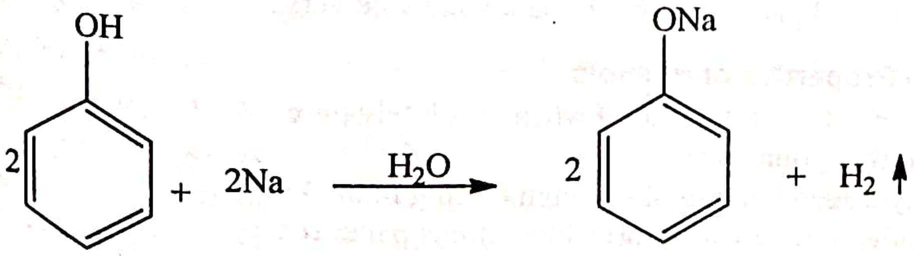


When bromination of phenol carried out in high polar solvent medium it gives white precipitate of 2, 4, 6-tribromophenol.



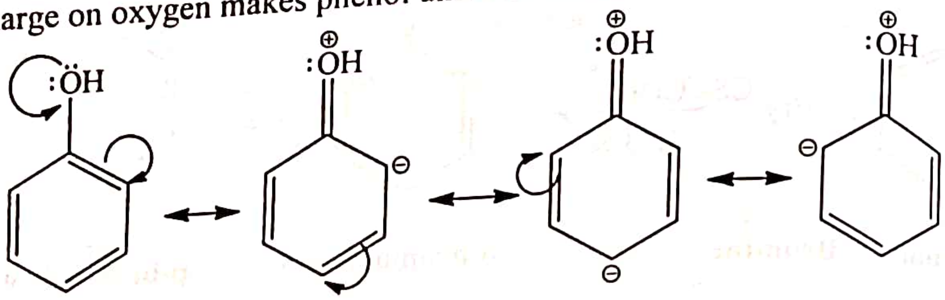
Acidity of Phenols

Phenol on reaction with sodium metal produces sodium phenoxide along with elimination of hydrogen gas. This reaction suggests that the phenol behaves as acidic in nature.

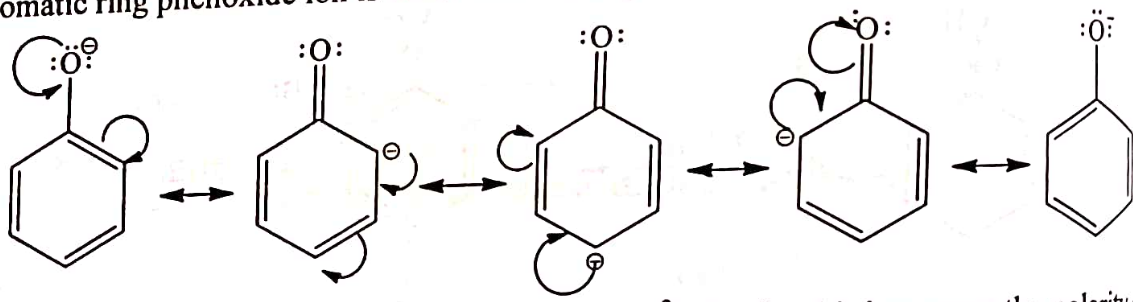


Unlike the alcohol the phenol easily donates the proton on reaction with bas form phenoxide ion. This is further stabilized by resonance delocalization of nega charge developed on oxygen atoms of phenol. Therefore phenol behaves as acidic, b is less acidic than the mineral acids and more acidic than alcohol. The more acidit phenol than alcohol is due to resonance stabilization of negative charge on oxygen at of phenol. This resonance delocalization is not possible in case of alcohol. The lone pair of electrons on the oxygen of phenol is in conjugation with the double b of benzene ring and it was resonancely stabilized. As oxygen develops a positive ch it will attract electron pair from bond present in between oxygen and hydrogen tow itself. This weakens the O-H bond and hydrogen atom can easily release as proto form phenoxy ion.

The resonance structure of phenol has charge separation bearing higher energ positive charge on oxygen makes phenol unstable than phenoxide ion.



Due to delocalization of only negative charge over the ortho and para positions aromatic ring phenoxide ion is more stable than phenol



The carbon of benzene ring in phenol is sp^{2}hybridised it increases the polarity C-OH bond which result in more ionization of phenol, hence phenol can lose the proto to form phenoxide ion because phenoxide ion is more stable than phenol itself.

Further the acidity of phenol increases as the electron withdrawing group present ortho and para position of phenol. The acidity decreases as the electron donating gro present at ortho and para position of phenol and vice versa.

4.4 Physical Properties of Phenols

1. It is colourless crystalline solid when absolutely pure.
2. It has melting point 315K
3. Due to hydrogen bonding it has high boiling point 455K
4. It has acidic in nature as it turns blue litmus paper red
5. It has sweet and tarry odour
6. It is sparingly soluble in water but completely soluble in alcohol and ether.

4.7 Uses of Phenol

1. Phenol is used in the preparation of Dettol which is antiseptic.
2. It is used in the preparation of plastics.
3. It is used in the preparation of agrochemicals like weedicides.
4. It is used in the preparations of phenolphthalein and some important dyes.
5. It is used in the preparation of phenol formaldehyde resins.

****

B. ETHERS AND EPOXIDES

Ethers are another important class of volatile organic compounds. In medicine the most common use of ether is anaesthetic agent than chloroform because ether is safer and less toxic than chloroform. It is regarded as the derivatives of alcohol and phenol where hydrogen atom of hydroxyl group of alcohol or phenol by alkyl group the alkoxy or aryloxy derivatives formed

The general formulas of ethers are R-O-R'

Where, R and R' may be same or different alkyl or aryl group

The most popular example of ether is the diethyl ether can be represented as

$$H_3C—\overset{H_2}{C}—O—\overset{H_2}{C}—CH_3$$

Diethyl Ether

On the basis of alkyl R group in ether they are of two types

A. Simple or Symmetrical ether
B. Mixed or Unsymmetrical ether

In the ether compounds if R and R' are same are called Simple or Symmetrical ether e.g.

$H_3C—O—CH_3$ **Dimethyl Ether**

$C_6H_5—O—C_6H_5$ **Diphenyl Ether**

$$H_3C—\overset{H_2}{C}—O—\overset{H_2}{C}—CH_3$$

Diethyl Ether

While In case of mixed or unsymmetrical ether R and R' are called Mixed or Unsymmetrical ether eg.

$H_3C—O—CH_2—CH_3$ **Ethyl methyl Ether**

$C_6H_5—O—CH_3$ **Methyl phenyl Ether**

$$C_6H_5—O—\overset{H_2}{C}—CH_3$$

Ethyl Phenyl Ether

4.8 Nomenclature of Ethers

As usual the ethers can be named by two ways

Common Name: in this method of nomenclature the names of ether derived from the by naming the two alkyl or aryl groups linked to the oxygen atom in alphabetical order followed by the name ether. If two alkyl groups attached to oxygen atom in ethers are same then prefix di is used before the name of alkyl or aryl groups.

$H_3C—O—CH_3$ **Dimethyl ether**

$H_3C—O—CH_2—CH_3$ **Ethyl methyl ether**

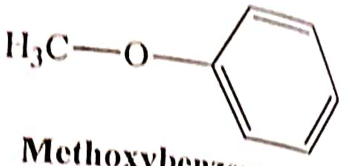
$C_6H_5—O—C_6H_5$ **Diphenyl ether**

IUPAC Name

In the IUPAC nomenclature of ether it is regarded as the alkoxy derivati hydrocarbon. In this system the larger alkyl group attached to oxygen atom regard the parent alkane. So it is named as alkoxyalkane,

$H_3C—O—CH_3$ Methoxymethane

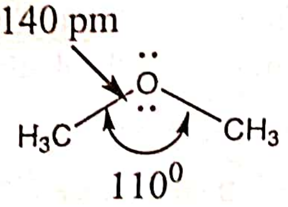
$H_3C—O—C_2H_5$ Methoxyethane



Methoxybenzene

4.7 Structure of Ether

The central oxygen atom in ether is sp3 hybridized. Due to which like molecule it is in tetrahedral geometry. But the bond angle is slightly larger than no tetrahedral angle. The C-O-C bond angle may be 110 to 111^0 and the C-O bond leng about 140 t0 141pm. The oxygen atom is more electronegative than carbon the hydr atom can be released as proton this make the ether acidic.



Structure of ether

4.8 Methods of synthesis of ethers

Ether can be synthesized by following methods

1. From alcohol or continuous etherification process

Excess of ethyl alcohol placed in distillation flask with concentrated small amo of sulphuric acid at 413 K it produces large amount of ether continuously. This proc becomes continuous and the process is known as continuous etherification process

$$\underset{\text{Ethyl alcohol}}{C_2H_5—OH} + \underset{\text{Sulphuric acid}}{H_2SO_4} \xrightarrow{-H_2O} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5—O—SO_3H} + H_2O$$

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5—O—SO_3H} + \underset{\text{Ethyl alcohol}}{C_2H_5—OH} \xrightarrow{-H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5}$$

2. Williamson's synthesis

This method of preparation involves the treatment of an alkyl halide with a suitab sodium alkoxide. This reaction was named to the credit of Alexander Williamson wh developed this method in 1850. This reaction involves the nucleophilic substitution halide ion from the alkyl halide by the alkoxide in via SN^2 mechanism.

Eg. When ethyl bromide is heated with sodium ethoxide gives diethyl ether.

$$\underset{\text{Ethyl bromide}}{C_2H_5—\boxed{Br}} \boxed{+ \; Na}\underset{\text{Sodium ethoxide}}{—O—C_2H_5} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + NaBr$$

4.9 Chemical Reactions of ether

The C-O-C linkage in ether is very strong and the molecule is quite stable and inert toward the hydrochloric acid but it can be broken by HI (Hydroiodic acid).

1. Action of HI in cold condition

The cold and dry HI (Hydro iodic acid) reacts with ether at 273 K, it breaks the C-O-C bond of ether, one molecule of alkyl halide and one molecule of alcohol generated.

$$\underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + HI \xrightarrow[\text{Cold}]{273\ K} \underset{\text{Ethyl Alcohol}}{C_2H_5—OH} + \underset{\text{Ethyl Iodide}}{C_2H_5—I}$$

In case of mixed ether or unsymmetrical ether the lower alkyl group converted into halide higher alkyl group converted into alcohol.

$$\underset{\text{Eethyl methyl ether}}{C_2H_5—O—CH_3} + HI \xrightarrow[\text{Cold}]{273\ K} \underset{\text{Ethyl Alcohol}}{C_2H_5—OH} + \underset{\text{Ethyl Iodide}}{H_3C—I}$$

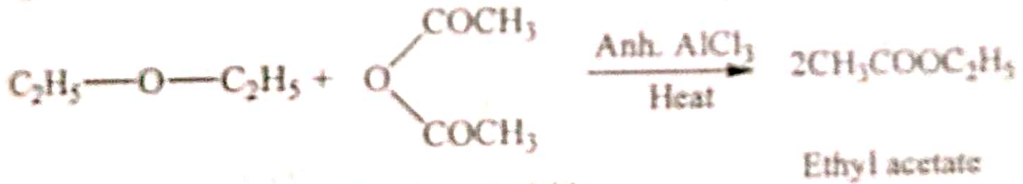
2. Action of HI in Hot condition

Diethyl ether when react with hydroiodic acid (HI) at 373 K or under hot condition the ether converted into ethyl iodide and water.

$$\underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + 2HI \xrightarrow[\text{Hot}]{373\ K} \underset{\text{Ethyl Iodide}}{2\,C_2H_5—I} + H_2O$$

3. Reaction of ether with acetic anhydride

Diethyl ether on reaction with acetic anhydride in presence of anhydrous aluminum chloride it gives ethyl acetate.



$$C_2H_5—O—C_2H_5 + O\begin{cases}COCH_3\\COCH_3\end{cases} \xrightarrow[\text{Heat}]{\text{Anh. }AlCl_3} 2CH_3COOC_2H_5$$

Ethyl acetate

Diethyl ether Acetic anhydride

4.10 Physical Properties of Ether

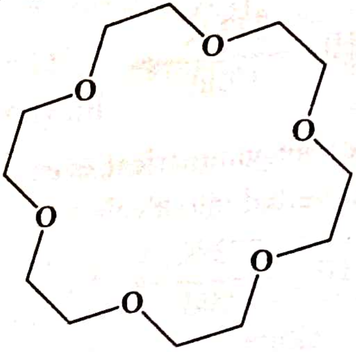
1. The lower ether are colourless volatile liquid
2. It have characteristic ether smell
3. This is highly flammable liquid
4. Ethers are slightly polar molecule.

4.11 Uses of Diethyl Ethers

1. In organic synthesis ethers are used as solvent medium.
2. It is also used as extracting solvent in industry.
3. Lower ethers are also used as anaesthestics.
4. It is used as refrigerant.
5. Mixture of diethyl ether and alcohol known as Natalite is used as substitute of petrol.
6. Diethyl ether used as industrial solvent in the preparation of resins, gums, oils and fats.

4.12 Crown ethers

Crown ethers are large heterocyclic rings of carbon and oxygen. This mole comes under the category of macrocyclic organic compounds. It is nothing but the typ ether in which C-O-C group of ether involved in the cyclic form. It was discovered b Charles J. Pederson and also regarded as macrocyclic polyether. The first crown e synthesized was the 18-crown-6-ethere it can be represented as,



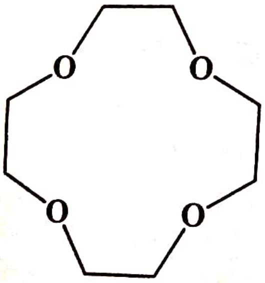
18-Crown-6-Ether

Crown ether can be named as n-crown-m, where

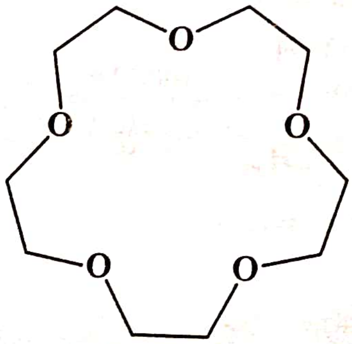
n= Total number of carbon and oxygen in the molecule

m=total number of oxygen atoms in the ring

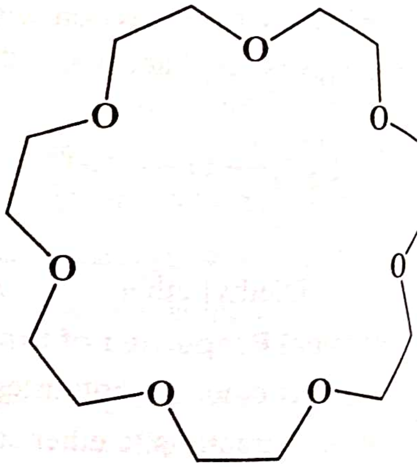
e.g. In 18-crown-6 there are total 18 atoms including carbon and oxygen in the molec of crown ether and the 6 oxygen involved inside the ring. Other examples of crown eth are as follow



12-crown-4

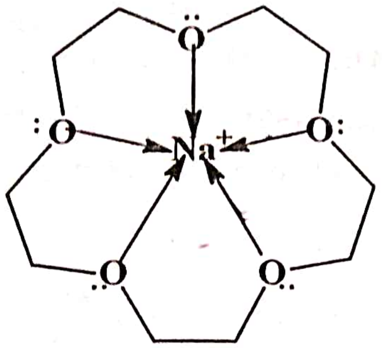


15-crown-5



21-crown-7

The crown ether has the cavity inside the ring and can be trapped by the metal. The lone paired of electron on the oxygen responsible to form the complex between the metal and crown ether ring. The metals like sodium potassium and lithium can form the strong bond with oxygen and form the complex compound. The crown ether molecule can acts as lig and and form coordination complex through oxygen. The crown ether molecule is selective against the selective metals. For example 15-crown-5 can bind with Na^+ ion by following complex formation.



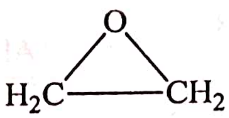
Coordination compound of crwon ether with Sodium ion through oxygen

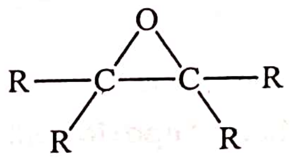
4.13 Applications of crown ethers

1. It is used as carrier agent in the reactions involving two immiscible solvent.
2. Due to selective nature against the selected ion it is used in isolation of metals from the sample.
3. It used for increasing solubility of ionic salts in nonpolar solvents.
4. It is also used to remove the radioactive isotopes from radioactive waste.
5. The derivative of 18-crwon-6 used to extracts two important elements cesium and strontium.

4.14 Ethylene oxide or Epoxide

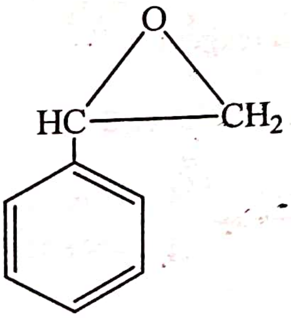
It is three membered highly unstable heterocyclic compounds. It comes under the type of ether, in this molecule the oxygen atom attached to two adjacent carbon atoms of hydrocarbon. The carbon atoms in the epoxide ring in sp^3 hybridization and deviation in the bond angle makes the epoxide ring unstable and highly reactive than the other simple ether. The ring can easily open when reacts either with acid or base. The simple representation of ethylene oxide is as follow.





Ethylene oxide

When the epoxide ring attached to the benzene ring the compound is known as styrene,



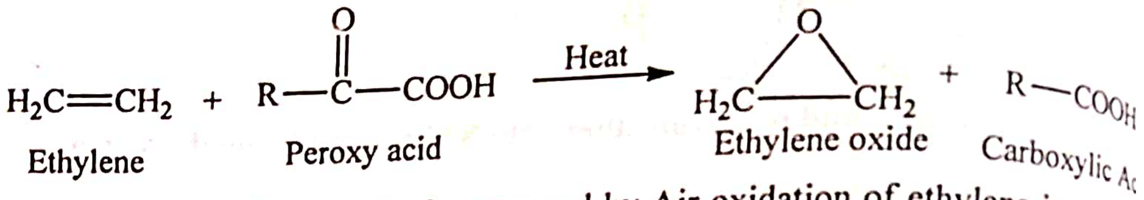
Styrene oxide or 2-phenyl oxyrane

4.15 Method of Synthesis of epoxide

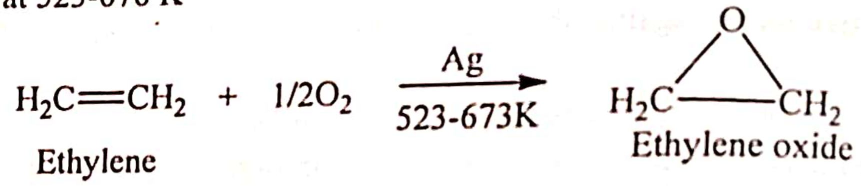
Ethylene oxide can be preapared by two methods

Synthesis from ethylene by using peroxy acid

Ethylene molecule on reaction with peroxy acid it gives ethylene oxide with the acetic acid.



Ethylene oxide can also be prepared by Air oxidation of ethylene in presen silver catalyst at 523-676 K

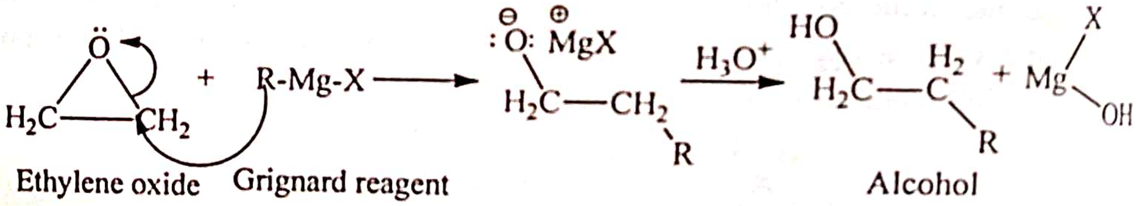


4.16 Chemical reactions of epoxide

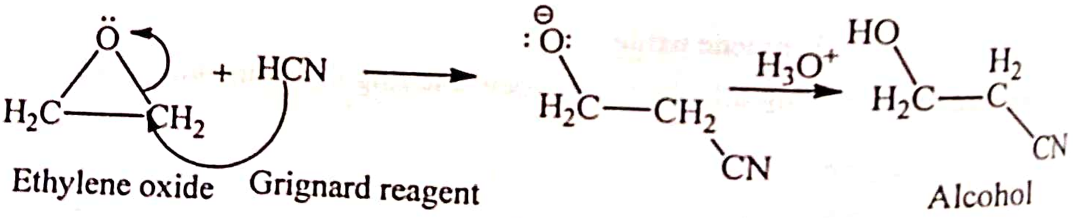
The ethylene oxide ring is with highly strain molecule. The ring can easily ope form the corresponding products. Some of the reactions of epoxide are discussed belo

1. Ring opening reaction of epoxide with Grignard reagent

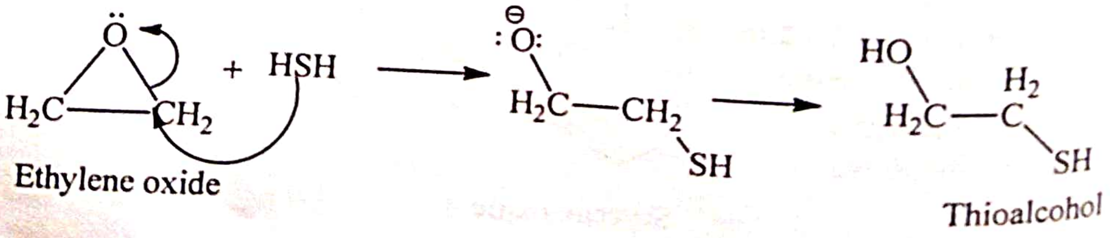
Epoxide on treatment with the Grignard reagent alkyl group of Grignard reagents ac nucleophile and open the reaction by SN2 fashion.



2. Ring opening reaction of epoxide with HCN



3. Ring opening reaction of epoxide with H_2S



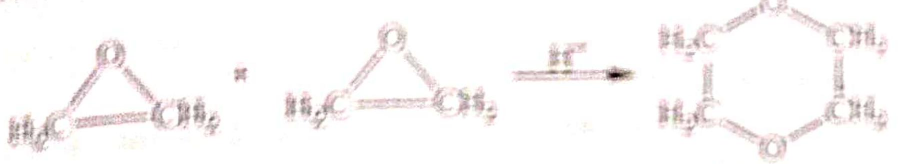
Reduction of epoxide with Zn + CH_3COOH

Ethylene oxide on treatment with zinc in acetic acid the ethylene oxide ring opened and get reduced to produce ethane-1,2-diol

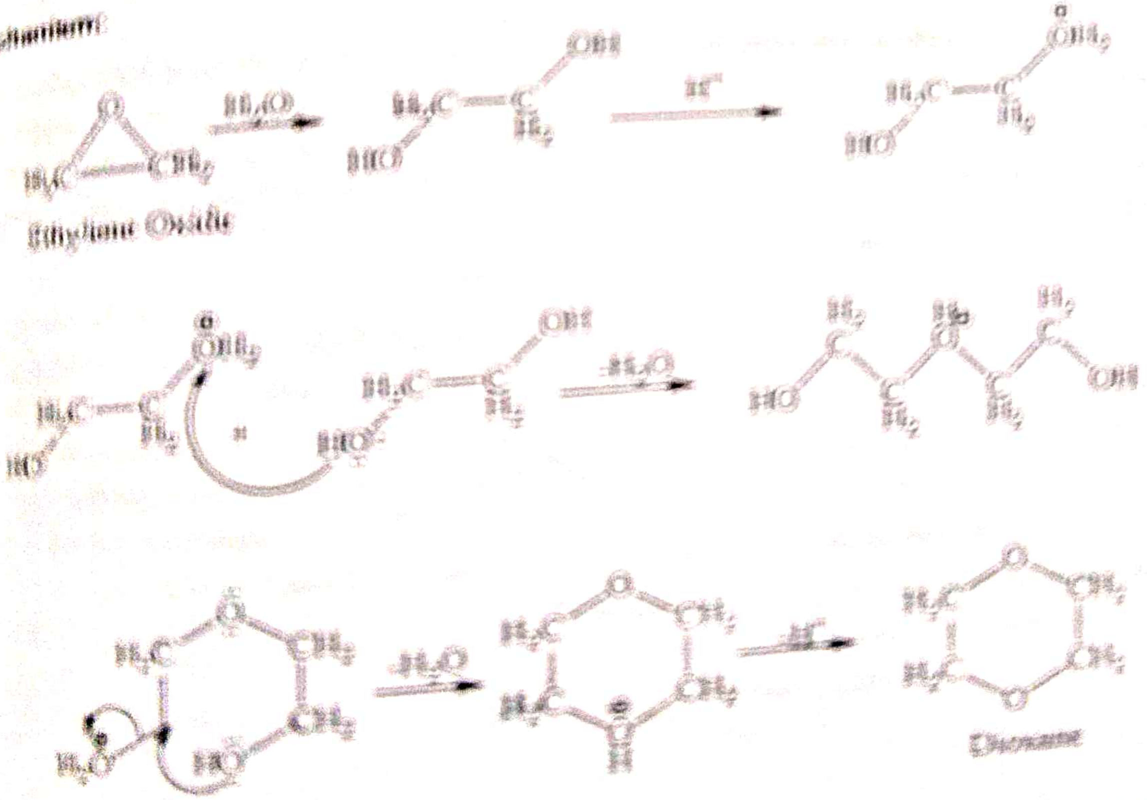

Ethylene Oxide ethane-1,2-diol

Dimerisation to dioxane (Mechanism)

Ethylene oxide undergoes the dimerisation reaction. When the two molecule of ethylene oxide reacts together in presence of acid the 1,4-dioxane compound is formed.


Ethylene Oxide Ethylene Oxide 1,4-Dioxane

Mechanism:

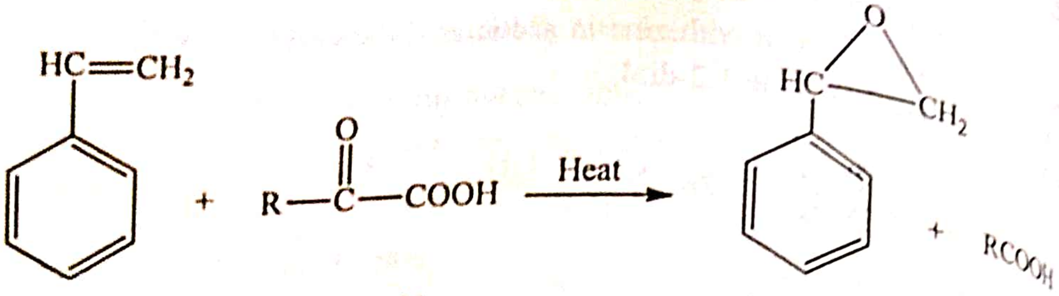

Ethylene Oxide

Dioxane

4.17 Styrene oxide

Styrene oxide is another important class of ether like epoxide. It is regarded as aromatic epoxide because the epoxide ring is attached to benzene ring.

It can be synthesized from styrene, when it is heated with peroxy acid it gives the styrene epoxide. It is the oxidation of styrene by peroxy acid.



Styrene Peroxy acid Styrene oxide

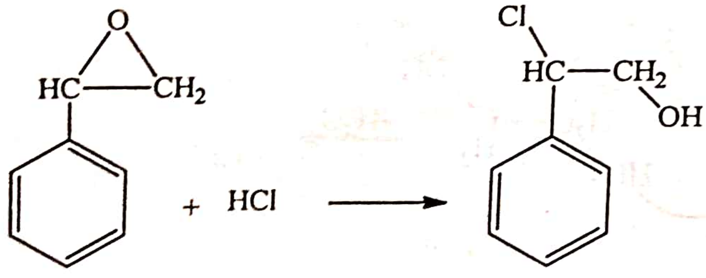
Ring opening reactions of styrene epoxide

The prominent reaction of styrene is the ring opening of tricyclic ring. It is be the high strain in the epoxide rings. Some of the reactions shown by styrene epoxid discussed below.

1. Ring opening reaction by acid

The oxygen atom of oxirane ring is electronegative than the carbon. The ca atoms become electrophilic and can attack the incoming nucleophile to open the ring. electrophilic character increases due the attack of H^+ over the electronegative oxy atom.

The styrene oxide reacts with the hydrochloric acid the ring opening takes place produces 2-chloro-1-phenyl ethanol is the main product. There are two sites to attack nucleophile on styrene oxide. The nucleophile always prefers the less crowded posit When this reaction carried out in the chloroform the product will be 2-chloro-1-phe ethanol.

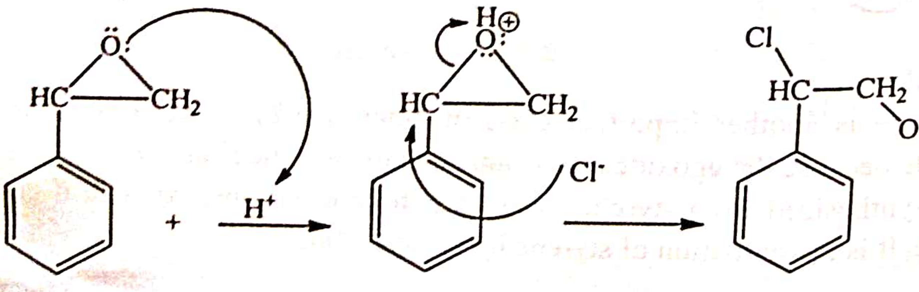


Styrene oxide 2-chloro-2-phenyl ethanol

Mechanism of ring opening reaction by acid

The hydrochloric acid used dissociate as

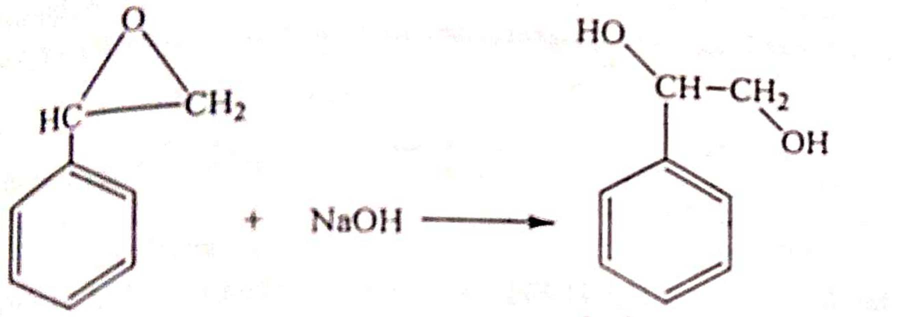
$$HCl \rightleftharpoons H^+ + Cl^-$$



Styrene oxide Oxonium Compound 2-chloro-2-phenyl ethanol

2. Ring opening reaction by base or alkali

In this reaction the attack of nucleophile takes place from more crowded position. This reaction proceeds by the SN^2 type of reaction and product will be 1-phenyl-1, 2-*ethane diol.*

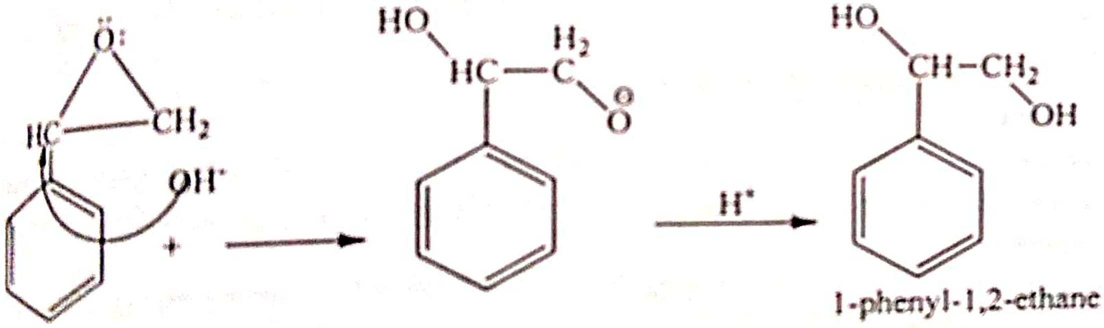


Styrene oxide

1-phenyl-1,2-ethane diol

Mechanism:

$$NaOH \rightleftharpoons Na^+ + OH^-$$

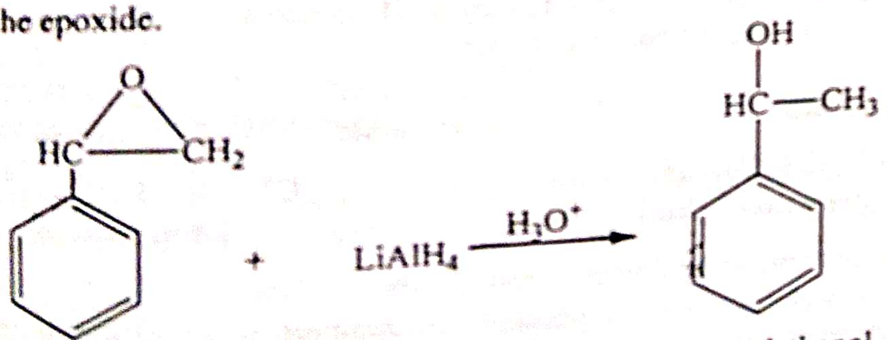


1-phenyl-1,2-ethane diol

Styrene oxide

Reduction of styrene epoxide by $LiAlH_4$

$LiAlH_4$ (Lithium aluminum hydride) is the reducing agent it reduces the styrene epoxide by opening the ring to form 1-phenyl-1, 2-ethane diol. This reaction proceeds by SN^2 nucleophilic substitution bimolecular way. This reaction is useful to synthesize the alcohol from the epoxide.



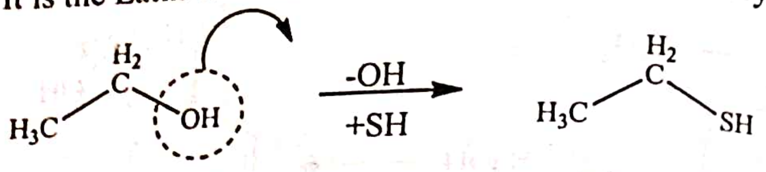
1-phenylethanol

Styrene epoxide

••••

C. THIOLS AND THIOETHERS

The Ethanethiol is the compounds looks like the ethanol, in this the OH group ethanol is replaced by SH group. This molecule was first reported by the scie William Christopher Zeise in 1834 he named $-SC_2H_5$ group as mercaptum. The str affinity of sulphur toward mercury to form mercaptides, hence the sulphur derivati name mercaptan. It is the Latin word mercurium captans means mercury capturing.



Ethyl alcohol

Ethanethiol

Its molecular formula is CH_3CH_2SH likewise the Ethanol CH_3CH_2OH. The ma functional group in the ethanethiol is -SH like the hydroxyl group (-OH) in ethanol. The SH group is known as mercaptan (ethyl-mercaptan), in this compound the sulphur ato isdirectly attached to the carbon atom hence it is regarded as organosulphur compound.

4.18 Nomenclature thiols:

Alkane thiols are named by two types of nomenclature such as common name an IUPAC name

Common name

In common name system the Alkanethiol are named by adding the word mercapta after the name of alkyl group attached directly to sulphur atom. For eg R-SH is named a alkyl mercaptan.

CH_3SH
methyl mercaptan

CH_3CH_2SH
ethyl mercaptan

$CH_3CH_2CH_2SH$
n-propyl mercaptan

$CH_3CH(SH)CH_3$
isopropyl mercaptan

$CH_3CH_2CH_2CH_2SH$
n-butyl mercatan

IUPAC name

In IUPAC nomenclature of thiols the compounds are named by adding the suffi thiols after the name of parent alkane. For eg R-SH is named as alkanethiol. All other rul of IUPAC is same like that of naming the alcohol.

CH_3SH
methanethiol

CH_3CH_2SH
ethanethiol

$CH_3CH_2CH_2SH$
propane-1-thiol

$CH_3CH(SH)CH_3$
propane-2-thiol

$CH_3CH_2CH_2CH_2SH$
1-butanethiol

4.19 Synthesis of ethanethiol from ethyl iodide

Ethanethiol molecule can be prepared by reaction of ethyl iodide with excess of KSH. This reaction undergo by SN^2 mechanism.

$$\underset{\text{ethyl iodide}}{CH_3\text{-}CH_2\text{-}I} + \underset{\text{potassium hydrogensulfide}}{KSH} \xrightarrow{\text{Heat}} \underset{\text{Ethanethiol}}{CH_3\text{-}CH_2\text{-}SH} + KI$$

4.20 Oxidation reactions of ethanethiols

1. **Reaction with hydrogen peroxide**

Hydrogen peroxide is the mild oxidizing agent it is on reaction with Ethanethiol it gets oxidized to producediethyl disulphide.

$$2CH_3\text{-}CH_2\text{-}SH + H_2O_2 \xrightarrow{\text{Heat}} CH_3\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH_3 + 2H_2O$$

Ethanethiol   Hydrogen Peroxide   diethyl disulphide

2. **Oxidation with Iodine (I_2)**

Iodine is the mild oxidizing agent, when reacts with ethane thiol molecule produces the diethyl disulphide.

$$2CH_3\text{-}CH_2\text{-}SH + I_2 \xrightarrow{\text{Heat}} CH_3\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH_3 + 2HI$$

Ethanethiol   Iodine   diethyl disulphide

4.21 Physical properties of thiols:

1. These are volatile liquid with unpleasant odors, as garlic and rotten eggs.
2. Lower members of thiol are gases while higher members are volatile liquids.
3. As compared to alcohol the hydrogen bonds in thiols are weak due to less polarity of S-H bond.
4. The boling point 35^0Cis lower than alcohol.
5. These are insoluble in water but readily soluble in organic solvents ether and alcohol.

4.22 Thioethers or Alkyl Sulphidesor Diethyl Sulphides:

This molecule is similar to the simple ether only the difference is the replacement of oxygen atoms in thioether by sulphur atom. Thioethers are also regarded as sulphide organic derivatives.

Like ether the thioethers have the general molecular formula R-S-R'. the alkyl group attached to sulphur may be same or different. The popular example of thioether is diethyl sulphide,

$$C_2H_5 \text{---} S \text{---} C_2H_5$$

Diethyl sulphide

These are of two types symmetrical and unsymmetrical thioethers depending on the alkyl group attached to sulphur atom.

Symmetrical thioetheres are those in which both the alky groups are same eg.

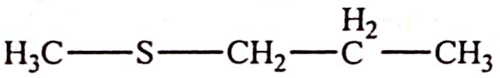
$$C_2H_5 \text{---} S \text{---} C_2H_5 \qquad H_3C \text{---} S \text{---} CH_3$$

Diethyl sulphide   Dimethyl sulphide

In unsymmetrical thioether both alky groups are different eg.

$$C_2H_5 \text{---} S \text{---} CH_3$$

ethyl methyl sulphide



$$H_3C \text{---} S \text{---} CH_2 \text{---} \overset{H_2}{C} \text{---} CH_3$$

methyl-n-propyl sulphide

4.23 Nomenclature of thioether

Thioether can be named by two types of method common name and IUPAC name

Common name

In this method thioether are named by adding the suffix sulphide after the nam alkyl group attached to sulphur atom. In case of symmetrical thioethers the prefix attached to the name of alkyl group. Whereas, unsymmetrical thioether are nam alphabetical order of first letter of alkane.

$H_3C—S—CH_3$

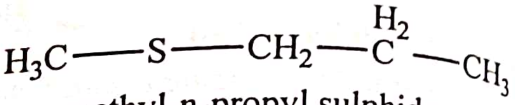
Dimethyl sulphide

$H_3C—H_2C—S—CH_2—CH_3$

Diethyl sulphide

$C_2H_5—S—CH_3$

ethyl methyl sulphide



$H_3C—S—CH_2—\overset{H_2}{C}—CH_3$

methyl-n-propyl sulphide

$C_6H_5—S—CH_3$

methyl phenyl sulphide

IUPAC Name

In this system the thioether regarded as sulphur derivatives of hydrocarbon. named as the word alkyl followed by thioalkaneeg to name the general thioethers R- it can be named as Alkyl thioalkane. In unsymmetrical thioetherThe larger group b considered as the parent hydrocarbon.

$H_3C—S—CH_3$

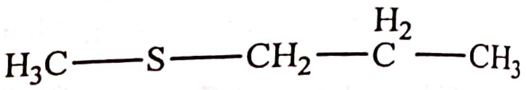
methyl thiomethane

$H_3C—H_2C—S—CH_2—CH_3$

ethyl thioethane

$C_2H_5—S—CH_3$

methyl thioethane



$H_3C—S—CH_2—\overset{H_2}{C}—CH_3$

1-methyl-thioprapane

$C_6H_5—S—CH_3$

thioanisol

4.24 Preparation of diethyl sulphide from ethyl bromide

1. It can be prepared by heating the ethyl bromide with potassium sulphide for diethyl sulphide.

$$\underset{\text{Ethyl bromide}}{2CH_3CH_2\text{-}Br} + \underset{\text{Pottasium sulphide}}{K_2S} \xrightarrow{\text{Heat}} \underset{\text{Diethyl sulphide}}{CH_3CH_2\text{-}S\text{-}CH_2CH_3} + 2KBr$$

2. It can also be prepared by reaction of ethyl bromide with sodium ethyl mercapti forms diethyl sulphide.

$$\underset{\text{Ethyl bromide}}{CH_3CH_2\text{-}Br} + \underset{\text{Sodium ethyl mercaptide}}{CH_3CH_2\text{-}S\text{-}Na} \xrightarrow{\text{Heat}} \underset{\text{Diethyl sulphide}}{CH_3CH_2\text{-}S\text{-}CH_2CH_3} + NaBr$$

4.25 Chemical Reaction of Thioethers

1. **Desulphurization with Raney Ni**

Diethyl sulphideon heating with the raney Ni it undergoes desulphurization t produce the n-butane.

$$CH_3CH_2\text{-}S\text{-}CH_2CH_3 + \text{Raney Ni} \xrightarrow[\text{Desulphurization}]{\text{Heat}} CH_3CH_2CH_2CH_3 + NiS$$

Diethyl sulphide butane Nickel sulfide

2. **Decomposition with alkali**

Diethyl sulphide on boiling with alkali undergoes hydrolysis to form ethyl alcohol.

$$CH_3CH_2\text{-}S\text{-}CH_2CH_3 + H_2O \xrightarrow{OH^-} 2CH_3CH_2OH + H_2S$$

Diethyl sulphide Ethyl alcohol

4.26 Physical Properties of thioethers

1. Diethyl thioether is a colourless oily, volatile, low boiling liquid with unpleasant smell.
2. The boiling point of thioethers are more than the corresponding ethers.
3. The boiling point diethyl thioether is about 92°C.
4. It is insoluble in water.
5. It is soluble in organic solvents like ether and alcohol.

EXERCISE

FILL IN THE BLANKS:

1. The molecular formula of phenol is ....
2. In benzene ring one of the hydrogen is replaced .... group the compounds form is phenol.
3. Due to mild acidic nature of phenol it is also known as ....
4. Bromination of phenol is another example of .... reaction of phenol.
5. Phenols are acidic in nature as it turns blue litmus paper ....
6. In the ether compounds if R and R' are same are called .... ether
7. In organic synthesis ethers are used as ....
8. Crown ethers are large heterocyclic rings of .... and ....
9. Epoxides are three membered .... ether
10. The SH group is known as ....
11. R-SH is named as ....
12. Thioethers are also regarded as .... organic derivatives.

SHORT ANSWER QUESTIONS:

1. Thiols have lower boiling points than corresponding alcohols.
2. Thioethers have higher boiling point than corresponding ethers.
3. Thiols and thioethers are insoluble in water.

EXPLAIN THE FOLLOWING:

1. Explain why phenols are more acidic than alcohols.
2. Explain the fries rearrangement
3. Explain the Reimer Tiemann

Write a note on: Williamson's synthesis.

How is diethyl ether prepared in laboratory? How does it react with (i) PCl_5 (ii) O_2 (iii) cold concentrated H_2SO_4 (iv) Con. HI

DESCRIPTIVE QUESTIONS:

1. Discuss different properties and uses of ether
2. Give general methods of preparation of epoxides.
3. Describe the general methods of preparation and chemical properties of thiols.
4. Describe the general methods of preparation and chemical properties of thioether

SELECT THE PROPER ANSWER FROM GIVEN ALTERNATIVE:

1. Commercially phenols can be obtained from:
   a) Coal- tar b) Benzene c) Gasoline d) Wood
2. Which of the following groups will increase the acidity of phenol?
   a) NO2 b) CN c) halogens d) all
3. Ethers have:
   a) Pungent odour b) Pleasant odour c) Fishy odour d) Vinegar odour
4. When diethyl ether is treated with hot HI, it forms:
   a) Ethyl iodide b) Acetyl iodide c) Propyl iodide d) Ethyl alcohol
5. Which of the following cannot be considered as use of ether?
   a) Inert solvent b) Anaesthetic
   c) Antipyretic d) Solvent of oil, fats and resins
6. Which class of organic compounds can be represented as R-S-R'?
   a) Esters b) Thiols c) Thioether d) Alcohols
7. Which one of the following is a thiol?
   a) CH_3SH b) CH_3COOH c) CH_3OH d) CH_3SCH_3
8. What is the IUPAC name of CH3CH2SH compound?
   a) Ethyl sulphide b) Ethanethiol
   c) Ethyl thioether d) Ethyl hydrogen sulphide
9. Which compound is a thioether?
   a) $CH_3CH_2CH_2SH$ b) $CH_3CH_2SCH_2CH_3$
   c) CH_3CH_2Br d) $CH_3CH_2SCH_2CHO$
10. Which functional group is present in thiols?
    a) R-O-R' b) -SCN c) -SH d) –NH
11. Thioethers are
    a) Sulphur analogues of ethers b) Nitrogen analogues of ethers
    c) Sulphur analogues of alcohols d) Sulphur analogues of alcohols
12. Which property is generally characteristic of thioethers?
    a) Their boiling points are lower than corresponding ethers.
    b) Their boiling points are higher than corresponding ethers.
    c) They are colourless.
    d) They have unpleasant order.

ANSWERS OF MCQ:

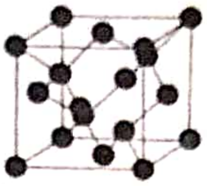
1 - a	2 - d	3 - b	4 - a	5 - c	6 - c
7 - a	8 - b	9 - b	10 - c	11 - a	12 - b

****

UNIT V

CRYSTALLINE STATE

5.1 Introduction



Diamond Cubic (DC)

In classical physics and general chemistry, **matter** is any substance that has mass and takes up space by having volume. The three states of matter are the three distinct physical forms which matter can take in most environments: solid, liquid, and gas. Other states, such as plasma, Bose-Einstein condensate, and neutron stars, may be present in extreme environments. Solid is one of the four fundamental states of matter. In solid state the component particles are held together by strong cohesive forces so that the molecules are tied together and contain the least amount of kinetic. A solid is characterized by structural rigidity and resistance to a force applied to the surface. Thus solids have definite shape, size and volume.

Characteristics of Solids

i) Interparticle distance is very small in solids i.e. the components are closely packed. Thus, free space between them is almost absent

ii) Density is higher due to close packing of particles

iii) Interparticle attraction forces are very strong in solids. So particles cannot leave their positions in solid. However, particles can vibrate about their mean position

iv) Rigidity is high. It is due to absence of translational motion of particles

v) Non-compressibility is due to rigidity. So there is almost no change in volume of solid on applying external pressure

vi) Definite shape, size and volume is due to rigidity and non-compressibility of solid

vii) Melting Points of solids are higher. The M.P. gives an idea about strength of interparticle attraction forces

Classification of Solids

Solids are of two types

(a) Crystalline solids; also called true solids

(b) Amorphous solid

a) Crystalline solids

The solids in which structural units (atoms, ions or molecules) are perfectly arranged in regular ordered and constantly repeating in three dimensional pattern to give a definite geometrical shape are known as crystalline solids.

Ex.: NaCl, sugar, diamond.

Characteristics of Crystals

1) The atoms are closely packed in a definite manner to form a characteristic three dimensional pattern

2) They have planner surfaces arranged in definite pattern

3) It has a similar environment around each particle throughout the solid

4) They have sharp edges and sharp melting point
5) They have definite interfacial angles
6) They are anisotropic i.e. their physical properties are different in different dir

b) Amorphous solid (from Greek = amorphous = shapeless)

It is defined as such solid which does not have any long range regularity, l ordered and periodicity in the internal arrangement of particles so that it does no any definite geometry e.g. rubber, plastics, starch etc.

Characteristics of amorphous solids

1) They have a random, irregular and non- periodic arrangement of component pa over a long range
2) They do not have flat faces, sharp edges and sharp melting point
3) They are considered as super cooled liquids with very high viscosity
4) They are isotropic i.e. their physical properties are independent of direction

Isotropy and Anisotropy

Amorphous substance are said to be isotropic because they exhibit the same of any property in all direction. Thus refractive index, thermal and elec conductivities coefficients of thermal expansion in amorphous solids are independe direction along which they are measured.

Crystalline substances on the other hand are anisotropic and the magnitude physical property changes with directions. For example, in a crystal of silver iodid coefficient of thermal expansion is positive in one direction and negative in o Similarly, velocity of light in a crystal may vary with direction in which it is meas Thus a ray of light passing through a Nicole prism splits into two components travelling with different velocity (double refraction).

Explanation of Isotropy and Anisotropy

In amorphous substance as in liquids the arrangement of particles is random disorder. Therefore all directions are equivalent and properties are independent direction.

On the other hand the particles in a crystal are arranged and well order. Thus arrangement of particles may be different in different directions. This is illustrate figure 5.1 in which a simple two dimensional arrangement of two different types particles has been shown when the property is measured along AB and CD, the value along CD will be different from that along AB. This is so because there is only one type of particle along AB while there are two types of particles in alternate position along CD. This explains why crystalline substances are anisotropic.

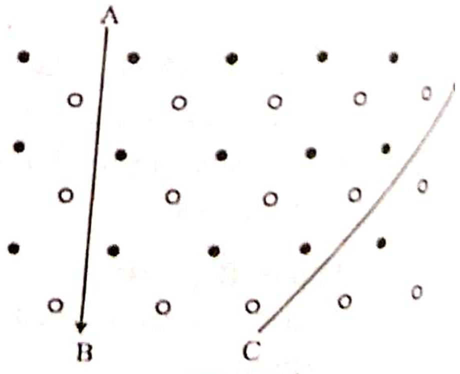


Fig. 5.1

5.2 Crystallography

Crystallography is a branch of science which deals with the study of geometry, properties and structure of crystals and crystalline substances. The science of crystallography is concerned with the enumeration and classification of all possible types of crystal structure and the determination of the actual structure of the crystalline solids. Today it includes not only regular solid but also other substances like plastics and rubber because it brings out principles of structure

Some common terms used in crystallography

a) **Crystallographic face or plane;** The flat surfaces containing component particles which define geometry of crystals so that particles are not present beyond this surface is known as crystallographic face or plane (Fig. 5.2).

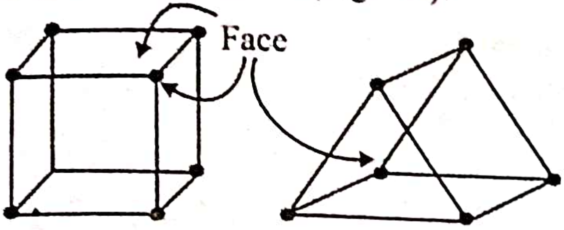


Fig. 5.2

b) **Crystallographic axes or edge:** It is line along which two adjacent faces intersect. There are three axes which are represented by X, Y & Z or a, b, & c. They are perpendicular to each other (Fig. 5.3).

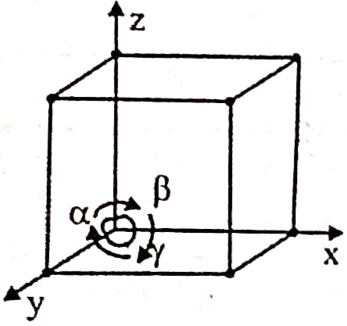


Fig. 5.3

c) **Crystallographic angles or interfacial angles;** These are defined as the angles at which two faces meet. These are represented α, β & γ (Fig. 5.3) such angles may be 90^0 or may not be 90^0

d) **Lattice point:** It is defined as representation of position occupied by component particle in crystal structure in the form of a dot or point (Fig 5.4). This lattice point represents only the position of particle. It does not at all represent shape, size, chemical nature etc. of the particle.

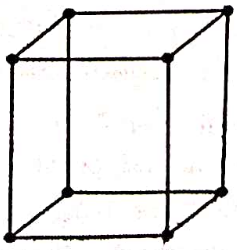


Fig. 5.4

e) **Crystal lattice or space lattice:** It is defined as representation of infinite lattice points repeated regularly in the three dimensional space.

So it is collection or array of large number of lattice points. Here each lattice p the space lattice has identical surroundings.

i) **Unidirectional lattice:** It is a set of lattice points arranged at equal distance straight line (Fig. 5.5a).

Fig. 5.5 (a)

ii) **Bidirectional lattice:** It is a set of lattice points arranged at equal distance X and Y axes (Fig.5.5b).

iii) **Three dimensional lattice:** (or space lattice): It is a set of lattice points a at equal distance along X, Y and Z axes (Fig. 5.5c).

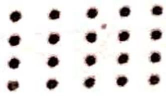


Fig.5.5 (b)

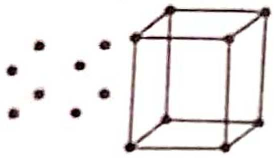


Fig.5.5 (c)

f) **Lattice planes:** These are defined as parallel equidistant planes containing l points (Fig. 5.6).

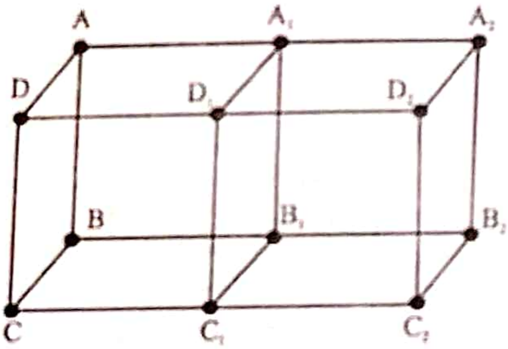


Fig. 5.6

Here planes ABCD, A_1 B_1 C_1 D_1 and A_2 B_2 C_2 D_2 are lattice planes similar remaining planes are also lattice plane.

g) **Unit Cell:**

It is defined as smallest geometrical portion of the crystal which represent crystal in shape, geometry, faces, symmetry and angles but not in size.

The unit cell shows all characters of given crystal, but it is smallest in size. unit cell on extension and repetition in all directions give the actual crystal given crystal is made up of a very large number of such unit cells adjacent to other in the three dimensional space. (Fig 5.7)

Thus naturally unit cell and actual crystal are made up of same compo particles i.e. atoms or ions or molecules. Here structure with thick and dotted line a unit cell. So a large number of such unit cells give space lattice.

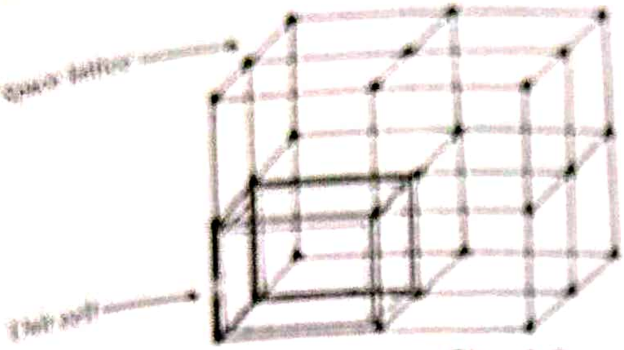


Fig. 5.7

5.3 Symmetry in Crystals

In crystallography, symmetry is used to characterise crystals, identify repeating parts of molecules. Also, the symmetry of physical properties of a crystal such as thermal conductivity and optical activity must include the symmetry of the crystal. Symmetry, is the fundamental property of the orderly arrangements of atoms found in crystalline solids. Each arrangement of atoms has a certain number of elements of symmetry, i.e., changes in the orientation of the arrangement of atoms seem to leave the atoms unmoved.

Symmetry and elements of symmetry

The given structure is said to have symmetry with respect to some process or operation if carried out on it then that structure is reproduced. Such process in known as symmetry operation. The planes, axes and center with reference to which symmetry operations are carried out are known as **elements of symmetry**.

A) Plane of symmetry

A crystal has plane of symmetry when an imaginary plane passing through the centre of crystal can divide it into two parts which are mirror images of each other.

Fig.5.8

Plane of symmetry for cubic crystal

The cubic crystal has two types of planes of symmetry

i) **Rectangular plane of symmetry**: It is an imaginary plane which passes through centre of two opposite faces (Fig 5.9 a).

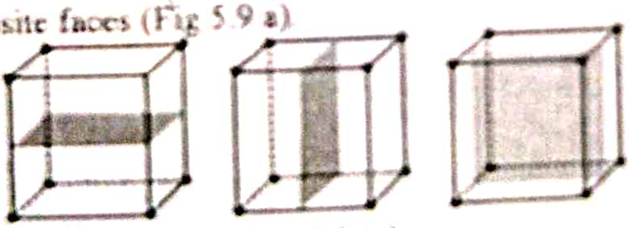


Fig. 5.9 (a)

Cubic crystal has six faces.

Hence, rectangular plane of symmetry for cubic crystals $= \dfrac{\text{Number of faces}}{2} = \dfrac{6}{2} = 3$

Therefore, cubic crystal has three rectangular plane of symmetry

ii) **Diagonal plane of symmetry:** It is such plane which passes diagonally thro opposite edges of cube (Fig.5.9 b)

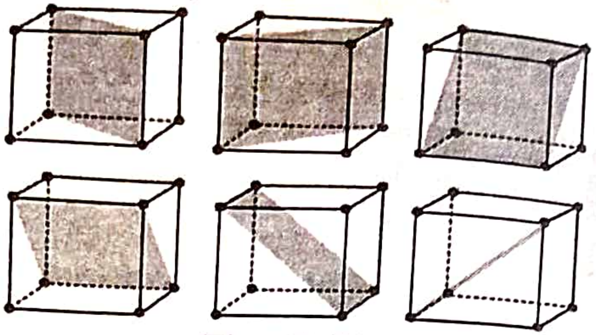


Fig. 5.9 (b)

Cubic crystal has twelve edges.

Hence, digonal plane of symmetry for cubic crystals $= \frac{\text{Number of edges}}{2} = \frac{12}{2} = 6$

Therefore, cubic crystal has six rectangular plane of symmetry

Total plane of symmetry for cubic crystal = rectangular plane of symmetry + diagonal plane of symmetry

= 3 + 6

= 9

Hence cubic crystal has total nine plane of symmetry.

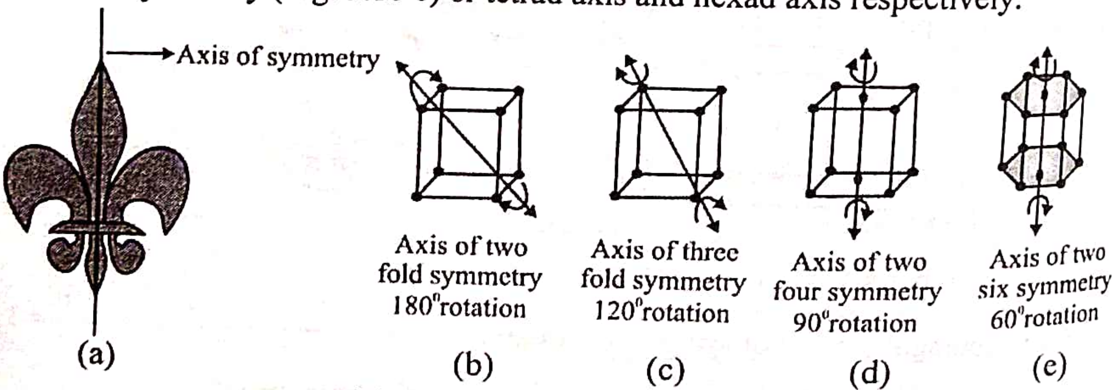
B) Axis of symmetry

An axis of symmetry is the imaginary line passing through centre of crystal suc that if the crystal is rotated through 360^0 then similar faces (or position) appears mor than one during a complete rotation. Crystal may have many fold of axes depending o the number of times the crystal appears unchanged. (Fig. 5.10 a)

i) If the crystal appears unchanged twice, during one rotation (i.e. after every 180^0) the axis is said to have two fold of symmetry or it is known as diad axis (Fig. 5.10 b).

ii) If the crystal has similar appearance thrice (i.e. after every 120^0) the axis is said to have three fold of symmetry or triad axis (Fig. 5.10 c).

iii) If the crystal shows similar appearance four times (i.e. after every 90^0) and six times (i.e. after every 60^0) the corresponding axis is said to have four fold (Fig. 5.10 d) and six fold symmetry (Fig. 5.10 e) or tetrad axis and hexad axis respectively.



(a)

Axis of two fold symmetry 180°rotation
(b)

Axis of three fold symmetry 120°rotation
(c)

Axis of two four symmetry 90°rotation
(d)

Axis of two six symmetry 60°rotation
(e)

Fig. 5.10 : Axis of symmetry

The cubic crystal has 13 axes of symmetry, six axes of two fold, four axes of three fold, and three axes of four fold.

3) Centre of symmetry

Centre of symmetry is a point in a crystal that any imaginary line drawn through it will meet the surface of the crystal at equal distance on either side. The cubic crystal has only one centre of symmetry. (Fig. 5.11)

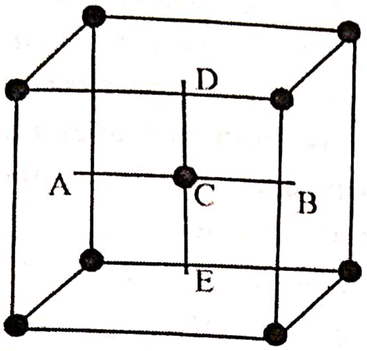


Fig. 5.11 : Centre of symmetry

Hence cubic crystal has total twenty three (nine plane +13 axis + one centre) element of symmetry.

5.4 Laws of Crystallography

Crystallography is based on three fundamental laws

i) Laws of constancy of interfacial angles
ii) Law of constancy of symmetry
iii) Law of rational indices

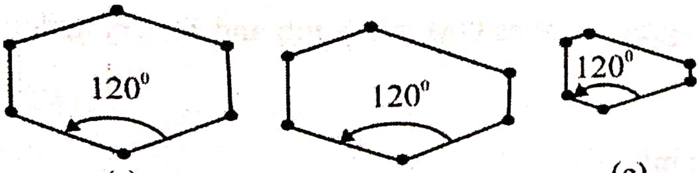
i) Laws of constancy of interfacial angles

This law was proposed by Steno in 1669. According to this law "The crystals of same substance can have different shape depending upon the number and size of faces, but the angle between the corresponding faces remains constant".

Or "Whatever may be the apparent shape of crystal, the interfacial angles are always same" Or "The interfacial angles for any given crystal is same and constant irrespective of its shape and its method of preparation"

Thus, a given crystal may be produced by different methods and under different conditions. The size and shape of faces may be different. However, angle between given set of faces remain same.

Ex. : A crystal of quartz has three different shapes as shown in Fig. 5.12 (a), (b) and (c) but the angle remains same at 120^0.



(a) (b) (c)

Fig. 5.12 : crystals of quartz

ii) Law of constancy of symmetry

According to this law "All crystals of the same substance have same elemen symmetry". The total number of planes, lines and centers of symmetries possessed a crystal is termed as the elements of symmetry of crystals.

iii) Law of rational indices or intercepts

This law was proposed by Hauy in 1784. We know that crystal lattice consist unit cells arrange in parallel planes. Thus each crystal plane lies parallel to the cry face as also to the unit cell face. These planes cut the three axis along the crystallographic axes (OX,OY,OZ). Hauy proposed that given crystal plane could described in terms of intercepts along the axes (Law of rational intercepts). T reciprocals of these intercepts are small whole numbers.

This law states that "intercepts made by any lattice plane on the crystallograph axes are integral multiples of unit cell intercepts". According to this law the interce of any plane of a crystal along the crystallographic axes are either equal to the u intercept or some small whole number multiples of them.

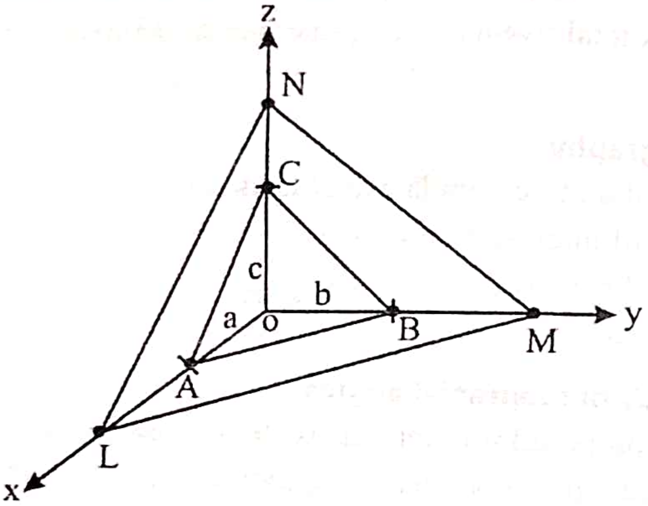


Fig. 5.13 : Law of rational indices

Ex. Let OX, OY, OZ represents the three crystallographic axes and ABC be a unit (standard) plane. So that OA = a, OB = b and OC = c. Then unit intercept will be a (OA), b (OB), c (OC). If any plane LMN when placed along same axes so that OL=x, OM=y and ON = z (Fig. 5.13) Then it gives the intercepts x (OL), y (OM), z (ON), then according to law of rational intercepts- the intercept of plane LMN of a crystal along the crystallographic axes OL is equal to the unit intercept or some small whole number multiples of them".

OR $OL = x = la$.

Similarly for crystallographic axes $OM = y = mb$ and for crystallographic axes $ON = z = nc$

Hence the ratio

$$x : y : z = la : mb : nc$$

Where, the multiplies l, m and n are either integral whole number or fraction of whole numbers. The coefficients of a, b, c in the ratio of intercepts are known as Weiss Indices.

Here l, m, n is known as Weiss indices. The reciprocal of these numbers $\left(\text{i.e. } \frac{1}{l}\frac{1}{m}\frac{1}{n}\right)$ are written together in brackets (h k l) to give the Miller indices of the plane under study.

According to hauy law of rational indices, the intercepts of any plane or face of a crystal on the crystallographic axes are either :

- Equal to the unit intercepts (a, b, c)
- Some simple whole number multiple of them are simple integers like 1, 2,3
- One or two intercepts may be infinity, when the crystal planes are parallel to one or two axes.

5.5 Weiss Indices

Indices mean indictor of crystal plane. It is important to study the crystal structure. The Weiss parameters, introduced by Christian Samuel Weiss in 1817, are the ancestors of the Miller indices. Weiss indices will help to determine the distance between parallel planes of the crystal. They give an approximate indication of a face orientation with respect to the crystallographic axes, and were used as a symbol for the face.

"The ratio of the distances from the origin at which a face intersects the crystallographic axes is known as Weiss Indices of plane".

OR "The coefficients in the ratio of intercepts are defined as Weiss Indices".

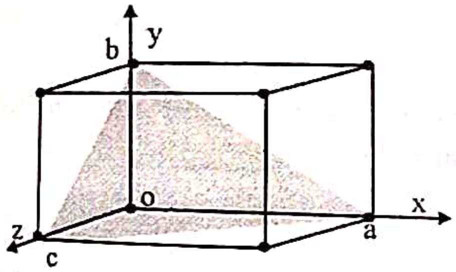
OR "Weiss indices are the ratio of the intercepts on that axis to the unit length of that axis".

Weiss indices = intercepts on that axis / unit length on that axis

Let ABC be unit plane and OX, OY, OZ are the crystallographic axes

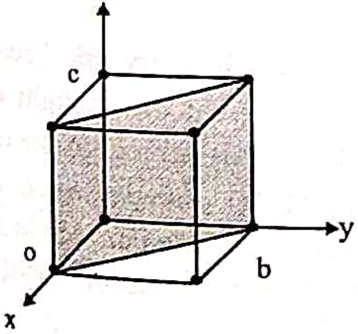
Unit length on crystallographic axes = a, b, c along OA, OB, OC

$$\text{Weiss Indices} = \frac{\text{intercepts on that axis}}{\text{unit length on that axis}}$$



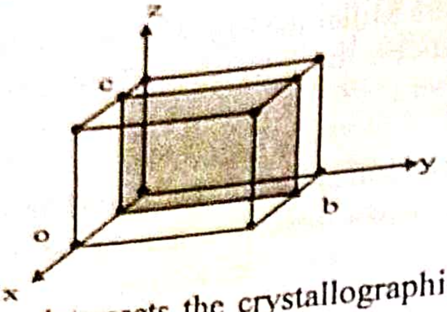
$$\text{Weiss indices} = \frac{a}{a}\frac{b}{b}\frac{c}{c}$$
$$= 1 \ \ 1 \ \ 1$$

Here given plane intersects the crystallographic OX, OY and OZ axis at unit length a,b and c respectively



$$\text{Weiss indices} = \frac{a}{a}\frac{b}{b}\frac{\infty c}{c}$$
$$= 1 \ \ 1 \ \ \infty$$

Here given plane intersects the crystallographic OX and OY at unit length a and b, b
is parallel to OZ.



$$\text{Weiss indices} = \frac{a}{2a}\ \frac{\infty b}{b}\ \frac{\infty c}{c}$$

$$= \frac{1}{2}\ \infty\ \infty$$

Here given plane intersects the crystallographic OX at half of the unit length a (i, a/2). But it is parallel to OY and OZ.

NOTE: In Weiss indices we used a, b, c for different crystallographic axes.

Conditions for Weiss Indices

In Weiss indices a, b, c values may be fraction, integers, positive, nega infinite but never be zero.

Hence from above we conclude that Weiss indices are undefined. So there need of Miller Indices.

5.6 Miller Indices

The concept of Miller indices was introduced by British scientist Will Hallowns. Miller indices are the mathematical notation to represent crystal planes an direction in crystal structure. These directions and planes could be in lattices o crystals. The number of indices will match with the dimension of the lattice or the crys "Miller Indices are the reciprocals of the distance from the origin at which a given intersects the three axes".

Or "Miller Indices of plane may be defined as the reciprocals of the intercepts which plane makes with the axes".

Or "It is reciprocal of Weiss indices".

In Miller indices, group of three integers (h k l) that shows the orientation plane or group of planes in a crystal. It is also denoted by M.I.

(hkl) represent the plane
{hkl} represents family of plane
[hkl] represents direction
<hkl> represents family of direction

Importance of Miller Indices

Miller indices define coefficients of imaginary planes in a crystal. Accordin the Bragg interpretation of X-ray diffraction (1912), X-rays can be thought of bei reflected by such planes, and produce a Bragg peak/ diffraction, subject to the conditi being followed as per Bragg's law. Now, since the Miller indices when arrang sequentially, themselves form a 3-D lattice, it gives rise to an elegant construction diffraction space. Such a construction leads to the reciprocal lattice, which wh superposed on the Ewald sphere in a particular way, allows one to construct the diffraction space. Thus, the entire diffraction by a crystal can now be seen as the image of the reciprocal lattice.

Conditions for Miller Indices

It can be integers positive, negative and zero but it never be infinite or fractions.

If Miller indices are negative it is denoted by bar on top of that indices.

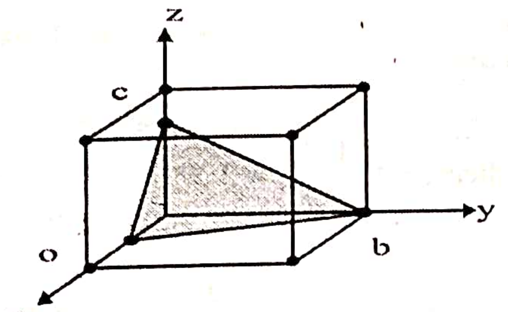
For example-M.I. is (-3 -2 1) then it can be written as $(\bar{3}\bar{2}1)$

Steps involved in Miller Indices

1) First find the Weiss indices by using steps described above
2) Now write reciprocals of Weiss indices
3) Find out LCM of denominators
4) Multiply each reciprocal by LCM
5) The values obtained are Miller Indices
6) Write the miller indices in parenthesis ( ) without space like (hkl)

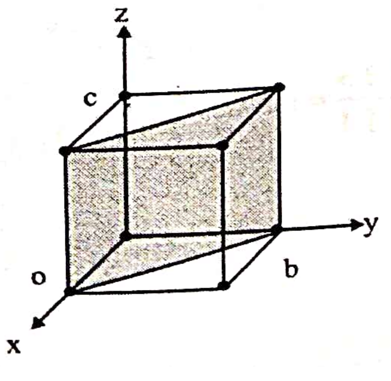
Q.1 : Find out the Weiss and Miller indices for following crystallographic planes.

a)



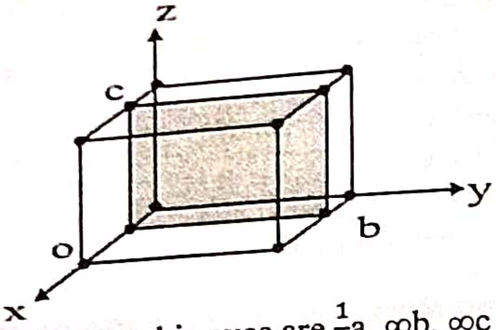
1) Here intercepts along crystallographic axes are $\frac{1}{2}a$, 1b, $\frac{3}{4}c$
2) Unit length on axis a,b,c
3) Weiss indices $=\frac{1a}{2a}\frac{b}{b}\frac{3c}{4c}=\frac{1}{2}1\frac{3}{4}$
4) Reciprocals of Weiss indices = 2 1 $\frac{4}{3}$
5) LCM = 3
6) Multiply by LCM $=2\times3 \quad 1\times3 \quad \frac{4}{3}\times3 \;=\; 6\;3\;4$
7) Miller Indices = (634)

b)



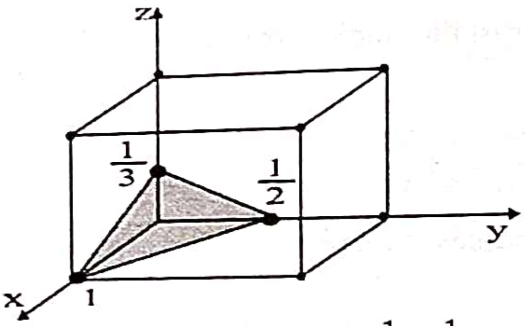
1) Here intercepts along crystallographic axes are 1a, 1b, ∞c
2) Unit length on axis a,b,c
3) Weiss indices $= \frac{a}{a}\frac{b}{b}\frac{\infty c}{c} = 1\ 1\ \infty$
4) Reciprocals of Weiss indices $= \frac{1}{1}\frac{1}{1}\frac{1}{\infty} = 1\ 1\ 0$
5) Miller Indices = (110)

c)



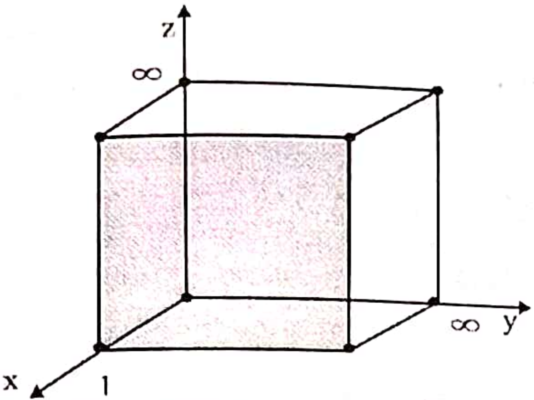
1) Here intercepts along crystallographic axes are $\frac{1}{2}$a, ∞b, ∞c
2) Unit length on axis a,b,c
3) Weiss indices $= \frac{1a}{2a}\frac{\infty b}{b}\frac{\infty c}{c} = \frac{1}{2}\ \infty\ \infty$
4) Reciprocals of Weiss indices $= 2\ \frac{1}{\infty}\frac{1}{\infty} = 2\ 0\ 0$
5) Miller Indices = (200)

d)



1) Here intercepts along crystallographic axes are a, $\frac{1}{2}$ b, $\frac{1}{3}$ c
2) Unit length on axis a, b, c
3) Weiss indices $= \frac{a}{a}\frac{b}{2b}\frac{c}{3c} = 1\ \frac{1}{2}\ \frac{1}{3}$
4) Reciprocals of Weiss indices $= \frac{1}{1}\frac{2}{1}\frac{3}{1} = 1\ 2\ 3$
5) Miller Indices = (123)

e)



1) Here intercepts along crystallographic axes are a, ∞b, ∞c
2) Unit length on axis a,b,c
3) Weiss indices $= \frac{a}{a}\frac{\infty b}{b}\frac{\infty c}{c} = 1\infty\ \infty$
4) Reciprocals of Weiss indices $= \frac{1}{1}\frac{1}{\infty}\frac{1}{\infty} = 1\ 0\ 0$
5) Miller Indices = (100)

Q.2 : Find out Miller indices if Weiss indices are

a) 2a, -3b, -3c
1) Here intercepts along crystallographic axes are 2a, -3b, -3c
2) Unit length on axis a,b,c
3) Weiss indices $= \frac{2a}{a}\frac{-3b}{b}\frac{-3c}{c} = 2-3-3$
4) Reciprocals of Wiess indices $= \frac{1}{2}\frac{1}{-3}\frac{1}{-3}$
5) LCM = 6
6) Multiply by LCM $= \frac{1}{2}\times 6 \frac{1}{-3}\times 6 \frac{1}{-3}\times 6 = 3\ \ -2\ \ -2 = 3\ \bar{2}\ \bar{2}$
7) Miller Indices = $(3\bar{2}\bar{2})$

b) 2a, b, c
1) Here intercepts along crystallographic axes are 2a, b, c
2) Unit length on axis a,b,c
3) Weiss indices $= \frac{2a}{a}\frac{b}{b}\frac{c}{c} = 211$
4) Reciprocals of Wiess indices $= \frac{1}{2}\frac{1}{1}\frac{1}{1}$
5) LCM = 2
6) Multiply by LCM $= \frac{1}{2}\times 2\frac{1}{1}\times 2\frac{1}{1}\times 2 = 1\ \ 2\ \ 2$
7) Miller Indices = (122)

c) 1 1 2

1) Here Weiss indices = 1 1 2
2) Reciprocal of Weiss indices $=\frac{1}{1}\frac{1}{1}\frac{1}{2}$
3) LCM = 2
4) Multiply by LCM $=\frac{1}{1}\times 2\frac{1}{1}\times 2\frac{1}{2}\times 2 = 2\quad 2\quad 1$
5) Hence Miller Indices = (221)

d) 2 ∞ 3

1) Here Weiss indices = 2 ∞ 3
2) Reciprocal of Weiss indices $=\frac{1}{2}\frac{1}{\infty}\frac{1}{3}$
3) LCM = 6
4) Multiply by LCM $=\frac{1}{2}\times 6\quad 0\times 6\quad \frac{1}{3}\times 6\quad = 3\quad 0\quad 2$
5) Hence Miller Indices = (302)

5.7 Seven crystal system and fourteen Bravais Lattices

Bravais showed from geometrical consideration that there are only 14 pos ways of arranging lattice points in space. These are named as Bravais lattices.

There are 32 different possible combinations of elements of symmetry. These known as 32 point groups. These 14 Bravais lattices or 32 point groups are grouped i types known as crystal families or crystal systems. The geometry of crystal ca defined in terms of 3 axes & 3 angles in such 7 families. These are summarize follows

1) Regular or cubic system: In this system the three axes have equal 90^0 angle tc another i.e. $\alpha = \beta = \gamma = 90^0$ and all the three axes are equal a = b = c. This system has types of lattices depending upon the shape of unit cells. Ex. NaCl, KCl, Alum.

a) **Simple cubic:** In this particles are only at the centre of the cube.

b) **Face centered:** In this particles are at the corner as well as at the center of ea the six faces of cube.

c) **Body centered:** In this the particles are at the corner as well as at the centre of c

2) Tetragonal system: In this system the three axes are at right angle to each other two lateral axes are equal i.e. $\alpha = \beta = \gamma = 90^0$ and a = b ≠ c. Ex. Thorite (THO_2), An (TiO_2), Cassiterite (SnO_2).

3) Rhombic system (Orthorhombic): In this system the three axes are at right ang each other but these three axes are unequal i.e. $\alpha = \beta = \gamma = 90^0$ and a ≠ b ≠ c Celestine ($SrSO_4$), Epsomite ($MgSO_4\ 7H_2O$), Olivine(Mg_2SiO_4) and Car ($KCl, MgCl_2\ 6H_2O$).

4) Monoclinic system: In this system only two axis are at right angle to each other and all the three axes are unequal i.e. $\alpha = \gamma = 90^0$, $\beta \neq 90^0$ and $a \neq b \neq c$. Ex. Mohr's salt, orthoclate, cryolite and borax.

5) Triclinic system: In this system out of three angles no one is at right angle to each other and all the three axes are unequal i.e. $\alpha \neq \beta \neq \gamma \neq 90^0$, and $a \neq b \neq c$. Ex- Blue vitrol, Albite, Potassium dichromate.

6) Rhombohedral or trigonal system: In this system only two axis are at right angle to each other and all the three axes are equivalent i.e. $\alpha = \gamma = 90^0$, $\beta \neq 90^0$ and $a = b = c$. Ex- Fe_2O_3, Al_2O_3.

7) Hexagonal system: In this system out of three axes only two axes are at right angle to each other and one axis is 120^0 and the two axes are equal while third axis is unequal with remaining two i.e. $\alpha = \beta = 90^0$, $\gamma = 120^0$ and $a = b \neq c$. Ex- Beryl, apatite, Zincite, ice.

Table: Seven Crystal Systems

S.N.	Crystal	Axial Intercepts	Axial Angles	Examples
1	Cube	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	NaCl, KCl, Alums
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	TiO_2, SnO_2
3	Rhombic	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	Rhombic sulphur (or orthorhombic KNO_3)
4	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^0$ $\beta \neq 90^\circ$	Monoclinic sulphur, $Na_2SO_4.10H_2O$
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$
6	Trigonal	$a = b = c$	$\alpha = \gamma = 90^0$ $\beta \neq 90^\circ$	Fe_2O_3, Al_2O_3 (or Rhombohedral)
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0 \gamma = 120^0$	ZnO, PbI_2, Cd, Ice

The French crystallographer Bravais in 1848 postulated that seven crystal systems can exist in 14 distinct types of configurations. These fourteen arrangements are known as Bravais Lattices. The 14 Bravais Lattices are as follow:

Crystal	Bravais lattices
1. Cubic crystal	Simple, face centred, body centred
2. Tetragonal	Simple , body centred
3. Rhombic (Orthorhombic)	Simple, base centred, body centred, face centred
4. Monoclinic	Simple , base centred
5. Triclinic	Simple
6. Trigonal (Rhombohedral)	Simple
7. Hexagonal	Simple

The fourteen Bravais lattices in seven crystal system shown below

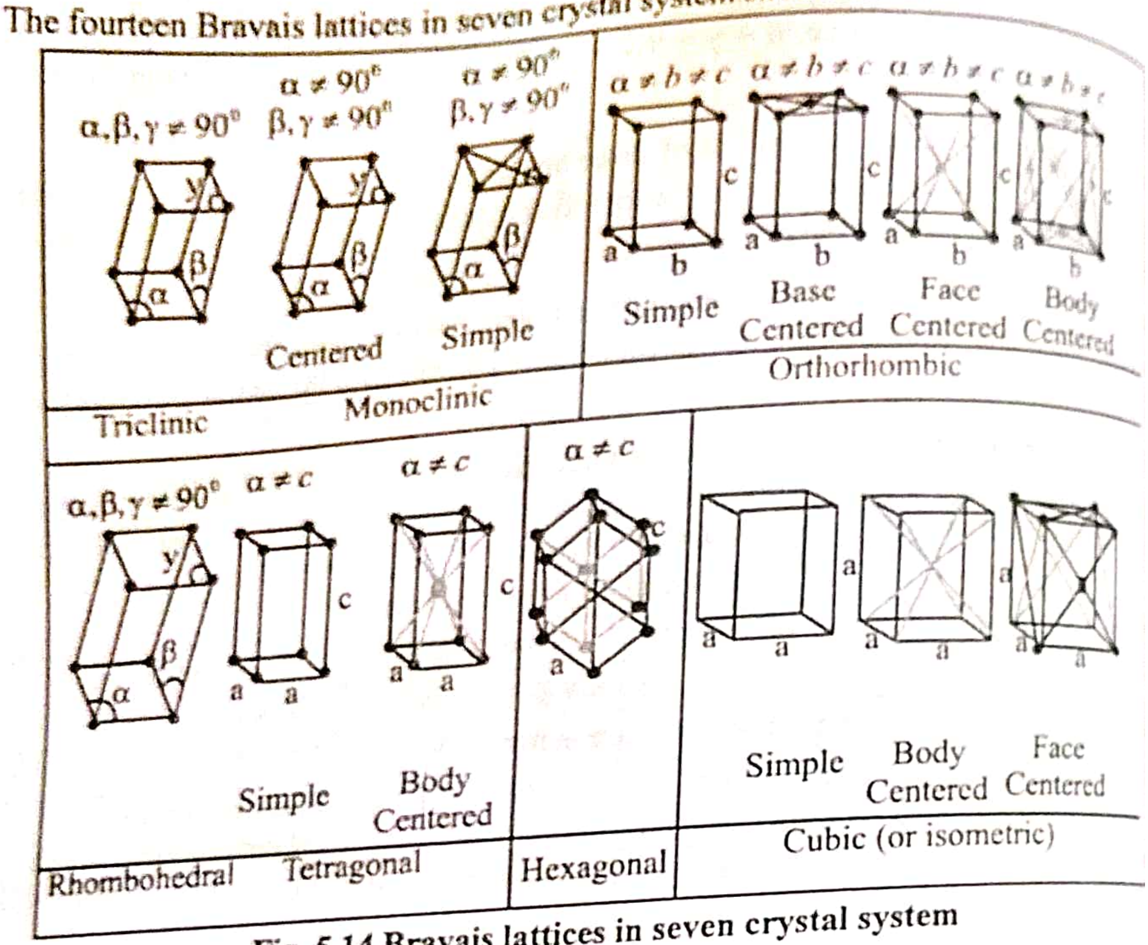
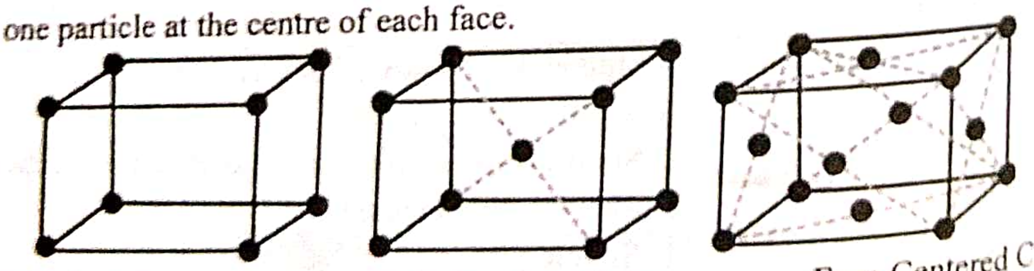


Fig. 5.14 Bravais lattices in seven crystal system

5.8 Bravais lattices for cubic crystals:

The cubic crystal has three types of Bravais lattices. It depends on the positi occupied by component particles in the unit cell. These are as follows.

1. **Simple cubic crystal (scc) or primitive:** It has component particles only at corners of the cube
2. **Body centred cubic crystal (bcc):** It has component particles at each corner as as one particle at the centre of cubic crystal.
3. **Face centred cubic crystal (fcc):** It has component particles at each corner as as one particle at the centre of each face.



Simple Cube (a) Body Centered Cube (b) Face Centered Cube (c)

Fig. 5.15 : Bravais lattices in seven crystal system

5.9 Calculation of number of constituent units in the cubic unit cell

The number of particles in the unit cell of simple (primitive), face centered and body centered cubic lattice are calculated as follow.

The number of such component particles present in the unit cell is known as lattice site and represented by Z.

1. **For simple cubic lattice (SCC):** In simple cubic lattice there is one particle at each corner of the cube, being all eight. Hence corner particle contributes only 1/8 to each cube.

$$\underset{\text{in one unit cell}}{\text{Number of particles}} = \underset{\text{corners}}{\text{number of}} \times \underset{\text{each corner particle}}{\text{contribution by}}$$

$$Z = 8 \times \frac{1}{8}$$

$$Z = 1$$

2. **For body centered cubic lattice (BCC):** In body centered cubic crystal particles are at each corner and one at centre of unit cell. The corner particles contribute 1/8 to the unit cell while the one particle at the centre contributes 1 to each unit cell.

$$\underset{\text{in one unit cell}}{\text{Number of particles}} = \underset{\text{corners}}{\text{number of}} \times \underset{\text{each corner particle}}{\text{contribution by}} + \underset{\text{central particle}}{\text{contribution by}}$$

$$Z = \left(8 \times \frac{1}{8}\right) + 1$$

$$Z = 2$$

3. **For face centered cubic lattice (FCC):** In face centered cubic crystal particles are at each corner and at centre of six faces. Particles present in the face of unit cell contributes only ½ to each unit cell.

$$\underset{\text{in one unit cell}}{\text{Number of particles}} = \underset{\text{corners}}{\text{number of}} \times \underset{\text{each corner particle}}{\text{contribution by}} + \underset{\text{Faces}}{\text{Number of}} \times \underset{\text{central particle}}{\text{contribution by}}$$

$$Z = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right)$$

$$Z = 4$$

The value of Z is related with density of crystal matter and molecular weight of it, by following equation.

$$Z = \frac{N_A \times a^3 \times D}{M}$$

Where,

N_A = Avogadro number (6.023×10^{23})
a = length of side of a cube in m
D = density of crystal matter in Kg/m^3
M = molar mass in Kg/mol

Problem 1: The length of side of unit cell of a cubic crystal in 4×10^{-8} m. The density of crystal matter is 1.2×10^{-3} Kg m^{-3}. If molar mass is 2.4×10^{-2} Kg $mole^{-1}$ then find out.

i) Type of lattice ii) Number of atoms in each unit cell ($N_A = 6.023 \times 10^{23}$)

Solution: Here $a = 4 \times 10^{-8}$ m, $D = 1.2 \times 10^{-3}$ Kg m^{-3}, $M = 2.4 \times 10^{-2}$ Kg mole^{-1},

$$N_A = 6.023 \times 10^{23}$$

$$Z = \frac{N_A . a^3 . D}{M}$$

$$Z = \frac{6.023 \times 10^{23} \times \left(4 \times 10^{-8}\right)^3 \times 1.2 \times 10^{-3}}{2.4 \times 10^{-2}}$$

$$Z = 1.9273 \cong 2$$

So this is the body centered lattice, since $Z = 2$ and number of atoms in each unit cell

Problem 2: Sodium has bcc lattice with density of 1x 10^{-3} Kg m^{-3} and molar ma 23 x 10^{-3} Kg mole^{-1}. Find out length of edge of its unit cell (given N_A = 6.023x 10

Solution: Here $D = 1 \times 10^{-3}$ Kg m^{-3}, $M = 23 \times 10^{-3}$ Kg mole^{-1}, $N_A = 6.023 \times 10^{23}$

$$Z = 2 \text{ since it is bcc}$$

$$Z = \frac{N_A . a^3 . D}{M}$$

$$2 = \frac{6.023 \times 10^{23} \times a^3 \times 1 \times 10^{-3}}{23 \times 10^{-3}}$$

$$a^3 = \frac{2 \times 23 \times 10^{-3}}{6.023 \times 10^{23} \times 1 \times 10^{-3}}$$

$$a = 4.3346 \times 10^{-10} \text{m}$$

Length of edge of unit cell of sodium = 4.3346×10^{-10} m = 4.3346 $\overset{o}{A}$

5.10 Interplanar distance d_{hkl} from Miller indices in cubic system

The perpendicular distance between two adjacent parallel lattice planes hav same Miller indices is called the inter planer spacing. The inter planar distance between two successive lattice is given by expression.

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

Where,

$h\,k\,l$ = Miller's indices

d_{hkl} = distance between two successive planes

a, b and c = length of unit cell

But for cubic crystal length of all side along crystallographic axes is sa (a=b=c) then above equation deduce to

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}}} \text{ OR } d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2 + l^2}{a^2}}} \text{ OR } d_{hkl} = \frac{\sqrt{a^2}}{\sqrt{h^2 + k^2 + l^2}} \text{ OR } d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Hence interplanar distance for cubic crystal is

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

i) Inter planar distance in simple cubic lattice.

In simple cubic lattice one unit is situated only at each corner of the cubic cell.

i) Interplanar distance for 100 planes in SCC.

In a simple cubic lattice, the (100) plane cut the X-axis and are parallel to Y and Z axes as shown in fig. 5.16

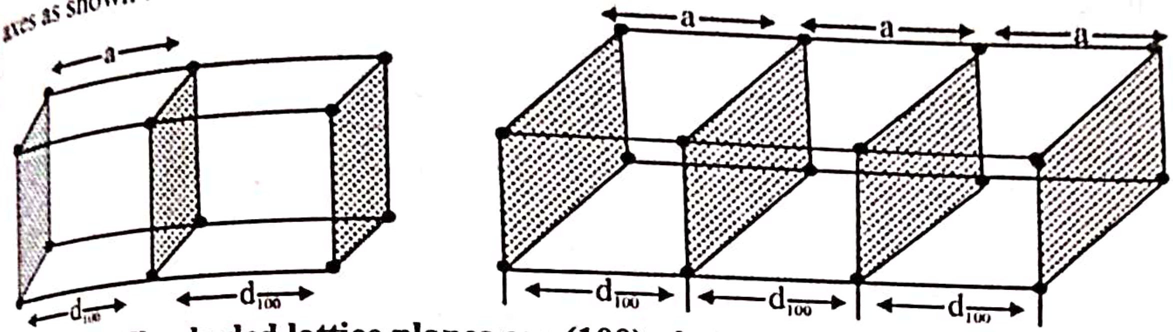


Fig. 5.16 : The shaded lattice planes are (100) planes in the simple cubic lattice

The interplanar distance for (100) plane is denoted by d_{100} and is calculated by using h=1, k=0, l=0 in equation.

$$d_{100} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = \frac{a}{\sqrt{1}} = a$$

ii) Interplanar distance for 110 plane in SCC.

The (110) plane cut across the X and Y axes but cut the Z axis at infinity i.e. parallel to Z axis as shown in fig. 5.17

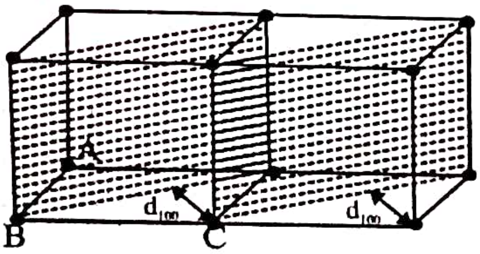


Fig. 5.17 : The shaded lattice plane is (110) plane in the simple cubic lattice

The interplanar distance for (110) plane is denoted by d_{110} and is calculated by using h=1, k=1, l=0 in equation.

$$d_{110} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}}$$

iii) Interplanar distance for 111 plane in SCC.

The (111) plane cuts all the three axes (X, Y & Z) and intercept each axis at the same distance from the origin as shown in fig. 5.18

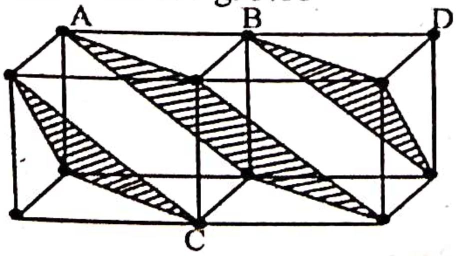


Fig. 5.18 : The shaded lattice planes are (111) planes in the simple cubic lattice

The interplanar distance for (111) plane is denoted by d_{111} and is calculated using h=1, k=1, l=1 in equation.

$$d_{111} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

Hence the ratio of interplanar distance for (100), (110), (111) plane in simple cubic latti will be

$$d_{100} : d_{110} : d_{111} = a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}}$$

or $$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

or $$d_{100} : d_{110} : d_{111} = 1 : 0.707 : 0.577$$

2) Interplanar distance in face centered cubic lattice.

In face centered cubic lattice one unit is situated at each corner and one unit at centre of each of the faces.

In FCC an additional plane can be passed through the middle. They pass throu the centre of front and back faces vertically.

i) Interplanar distance for 100 plane of FCC.

In FCC there is an additional plane (100) between two successive 100 plane, t the interplanar distance for 100 plane of FCC will be half of the cubic lattice fig 5.19.

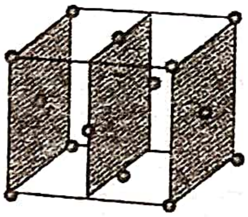


Fig. 5.19 : The shaded lattice planes are (100) planes in the face centered cubic lattice, additional plane is present in the middle

The interplanar distance for 100 plane of FCC will be half the distance of SCC

$$d_{100} = \frac{a}{2}$$

ii) Interplanar distance for 110 plane of FCC:

Interplanar distance for 110 plane of FCC is half of the interplanar distance 110 plane of simple cubic lattice. fig.5.20

$$d_{110} = \frac{a}{2\sqrt{2}}$$

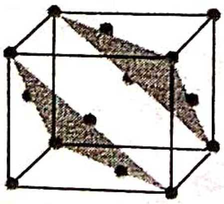


Fig. 5.20 The shaded lattice planes are (110) planes in the face centered cubic latti additional plane is present on the two sides

nterplanar distance for 111 plane of FCC:

The interplanar distance for 111 plane of FCC is same as that for a simple cubic ice. This is because (111) plane pass through the centre of all the faces of the face entered lattice. fig. 5.21

$$d_{111} = \frac{a}{\sqrt{3}}$$

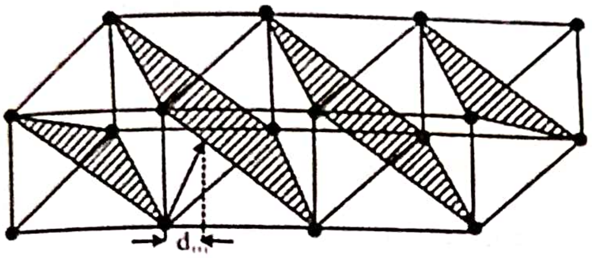


Fig. 5.21 : The shaded lattice planes are (111) planes in the face centered cubic lattice.

ence the ratio of interplanar distance for (100), (110), (111) plane in face centerd cubic ttice will be

$$d_{100} : d_{110} : d_{111} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}}$$

r $$d_{100} : d_{110} : d_{111} = \frac{1}{2} : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}}$$

r $$d_{100} : d_{110} : d_{111} = 1 : 0.707 : 1.154$$

Inter planar distance in body centered cubic lattice.

In body centered cubic lattice one unit is situated at each corner and one at the ntre of the cube. In BCC there is an additional plane passing through structural unit.

nterplanar distance for 100 plane of BCC.

In BCC there is an additional plane (100) between two successive 100 plane, thus e interplanar distance for 100 plane of BCC will be half of the cubic lattice.fig. 5.22

$$d_{100} = \frac{a}{2}$$

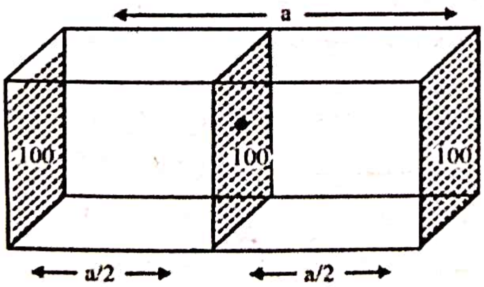


Fig. 5.22: The shaded lattice planes are (100) planes in the body centered cubic lattice, additional plane is present in the middle

Interplanar distance for 110 plane of BCC.

The 110 plane passes through the structural unit in the centre of the cube, hence terplanar distance is same as that of simple cubic lattice. fig.5.23

Problem 1: The length of edge of a cubic lattice is 2.5 A^0. Calculate interplanar distance for its 231 planes.

Solution : $$d_{231} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Here a= 2.5, h = 2, k = 3, $l = 1$

$$d_{231} = \frac{2.5}{\sqrt{2^2 + 3^2 + 1^2}} = \frac{2.5}{\sqrt{14}} = 0.6682\, A^0$$

Problem 2: Interplanar distance for 301 planes was found to be 0.75 A^0. Calculate length edge of its cubic lattice.

Solution : $$d_{301} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Here d_{301}= 0.75 A^0, h = 3, k = 0, $l = 1$

$$0.75 = \frac{a}{\sqrt{3^2 + 0^2 + 1^2}}$$

$$0.75 = \frac{a}{\sqrt{10}} = \frac{a}{3.162}$$

$$a = 2.3715 A^0$$

5.11 Bragg's Equation and Experimental Methods

W.L. Bragg and W.H. Bragg introduced a simple method to study structure of a crystal. X-ray diffraction was used to study internal structure of crystal. They obtained an equation known as Bragg's equation.

Principle: The crystal has a perfectly ordered arrangement of its component particles. It has parallel and equally spaced lattice planes. Thus, the distance between particles and also between lattice planes is same. Such structure acts as a reflection /diffraction grating for X- rays. Here X- rays are used because wavelength of X-rays and interparticle distances are of the same order.

Derivation of Bragg's equation: Consider some given crystal under study. It has very ordered arrangement of its components and lattice planes. Suppose XY, X_1Y_1 and X'Y' etc. are such lattice planes of crystal. Suppose 'd' is the distance between any two successive parallel planes. Bragg's obtained equation for this interplanar distance in terms of wavelength of X-rays, the glancing angle (θ) and the order of reflection (n).

The monochromatic X-rays of known wavelength are incident on first plane. (such X-rays are known as primary X-rays) .The component particle (atom) is the deflecting centre for such X-rays. Let AB is an incident X-rays on first plane at glancing angle θ, The X-ray is reflected from the first plane along BC.

However, some X-rays do not come in contact with any deflecting centre of first plane. So they penetrate the crystal and reach the second plane. They are reflected from this second plane and so on (Fig. 5.25)

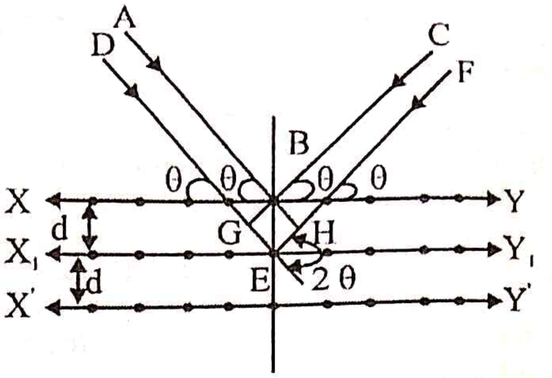


Fig. 5.25 : diagram of Bragg's law

Suppose DE is the X-ray which is incident on the 2nd plane X_1Y_1, and EF reflected X-ray from this plane (Fig. 5.25). It shows that the incident X-ray i required to travel some excess/additional distance than X-rays AB (because it re inner plane). This excess distance traveled is known as path difference (GE+ E depends on glancing angle θ and also on interplanar distance d. This path diffe according to Bragg's must be integral multiple of wavelength λ of X-rays for constr interference of reflected X-rays from these planes.

So total path difference = EG + EH .... (1)

In right angle triangle BGE we get <GBE = θ

Hence EG/BE = sin θ or EG= BE x Sin θ

$$EG = d \times \sin\theta$$

Similarly for right angle triangle BHE we get < HBE = θ

Hence EH/BE = sin θ or EH= BE x sin θ

$$EH = d \times \sin\theta$$

Total path difference = d sin θ + d sin θ

or Total path difference = 2d sin θ .... (2)

According to Bragg's this total path difference is integral multiple of wavel λ for constructive interference.

Total path interference = n λ

Where n=1, 2, 3, 4, etc. and is known as order of reflection

Hence eq. (2) becomes **$n\lambda = 2d \sin\theta$**

This is Bragg's equation.

b) Experimental method for determination of crystal structure

There are different methods for determination of internal structure of crystal. basic principle of all these methods is the study of X-ray diffraction from a given cry These methods are for different order of reflections from different sets of parallel pl (100,110,111).

5.12 Bragg's X-ray spectrometer method: The apparatus used is known as Bragg's ray spectrometer. It is illustrated in (Fig. 5.26).

The different parts of it are as follows-

1. X-ray generator /source (A): Here A is X-ray generator tube. X-rays produced are passed through filter (F as screen), this gives monochromatic X-rays. These pass through slits S_1 and S_2. This gives a sharp and narrow beam of monochromatic X-rays. These are known as primary X- rays and are of known wavelength.

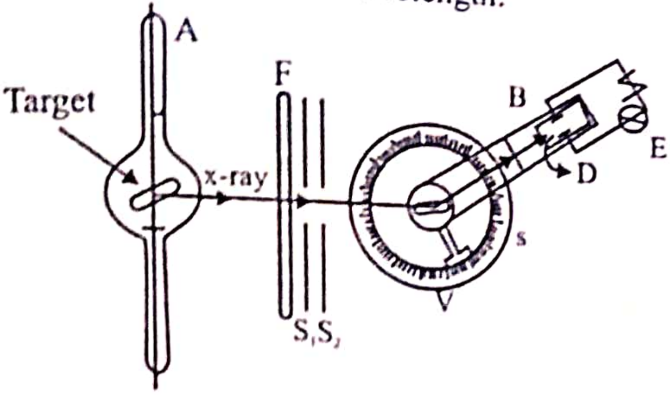


Fig. 5.26

2. Turn table (T): This table (T) is connected to the ionization chamber (B) .The crystal (C) under study is placed on this table (T). The glancing angle is recorded by vernier (V)

3. Ionization Chamber (B): It contains some suitable gas which is ionized by reflected X-rays generally SO_2 or methyl bromide gas is used. One electrode of chamber (B) is connected to positive terminal of battery and to electrometer (E) and other electrode is connected to the negative terminal of battery. This chamber (B) is mounted on arm of turn table (T).Thus (T) and (B) are so adjusted that when (T) rotates through angle θ then (B) rotates through 2θ . Thus all reflected X-rays from crystal shall enter (B).

4. Procedure/ Working

a) The beam of monochromatic X-rays of known wavelength passes into ionization chamber in absence of crystal. This is considered as initial position.

b) Now crystal under study is placed on the turn table (T). This crystal is now exposed to the same X-rays.

c) Small glancing angle is used to start with experiment. The reflected X-rays enter ionization chamber (B).Thus gas inside it is ionized giving current. The intensity strength of ionization current produced is recorded by electrometer.

d) The ionization chamber is moved on circular scale (s) independent of turn table (T), Thus, greater is the intensity of reflected X-rays then greater is ionization and so higher is the strength of current recorded.

e) Now slowly glancing angle is increased by rotating turn table (T) about the vertical axis. Similarly ionization chamber is rotated about the same vertical axis, but at an angle twice greater than that for turn table (T).

f) The intensity of current produced is noted for each glancing angle used. This procedure is repeated for all important planes of crystal (i.e. 100, 110 and 111 planes etc.)

g) The graph is plotted between different glancing angles used and intensity recorded by electrometer. This graph is known as X-ray diffraction pat 5.27)

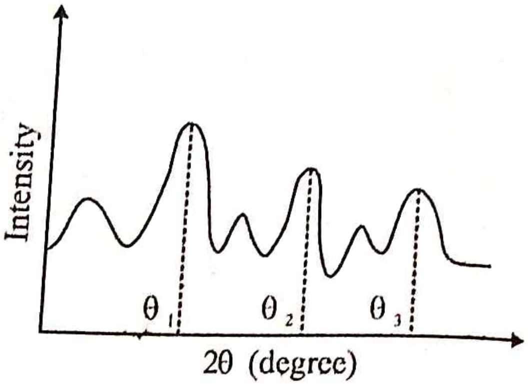


Fig. 5.27

h) θ_1, θ_2, θ_3 etc. glancing angle giving maximum intensity of current for differe of reflection (i.e. n- 1, 2, 3 etc). This ɵ is obtained separately for 100, 110 planes.

i) These values of n and θ are substituted in Bragg's equation i.e. $n\lambda = 2d\sin\theta$

$$d = \frac{n\lambda}{2d\sin\theta}$$

$$d_{100} = \frac{n\lambda}{2d\sin\theta_1}$$

Similarly $$d_{110} = \frac{n\lambda}{2d\sin\theta_2} \quad \text{and} \quad d_{111} = \frac{n\lambda}{2d\sin\theta_3}$$

This is used to calculate ratio of interplanar distance.

$$d_{100} : d_{110} : d_{111} = \frac{n\lambda}{2d\sin\theta_1} : \frac{n\lambda}{2d\sin\theta_2} : \frac{n\lambda}{2d\sin\theta_3}$$

$$d_{100} : d_{110} : d_{111} = \frac{1}{\sin\theta_1} : \frac{1}{\sin\theta_2} : \frac{1}{\sin\theta_3}$$

The value of this ratio is used to know type of crystal lattice (as scc, fcc,bcc etc.)

Problem 1 : The first order reflection maxima from 100, 110 and 111 planes of a c were observed at glancing angles of 11.270, 16.300 and 20.70 respectively. Find out of crystal lattice if wavelength of X-rays is 0.154 nm.

Solution:

Here, $\theta_1 = 11.270$, $\theta_2 = 16.300$, $\theta_3 = 20.70$, $n = 1$, $\lambda = 0.154$ nm

$$d_{100} : d_{110} : d_{111} = \frac{n\lambda}{2d\sin\theta_1} : \frac{n\lambda}{2d\sin\theta_2} : \frac{n\lambda}{2d\sin\theta_3}$$

$$= \frac{0.154}{2\sin 11.27} : \frac{0.154}{2\sin 16.30} : \frac{0.154}{2\sin 20.70}$$

$$= \frac{1}{0.1934} : \frac{1}{0.2806} : \frac{1}{0.3535}$$

$$= 1 : 0.690 : 0.550$$

Thus it is nearly same as for scc. Thus given crystal is scc lattice.

Problem 2 : The first order reflection maxima was noted at 5.90 for 100 planes of scc. Calculate the wavelength of X-rays, if interplanar spacing was 0.282 nm.

Solution : here n =1, d= 0.282, $\theta = 5.90$

$$d = \frac{n\lambda}{2d\sin\theta}$$

$$\lambda = \frac{2\times0.282\times\sin 5.9}{1}$$

$$= 2\times0.282\times0.1027$$

$$\lambda = 0.05792$$

Problem 3: Calculate the glancing angle for first order reflection for 100 planes of fcc. X-rays of wavelength of 0.154 nm are used. Given spacing of 100 planes is 0.315 nm.

Solution: here n = 1, $\lambda = 0.154$ nm d = 0.315

$$n\lambda = 2d\sin\theta$$

$$\sin\theta = \frac{n\lambda}{2d}$$

$$\sin\theta = \frac{1\times0.154}{2\times0.315}$$

$$\sin\theta = 0.2444$$

$$\theta = \sin^{-1}0.2444$$

$$\theta = 14.5^0$$

5.13 Structure of some Common Crystals

A. Structure of NaCl (Common salt)

1. NaCl is an ionic solid. It's component are Na^+ ions and Cl^- ions. These are deflecting centersof X-rays.
2. X-ray diffraction was studied for this crystal by Bragg's method.
3. It was observed that intensities of reflection decrease with increase in order of deflection for 100and 110 planes. So 100 and 110 planes have equal number of Na^+ and Cl^- ions.
4. It was observed that odd number order deflection (i.e. 1st, 3rd order etc.) from (111) planes show minimum intensity. However even number order reflections (i.e. 2nd, 4th order etc.) from (111) planes show maximum intensity.
5. It shows that successive (111) planes are not identical but are alternately arranged i.e. (111) planes have either only Na^+ ions or only Cl^- ions.
6. The glancing angles for first order reflections giving maximum are observed as follows.

$\theta = 5.90$ ....for 100 plane
$\theta = 8.40$ ....for 110 plane
$\theta = 5.20$ ....for 111 plane

$$d_{100} : d_{110} : d_{111} = \frac{1}{\sin 5.9} : \frac{1}{\sin 8.4} : \frac{1}{\sin 5.2}$$

$$= 1 : 0.704 : 1.14$$

7. This ratio shows that NaCl has fcc lattice, but NaCl crystal lattice is formed by th interpenetration of the two faces. (One of Na^+ and the other of Cl^-)

8. Here each Na^+ ion is surrounded by six Cl^- ions. Similarly each Cl^- ion is surrounde by six Na^+ ions. So coordination number is six. (NaCl is known as six -s coordination crystal). These ions are alternately arranged i.e. two +ve ions a separated by one Cl^- ion and vice versa.

9. If each Na^+ ion (surrounded by six Cl^- ions) is arranged at corner of a cub then each Cl^- ion (surrounded by six Na^+ ions) is arranged at the centre of th edge.

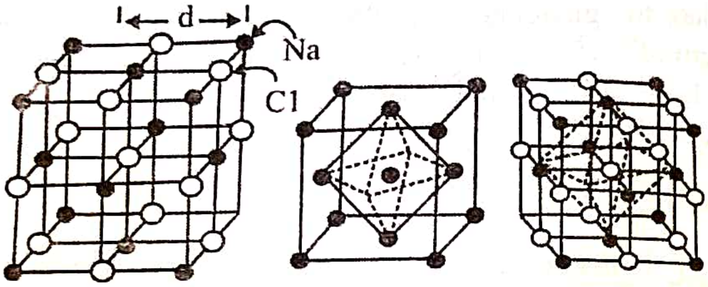


Fig. 5.28

10. To prove that unit cell of NaCl has four molecules of NaCl.

a) NaCl is fcc lattice and has Na^+ and Cl^- ions as component ions.

$$\text{Number of NaCl molecules in unit cell} = \text{Number of } Na^+ \text{ ions in unit cell} + \text{Number of } Cl^- \text{ ions in unit cell}$$

b) Here Na^+ ions are present at each of eight corners as well as centre of each face

Number of Na^+ ions = Contribution by corners + Contribution by faces.

$$= \left(\frac{1}{8}\times 8\right) + \left(\frac{1}{2}\times 6\right)$$

$$= 1 + 3$$

$$= 4$$

c) Here Cl^- ions are at the centre of each of 12 edges as well as one at centre complete unit cell.

Number of Cl^- ions = Contribution by edges + Contribution by centre

$$= \left(\frac{1}{4}\times 12\right) + 1\times 1$$

$$= 3 + 1$$

$$= 4$$

Number of molecules in unit cell of NaCl = 4 Na^+ ions + 4 Cl^- ions

= 4 NaCl molecules

Hence it is proved that unit cell of NaCl has four molecules of NaCl.

B. Structure of KCl (*sylvite*)

1. KCl is ionic crystal. It's components are K^+ and Cl^- ions. These are the deflecting centre for X-rays.
2. The glancing angles giving maxima for it's different planes are as follows.

   $\theta = 5.38^0$ ....for 100 plane

   $\theta = 7.61^0$..........................for 110 plane

   $\theta = 9.38^0$..........................for 111 plane

$$d_{100} : d_{110} : d_{111} = \frac{1}{\sin 5.38} : \frac{1}{\sin 7.61} : \frac{1}{\sin 9.38}$$
$$= 1 : 0.707 : 0.577$$

3. This shows that KCl should be a scc lattice.
4. However KCl should be fcc like NaCl. It is because KCl is is omorphous with NaCl.
5. Thus KCl is fcc lattice like NaCl .It is also six-six coordination crystal.

Anomalous behavior of KCl towards X-Ray

Why KCl behave like scc toward X-rays? This is explained as follows-.

a) The intensity of reflection of X-rays depends on number of electrons present in the reflecting centers.

b) Consider NaCl crystal which has Na^+ ions and Cl^- ions as the reflecting centers. Here Na^+ ion have 10 electrons and chloride ions have 18 electrons. Thus both have different number of electrons and hence different capability to diffract X-rays.

c) Consider KCl crystal which has K^+ and Cl^- ions as the reflecting centers. Here both have same number of electron (18 each). Thus intensities of reflections given out by planes with K^+ ions only and Cl^- ions only are same so X-rays cannot distinguish between planes with only K^+ ions or with only Cl^- ions.

d) This also explains why reflections from (111) planes are absent .Thus KCl behaves as scc towards X-rays.

EXERCISE

FILL IN THE BLANKS:

1. Crystals have planner surfaces arranged in .... pattern.
2. Crystals have .... melting point.
3. Cubic crystal has totaled nine ...., of symmetry.
4. The cubic crystal has .... axes of symmetry.
5. All crystals of the same substance have .... elements of symmetry.
6. The coefficients in the ratio of intercepts are defined as ....
7. Miller Indices are the .... of the distance from the origin at which a given face intersects the three axes.
8. The 32 classes of crystals are grouped into .... crystal system.
9. In simple cubic system the particles are only at the .... of the cube.
10. The number of particles in the unit cell of scc is ....
11. Number of molecules in unit cell of NaCl is ....

SHORT ANSWER QUESTIONS:

1. Define
   - i) crystalline solid
   - ii) Plane of symmetry
   - iii) Axis of symmetry
   - iv) Centre of symmetry
   - v) Weiss Indices
2. State the law of constancy of interfacial angles.
3. State the law of Symmetry.
4. State the law of rational indices or intercepts.
5. Calculate the interplanar distance for 100 plane in scc.
6. Calculate the interplanar distance for 111 plane in scc.
7. Calculate the interplanar distance for 110 plane in fcc.
8. Explain
   - i) Face centered cubic system
   - ii) Body centered cubic system
   - iii) Tetragonal system
   - iv) Rhombic system (Orthorhombic)
   - v) Monoclinic system
   - vi) Triclinic system
   - vii) Hexagonal system
   - viii) Rhombohedral or trigonal system
9. Calculate the number of constituent units in the cubic unit cell for scc.
10. Calculate the number of constituent units in the cubic unit cell for fcc.
11. Calculate the number of constituent units in the cubic unit cell for bcc.

DESCRIPTIVE QUESTIONS:

1. Establish that NaCl crystal belongs to fcc lattice.
2. Prove that unit cell of NaCl is composed of 4 NaCl molecules.
3. What are the factors on which intensity of reflected X-ray depends.
4. Explain why NaCl and KCl show different behavior towards X-ray.
5. Derive Bragg's equation for diffraction of X-ray by crystal.
6. Describe Bragg's spectroscopic method for determination of crystal structure.
7. Explain the structure of KCl on the basis of X- ray diffraction.
8. Find out miller indices if Weiss indices are
   i) 2 : 4 : 3 ii) 1 : ∞ : ¼ ii) 2 : 2 : 3 iii) 1/2 : 2/3 : ∞
   [**Answer :** i) 634 ii) 104 iii) 332 iv) 430]
9. X- ray of wavelength 0.0579 nm were incident on a scc. The second order defl maximum was observed at 11.9^0. Calculate interplanar spacing. (Ans.- 0.281 nm
10. Third order reflection maximum from 100 planes of bcc was observed at gla angle of 18.2^0 Calculate wavelengths of X-rays if side of cube is 6A^0.
    (Ans.- λ = 0.6192 A^0)
11. The length of side of unit cell of a cubic crystal is 4 X 10^{-8} m. The density of c is 1.2 X 10^{-3} kg m^{-3}. If the molar mass is 24 x 10^{-3} kg mol^{-1}, find out (i) num atoms in each unit cell (ii) type of lattice (N_A- 6.023 x 10^{23})
    [Ans.- i) 1.9273 ii) Body centered lattice]
12. The first order reflection maxima was noted as 5.9^0 from 100 planes of scc. Cal wavelength of X-rays if interplanar spacing was 0.282 nm. (Ans.- λ = 0.05792
13. The length of edge of cubic lattice is2.5 A° Calculate the interplanar distance (231) planes. (Ans. 0.6682 A°)
14. Calculate glancing angel for first order reflection from 100 planes of d_{100} = 0.315 nm and wavelength of X-rays was0.16 nm.(Ans. $\theta = 14.7^0$)

A metal has bcc lattice. The first order reflection maximum from 200 planes was observed at 16° 6' with X-rays of wavelength 0.154 nm. Calculate edge length of unit cell. (Ans. a = 0.56 nm)

Sodium has bcc lattice with density of 1×10^3 kg m^{-3} and molar mass of 23×10^{-3} kg mol^{-1} find out length of edge of its unit cell. (Given $N_0 = 6.023 \times 10^{23}$) (Ans. $a = 4.3346 \times 10^{-10}$ m)

ELECT THE PROPER ANSWER FROM GIVEN ALTERNATIVE:

Which is not true about the solid state?

a) They have definite shape and volume

b) They have high density and low compressibility

c) The particles can move easily from one place to another

d) They have high attractive forces among molecules

Amorphous solids do not have

a) sharp melting point b) characteristic geometrical shapes

c) regularity of the structure d) all of these

A crystalline solid has ....

a) irregular geometrical shape b) sharp melting point

c) non planner surface d) loosely packed atoms

Amorphous substances are isotropic because

a) They have same value of any property in all directions

b) They have different values of physical properties in different directions

c) They have definite geometrical shape

d) None of the above

The elements of symmetry are

a) plane of symmetry b) axis of symmetry

c) centre of symmetry d) all of these

The amorphous solid among the following is

a) table salt b) diamond c) plastic d) graphite

A crystalline solid does not have one of the following properties.

a) anisotropy b) sharp melting points

c) isotropy d) definite and regular geometry

The Bragg's equation for diffraction of X-rays is ....

a) $n\lambda = 2d2 \sin\theta$ b) $n\lambda = 2d\sin\theta$

c) $n\lambda = 2d\sin2\theta$ d) $n\lambda = d\sin\theta$

In Bragg's equation $n\lambda = 2d\sin\theta$, 'n' represents

a) the number of moles b) the principal quantum number

c) the Avogadro's number d) the order of reflection

Which of the following is a crystalline solid?

a) diamond b) glass c) rubber d) paper

The flat surfaces containing component particles which define geometry of crystals so that particles are not present beyond this surface is known as ....

a) Crystallographic axes b) Crystallographic plane

c) Crystallographic angle d) none of these

A cubic crystal possesses a total of .... elements of symmetry.

a) 20 b) 23 c) 22 d) 12

13. There are .... crystal systems.
a) 7 b) 5 c) 9 d) 3

14. The indices used to denote the direction of a plane of crystal are ....
a) rational indices b) Miller indices
c) Bragg's indices d) none of the above

15. Law of constancy of interfacial angles was proposed by ....
a) Braggs b) Laue c) Steno d) Hauy

16. The Miller indices are often used in the area of ....
a) Amorphous substances b) ionic crystal
c) single crystal d) hydrogen crystal

17. According law of constancy of interfacial angles crystals of same substance having different shape, the angle between corresponding faces ....
a) remains constant b) different
c) some are same and some different d) differ by specific angle

18. Law of rational indices or intercepts ....
a) Braggs b) Laue c) Steno d) Hauy

19. "The intercept of any face of a crystal along the crystallographic axes are either equal to unit intercepts (a, b, c) or simple whole number multiples of them." It is the statement of ....
a) law of symmetry b) law of constancy of interfacial angles
c) law of rational indices d) Bragg's law

20. According to law of symmetry all crystals of the same substance have same ....
a) elements of symmetry b) axis
c) angle d) lattice point

21. The reciprocals of the intercepts made by a plane with crystallographic axes are called ....
a) Weiss indices b) Miller indices
c) Bragg indices d) Laue indices

22. The ratio of the distances from the origin at which a face intersects the crystallographic axes are known as ....
a) Weiss indices b) Miller indices c) Bragg indices d) Laue indices

23. The interplaner distance ratio of 100, 110 and 111 planes for simple cubic crystal (SCC) is ....
a) 1 : 0.707 : 0.577 b) 1 : 0.707 : 1.154
c) 1 : 1.414 : 0.577 d) 1 : 0.577 : 1.414

24. Bravais lattices depend on the shapes of ....
a) lattice b) cubic crystal c) unit cell d) none of these

25. In a face-centered cubic lattice, a unit cell is shared equally by how many unit cells?
a) 8 b) 4 c) 2 d) 6

26. What type of lattice is found in potassium chloride crystal?
a) Face centered cubic b) Body centered cubic
c) Simple cubic d) Simple tetragonal

27. The number of atoms present in unit cell of a monoatomic substance of simple cubic lattice is ....
a) 1 b) 2 c) 3 d) 6

28. The smallest geometrical portion of the crystal which represents the crystal in shape, geometry, faces, symmetry and angle.
a) lattice point b) crystal lattice c) unit cell d) lattice plane

29. Cubic crystal has total .... plane of symmetry.
a) 6 b) 7 c) 9 d) 11

30. The cubic crystal has .... axes of symmetry.
a) 11 b) 13 c) 15 d) 17

31. A line along which two adjacent faces interest with each other is known as ....
a) Crystallographic edge b) Perpendicular line
c) Crystallographic bond d) Parallel lines

32. The angle at which two faces of the crystal, intersect with each other is known as ....
a) Acute angle b) Interfacial angle c) Right angle d) Straight angle

33. Representation of the infinite set of lattice points repeated regularly in the three dimensional space is known as ....
a) Crystal lattice b) Lattice planes c) Unit cell d) Lattice point

34. "Any plane containing atoms, ions, or molecules cuts crystallographic axes giving intercepts is either equal to unit cell intercepts or some small whole number multiples of unit cell intercepts." this law is known as ....
a) Law of symmetry b) Law of equality
c) Law of rational indices d) Law of constancy of interfacial angle

35. The interplaner distance ratio of 100, 110 and 111 planes for face centered cubic crystal (FCC) is ....
a) 1 : 0.707 : 0.577 b) 1 : 0.707 : 1.154
c) 1 : 1.414 : 0.577 d) 1: 0.577 : 1.414

36. Total number of component particles present in face centred cubic (FCC) lattice is ...
a) 1 b) 2 c) 3 d) 4

37. Total number of component particles present in the body centred cubic crystal (BCC) lattice is ....
a) 1 b) 2 c) 3 d) 4

38. The Miller indices for the Weiss indices (1 2 3) are ....
a) 312 b) 321 c) 632 d) 123

39. In Bragg's X-spectrometer, when turn table rotate through angle θ , then Ionization chamber rotate through .... angle so as to catch diffracted X-ray from the crystal.
a) 3θ b) 2θ c) θ d) 4θ

40. The unit cell of NaCl has .... molecules of NaCl.
a) 1 b) 2 c) 3 d) 4

41. In the Ionization chamber of Bragg's spectrometer which gas is generally used ....
a) Hydrogen b) Oxygen c) Methyl bromide d) Carbon dioxide

42. NaCl is example of ....
a) FCC b) BCC c) SCC d) Non of the above

43. How many Bravais lattice crystal systems are there for cubic system?
a) 2 b) 3 c) 1 d) 4

44. Crystalline solids are also called as ....
a) Metal solids b) False solids c) True solids d) Non-solids

45. The interplaner distance ratio of 100, 110 and 111 planes for body centered cubic crystal (BCC) is ....
   a) 1 : 0.707 : 0.577
   b) 1 : 0.707 : 1.154
   c) 1 : 1.414 : 0.577
   d) 1: 0.577 : 1.414

46. In tetragonal system the three axes are ....
   a) $a = b = c$
   b) $a \neq b \neq c$
   c) $a \neq b = c$
   d) $a = b \neq c$

47. In Monoclinic system the three axes are ....
   a) $a = b = c$
   b) $a \neq b \neq c$
   c) $a \neq b = c$
   d) $a = b \neq c$

48. In Regular or cubic system the angle between three axis is ....
   a) $\alpha = \beta = \gamma = 90^0$
   b) $\alpha = \beta = 90^0 \gamma \neq 90^0$
   c) $\alpha \neq 90^0\ \beta = \gamma = 90^0$
   d) $\alpha = \gamma = 90^0 \beta \neq 90^0$

49. In triclinic system the angle between three axes is ....
   a) $\alpha = \beta = \gamma = 90^0$
   b) $\alpha = \beta = 90^0 \gamma \neq 90^0$
   c) $\alpha \neq 90^0\ \beta = \gamma = 90^0$
   d) $\alpha \neq \beta \neq \gamma \neq 90^0$

50. How many Bravais lattice crystal systems are there for hexagonal system?
   a) 1
   b) 2
   c) 3
   d) 4

ANSWERS OF MCQ:

1 - c	11 - b	21 - b	31 - a	41 - c
2 - d	12 - b	22 - a	32 - b	42 - a
3 - c	13 - a	23 - b	33 - a	43 - b
4 - a	14 - b	24 - c	34 - c	44 - c
5 - d	15 - c	25 - d	35 - b	45 - c
6 - c	16 - c	26 - a	36 - d	46 - d
7 - c	17 - a	27 - a	37 - b	47 - b
8 - b	18 - d	28 - c	38 - c	48 - a
9 - d	19 - c	29 - c	39 - b	49 - d
10 - a	20 - a	30 - b	40 - d	50 - a

****

UNIT VI

CHEMICAL KINETICS

Chemical kinetics is the branch of physical chemistry which deals with the study of the rate or speed or velocity of the chemical reactions proceeding under given conditions of the temperature, pressure and concentration with the elucidation of their mechanism. Chemical kinetics includes methods of determination of rate of reactions, order of a reaction, factors affecting rate of reaction, effect of temperature on reaction rates, Arrhenius equation, activation energy and its determination using Arrhenius equation. The knowledge of the rate of reactions is very valuable to understand the chemical of reactions.

6.1 Rate or Velocity or Speed of Chemical Reaction

Let us consider a simple reaction of the type,

$$\underset{\text{reactant}}{A} \qquad \rightarrow \qquad \underset{\text{product}}{B}$$

Here reactant 'A' is consumed and product 'B' is formed. As the reaction precedes concentration of reactants decreases while that of the product increases.

The rate or speed or velocity of a chemical reaction is defined as,

'The decrease in concentration of any one of its reactant per unit time or increase in the concentration of any one of its product per unit time.'

OR

'The rate of change of concentration of either reactant or product per unit time.'

It is denoted as

Hence, $$\text{Rate} = r = \frac{dx}{dt} = -\frac{dC_A}{dt} = +\frac{dC_B}{dt} \qquad \text{..........} (1)$$

Where, dx is the change in concentration of either reactant or product,

dt is the time interval.

According to law of mass action rate of any chemical reaction directly varies with the active mass of the reactants i.e. C_A or $[A]$

$$\therefore r = \frac{dx}{dt} = -\frac{dC_A}{dt} = +\frac{dC_B}{dt} \alpha C_A$$

OR $$r = -\frac{dC_A}{dt} = kC_A \qquad \text{OR} \qquad r = -\frac{d[A]}{dt} = k[A] \qquad \text{..........} (2)$$

Where, dC_A or $d[A]$ is infinitesimal decrease in the concentration of 'A' in an infinitesimal interval of time, 'dt'

-ve sign indicates decrease in concentration of 'A'.

dC_B or $d[B]$ is infinitesimal increase in the concentration of 'B' in an infinitesimal interval of time, 'dt'

+ve sign in equation indicates the concentration of product is increasing, with time k is known as the *rate constant* of a reaction.

Velocity Constant or Rate Constant

Consider a simple reaction of the type

$$\underset{\text{reactants}}{A + B} \rightarrow \underset{\text{product}}{P}$$

Rate of this reaction is given by

$$r = \frac{dx}{dt} = kC_A.C_B \qquad \text{.........(3)}$$

If the concentration of each of the reactants A and B is unity i.e. $C_A.C_B = 1$, then equation (3) becomes

$$r = \frac{dx}{dt} = k \qquad \text{.........(4)}$$

Definition of Rate Constant (k): Rate constant or velocity constant of a reaction at a given temperature is defined as *'It is equal to the rate of reaction when the concentration of each of the reactant is unity.'*

Units of Rate Constant (k)

Let us consider the general reaction

$$aA + bB + \ldots.. \rightarrow lL + mM + \ldots\ldots$$

rate of this reaction is given by,

$$r = \frac{dx}{dt} = -\frac{1}{a}\frac{dC_A}{dt} = -\frac{1}{b}\frac{dC_B}{dt} = +\frac{1}{l}\frac{dC_L}{dt} = +\frac{1}{m}\frac{dC_M}{dt} = kC_A^a.C_B^b \ldots\ldots$$

Hence, rate is directly proportional to product of concentrations of reacting species raised to power their number of moles.

Now, if time is expressed in second or minute and $C_A=C_B$... in mol dm^{-3} then, rate of the reaction is expressed as **mol dm^{-3} sec^{-1} or mol dm^{-3} min^{-1}**

Substituting these dimensions in above rate equation, we get

$$\frac{\text{moldm}^{-3}}{\text{sec}} = k\left(\text{moldm}^{-3}\right)^a \times \left(\text{moldm}^{-3}\right)^b \times \ldots\ldots$$

OR $$\text{moldm}^{-3}\,\text{sec}^{-1} = k\left(\text{moldm}^{-3}\right)^a \times \left(\text{moldm}^{-3}\right)^b \times \ldots\ldots$$

OR $$\text{moldm}^{-3}\,\text{sec}^{-1} = k\left(\text{moldm}^{-3}\right)^{(a+b+c+\ldots)}$$

O $$\therefore k = \frac{\text{moldm}^{-3}\,\text{sec}^{-1}}{\left(\text{moldm}^{-3}\right)^{(a+b+c+\ldots)}}$$

$$k = \left[\text{moldm}^{-3}\right]^{[1-(a+b+c+\ldots)]}\text{sec}^{-1}$$

Reactions rate has the units of concentration divided by time. We express concentrations in moles per litre (mol/litre or mol/l or mol l^{-1}) but time may be given in any convenient unit second (s), minutes (min), hours (h), days (d) or possible years. Therefore, the units of reaction rates may be

mole/litresec	or	$mol\,l^{-1}\,s^{-1}$
mole/litremin	or	$mol\,l^{-1}\,min^{-1}$
mole/litrehour	or	$mol\,l^{-1}\,h^{-1}$ and,so on

6.2 Factors Influencing the Rate of Reaction

The following principal factors influence (affect) the rates of chemical reactions.

I) Concentration of reactants: The rate of chemical reaction is directly proportional to the concentration of reacting substances raised to power of their number of moles. This has only exception of zero order reactions. Since reactants are continuously consumed during the course of a reaction, concentration of reactants decreases with the time. The variation of concentration (rate of reaction) with time is shown in figure 1. The rate is highest in the beginning and continuously decreases with the time as shown in graph I. Theoretically, a reaction is never complete, but for all practical purposes, it is assumed that the reaction slow after some time that it may be taken to be completed. Reverse is the case with the concentration of the products as shown in graph II.

II) Effect of temperature: Increase in temperature leads to an increase in the rate of the reaction. Reaction rate which is negligibly slow at ordinary temperatures, may become appreciable and even explosive at elevated temperatures. It is observed that with a rise of 10°C the rate constant is approximately doubled or tripled.

III) Solvent: Solvent also plays the vital role in determining rates of reactions. Rate of reaction increases or decreases with change of solvent, which depends upon the nature of the reaction.

IV) Catalyst: The rates of certain reactions are increased due to presence of certain substances in the reacting system, known as catalyst.

e.g. MnO_2 speeds up decomposition of potassium chlorate.

V) Pressure: Rates of the gas phase reactions are also affected by pressure. Higher the pressure, more is the rate of reaction. Thus concentration and pressure affect the rate of reaction in the same manner.

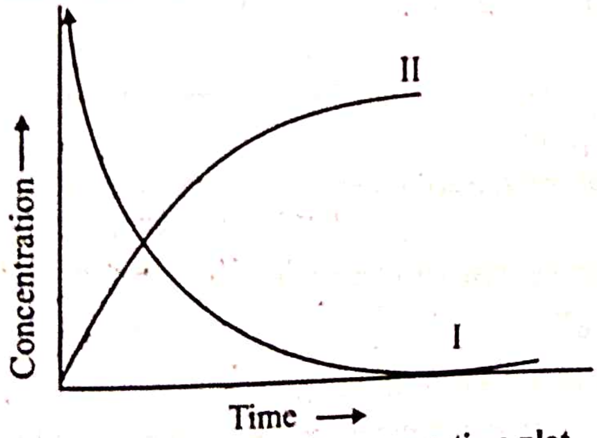


Fig. 6.1 : Concentration versus time plot

6.3 Rate Law

The rate of a given reaction depends on concentration of reactants at given time. The exact relation between concentration and rate is determined by measuring the reaction rate with different initial reactant concentrations. By a study of numerous reactions, it is shown that: ***the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.***

Thus, for a substance an undergoing reaction, $\text{rate} \; \alpha \; [A]^n$

Or $\text{rate} = k\,[A]^n$

For a reaction $2A + B \longrightarrow \text{Products}$

The reaction rate with respect to A or B is determined by varying the concentration of one reactant, keeping that of the other constant. Thus, the rate of reaction may be expressed as

$$\text{rate} = k[A]^m[B]^n$$

Above expressions of rate tells us the relation between the rate constant and concentration of reactants. The power (exponent) of concentration n or m in the rate law is usually a small whole number integer (1, 2, 3) or fractional. The proportionality constant k is called the **rate constant** for the reaction.

6.4 Order of Reaction

It is an experimentally determined quantity. It is obtained from the rate equation applicable to the reaction. It is not necessary that concentration of all the reactants taking part in a reaction can determined the rate of reaction. In the rate equation only those reactant appears whose concentration undergo a measurable change during the reaction. Thus, a new term introduced, order of reaction, which is defined as-

'The order of a reaction is given by the number of reacting atoms or molecules whose concentration alter during the chemical change.'

OR

'The order of a reaction is the total number of atoms or molecules whose concentration determines the velocity of a reaction.'

OR

'The order of a reaction is defined as the sum of the powers of the concentration terms in the rate law equation.'

On the basis of order, reactions are classified as zero, first, second or third order reactions.

Let us consider the example of are action which has the rate law

$$\text{rate} = k[A]^p[B]^q$$

The order of such reaction is $(p + q)$.

The order of a reaction can also be defined with respect to a single reactant. Thus, the reaction order with respect to A is p and with respect to B it is q. The overall order of reaction $(p + q)$ may range from 1 to 3 and can be fractional.

Rate Law	Reaction Order
rate = $k\,[CO_2]$	1
rate = $k\,[H_2]\,[N_2]$	$1 + 1 = 2$
rate = $k\,[NO_2]^2$	2
rate = $k\,[[H_2]\,[I_2]^2$	$1 + 2 = 3$
rate = $k\,[CHCl_3]\,[Cl_2]^{1/2}$	$1 + \frac{1}{2} = 1\frac{1}{2}$

Reactions may be classified according to the order. If in the rate law (1) above

$p + q = 1$, **it is first order reaction**

$p + q = 2$, **it is second order reaction**

$p + q = 3$, **it is third order reaction**

6.5 Molecularity of a Reaction: Molecularity is defined as total number of molecules of various reactants taking part in a chemical reaction as represented by a balance chemical equation. On the basis of molecularity reactions are classified as unimolecular, bimolecular, trimolecular and so on depending up on the number of molecules involved in a reaction.

a) Unimolecualr reaction: A unimolecular reaction is one in which only one molecule of reactant is involved.

In general it is represented as

$$A \longrightarrow \text{product}$$

For example

i) $Br_2 \longrightarrow 2Br$

ii) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

b) Bimolecualr reaction: A bimolecular reaction is one in which two molecules of reactants are involved.

In general it is represented as

$A + A \longrightarrow \text{product}$

OR $A + B \longrightarrow \text{product}$

For example

i) $2HI \longrightarrow H_2 + I_2$

ii) Hydrolysis of methyl acetate in presence of mineral acid

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

c) Termolecular Reactions: A termolecular reaction is one in which three molecules of reactant are involved.

In general it is represented as

$3A \longrightarrow \text{product}$

OR $2A + B \longrightarrow \text{product}$

OR $A + B + C \longrightarrow \text{product}$

For example

i) $2NO_{(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)}$

ii) $2NO_{(g)} + Cl_{2(g)} \longrightarrow 2\,NOCl_{2(g)}$

Difference between Order and Molecularity

Order of Reaction	Molecularity
1. It is the **sum of powers** of the concentration terms in the rate law expression.	1. It is number of **reacting species** undergoing simultaneous collision in the elementary or simple reaction.
2. It is an **experimentally** determined value.	2. It is a **theoretical** concept.
3. It can have **fractional** value.	3. It is always a **whole number.**
4. It can assume **zero value.**	4. **It cannot have zero value.**
5. Order of a reaction **can change** with the conditions such as pressure, temperature, concentration.	5. Molecularity is **invariant** for a chemical equation.
6. It **cannot be obtained** from the single balanced equation.	6. It is **obtained** from a balanced chemical equation.
7. It do not consider the molecules of a catalyst and that of the reactant taken in large excess.	7. It considers the molecules of a catalyst and that of the reactant taken in large excess.

Problem 1: Write the differential rate equations for the following reactions, assuming them to be elementary reactions :

a) $A + 2B + 3C \longrightarrow \text{Products}$

b) $A + 3B \longrightarrow 2C + D + 2E$

Solution: a) Rate, $r = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = -\frac{1}{3}\frac{d[C]}{dt}$

b) Rate, $r = -\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = \frac{d[D]}{dt} = \frac{1}{2}\frac{d[E]}{dt}$

Problem 2: The rate of the homogeneous gaseous reaction $2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$ is doubled when the chlorine concentration is doubled but increases by a factor of eight when the concentrations of both the reactants are doubled. Determine the overall order of the reaction and the order with respect to NO and Cl_2.

Solution : Rate = $k[NO]^a\,[Cl_2]^b$ where we have to determine a and b.

If a = 0 and b = 1 (overall first-order), then $r = k_1[Cl_2]$

A little reflection will show that this is not at all acceptable

If a = 1, b = 1 (overall second-order), then $r = k_2[NO][Cl_2]$

Doubling the concentration of both the reactants will increase the rate by a factor of 4, which is not given.

If a = 0, b = 2 (overall second-order), then $r- = k_2[Cl_2]^2$

Doubling the concentration of Cl_2 will increase the rate by a factor of 4 which, too, is not given.

If a = 1, b = 2 (overall third-order), then $r = k_3[NO][Cl_2]^2$

Doubling the concentrations of both the reactants will, no doubt, increase the rate by a factor of 8 but doubling the concentration of Cl_2 alone will increase the rate by a factor of 4, which again, is not given. The other alternative for a third-order reaction is a =2, b=1 so that $r = k_3[NO][Cl_2]^2$. We immediately see that this rate equation satisfies both the given conditions. Hence, overall the reaction is of the third order, being of the second order in NO and of the first order in Cl_2.

Problem 3: Write the units of the rate constants for a (i) zeroth-order (ii) half-order (iii) first-order (iv) $\frac{3}{2}$ -order (v) second-order (vi) $\frac{5}{2}$ -order and (vii) third-order reaction.

Solution: The units of the rate constant for the nth-order reaction are given by $(dm^3)^{n-1}$ mol^{n-1} s^{-1}.

i) n = 0, the units are dm^{-3} mol s^{-1}

ii) n = 1/2, the units are $(dm^3)^{-1/2}$ $mol^{1/2}$ s^{-1}

iii) n = 1, the units are s^{-1}

iv) n = 3/2, the units are $(dm^3)^{1/2}$ $mol^{-1/2}$ s^{-1}

v) n = 2, the units are dm^3 mol^{-1} s^{-1}

vi) n = 5/2, the units are $(dm^3)^{3/2}$ $mol^{-3/2}$ s^{-1}

vii) n = 3, the units are dm^6 mol^{-2} s^{-1}

6.6 Zero Order Reactions

A reaction is said to be of zero order when it's rate is independent of the initial concentration of the reactants. Consider-

$$A \rightarrow \text{Product}$$

At time, t = 0   a   0

t = t,   (a - x)   x

Suppose 'a' mol dm^{-3} is initial concentration and '(a - x)' mol dm^{-3} be the concentration of reactant after time 't'. The rate of above reaction is given as -

$$\text{Rate} = r = \frac{dx}{dt} = k_0 (a-x)^0 \qquad \text{..........(5)}$$

Where, 'k_0' is a rate constant or velocity constant

$$\therefore \frac{dx}{dt} = k_0 \qquad \left[\text{Since}, (a-x)^0 = 0\right]$$

i.e. $\quad dx = k_0 dt$ ....(6)

Integrating equation (6) within the limits,

$$\int_{X=0}^{X=X} dx = \int_{t=0}^{t=t} k_0 dt \qquad \text{i.e. } x = k_0 t \qquad \text{..........(7)}$$

This is zero order rate law equation.

Characteristics of Zero Order Reaction

I) Unit of k_0

We know that for zero order reaction, the rate law equation is

$x = k_0 t$

$$\text{OR}\quad k_0 = \frac{x}{t} = \frac{\text{moldm}^{-3}}{\text{sec}} = \text{moldm}^{-3}\text{sec}^{-1}$$

ii) **Half life:** Half life of reaction is the time required to complete half of the reaction. It is represented by $t_{1/2}$.

The zero order rate law equation

$x = k_0 t$

Thus, when, $t = t_{1/2}$, $x = \frac{a}{2}$

Substitute these values in above equation,

We get, $\frac{a}{2} = k_0 t_{1/2}$

$\therefore t_{1/2} \propto a$

Hence half life of zero order reaction is directly proportional to initial concentration of reactant.

iii) **The graphical representation**

The zero order rate law equation, $x = k_0 t$

This is in the form of $y = mx$

i.e. when the graph is plotted between 'x' values on Y-axis and 't' values an X-axis. Straight line is obtained with slope, k_0 as shown in Figure 2.

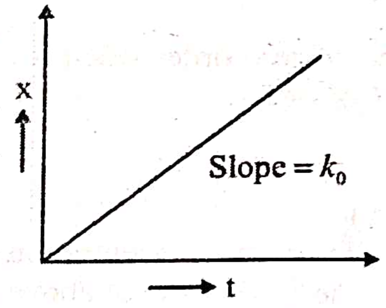


Fig. 6.2 : Linear plot of 'x' versus 't'

Examples of Zero Order Reaction

1) **Reaction between acetone and Bromine**

$CH_3COCH_3 + Br_2 \rightarrow CH_3COCH_2Br + HBr$

This reaction proceeds with same rate irrespective of concentration of Br_2 and so reaction is said to be zero order with respect to Br_2.

2) **Decomposition of Phosphine**

$4PH_3 \xrightarrow{Mo/W} P_4 + 6H_2$

Decomposition of phosphine on the surface of molybdenum or tungsten at high pressure P is zero order reaction

3) **Reaction of acetone and Iodine**

$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$

The reaction is zero order with respect to iodine concentration since reaction rate is independent of concentration of iodine.

6.7 First Order Reaction

When the rate is depends on the change in initial concentration of single reactant, the reaction is 'first order'. Consider a reaction.

	A	$\rightarrow$ Product
At time, $t = 0$	a	0
$t = t$,	$(a - x)$	x

Suppose 'a' mole dm^{-3} be the initial concentration of reactant 'A' and 'x' mol dm^{-3} be the concentration of product after time, 't'. The rate of the reaction is given as-

$$r = \frac{dx}{dt} \alpha (a\text{-}x)$$

i.e.
$$\frac{dx}{dt} = k_1 (a\text{-}x) \qquad \text{..........} (8)$$

Where, k_1 is first order rate constant (or velocity constant). Equation (8) can be written as-

$$\frac{dx}{(a\text{-}x)} = k_1 dt \qquad \text{..........} (9)$$

Integrating the equation (9), we get

$$\int \frac{dx}{(a\text{-}x)} = \int k_1 dt$$

$$-\ln(a - x) = k_1 t + C \qquad \text{..........} (10)$$

Where 'C' is integration constant which can be evaluated from initial condition of reaction as at t = 0, x= 0.

$$\therefore -\ln a = C \qquad \text{..........} (11)$$

From equations (10) and (11) we get,

$$-\ln(a - x) = k_1 t - \ln a$$

OR
$$\ln a - \ln(a - x) = k_1 t$$

OR
$$k_1 = \frac{1}{t} \ln\left(\frac{a}{a - x}\right) \qquad \text{..........} (12)$$

OR
$$k_1 = \frac{2.303}{t} \log\left(\frac{a}{a - x}\right) \qquad \text{..........} (13)$$

This equation (13) is known as the integrated rate law (kinetic equation) of first order reaction.

Characteristics of First Order Reaction

I) Unit of k_1

We know that rate law for the first order reaction is

$$k_1 = \frac{2.303}{t} \log\left(\frac{a}{a - x}\right)$$

$$k_1 = \frac{2.303}{sec} \log\left(\frac{mol dm^{-3}}{mol dm^{-3}}\right)$$

$$k_1 = sec^{-1}$$

ii) Graphical representation

We have,

$$k_1 = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

$$k_1 t = 2.303\log\left(\frac{a}{a-x}\right)$$

$$\log\left(\frac{a}{a-x}\right) = \left(\frac{k_1}{2.303}\right)\times t$$

This is in the form of $y = mx$

Hence, when a graph is plotted between 't' and $\log\left(\frac{a}{a-x}\right)$, we get a straight line passing through origin and having slope $\frac{k_1}{2.303}$ shown in figure 3.

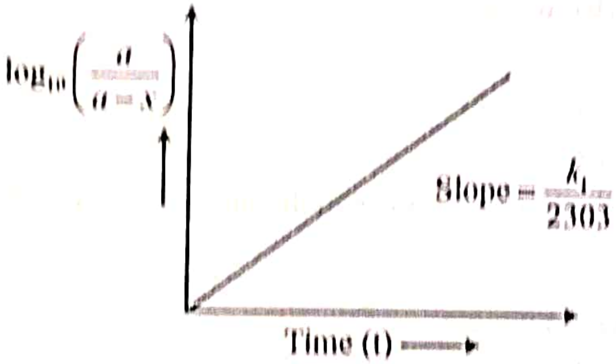


Fig. 6.3 : The plot of $\log\left(\frac{a}{a-x}\right)$ versus time (t)

Now, $k_1 t = 2.303\log\left(\frac{a}{a-x}\right)$

OR $k_1 t = 2.303\log a - 2.303\log(a-x)$

OR $2.303\log(a-x) = -k_1 t + 2.303\log a$

OR $\log(a-x) = -\left(\frac{k_1}{2.303}\right)t + \log a$ ....(14)

This is in the form of $y = mx + C$

Thus, when a graph is plotted between 't' and $\log(a-x)$, we get a straight line with slope $-\left(\frac{k_1}{2.303}\right)$ and intercept log a as shown in figure 4.

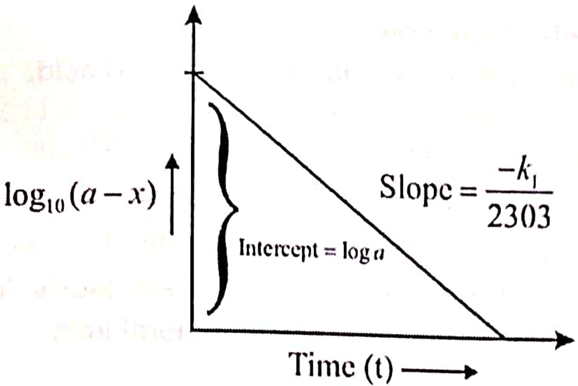


Fig. 6.4 : The plot of log(a-x) versus time

iii) Half life

Half life of reaction is the time required to complete half of the reaction. It is represented by $t_{1/2}$.

The first order rate law equation

$$k_1 = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

Thus, when $t = t_{1/2}$, $x = \frac{a}{2}$

Substitute these values in above equation, we get

$$k_1 = \frac{2.303}{t_{1/2}}\log\left(\frac{a}{a-\frac{a}{2}}\right)$$

OR $$k_1 = \frac{2.303}{t_{1/2}}\log\left(\frac{a}{a-\frac{a}{2}}\right)$$

OR $$k_1 = \frac{2.303}{t_{1/2}}\log 2$$

OR $$t_{1/2} = \frac{2.303}{k_1}\log 2 = \frac{0.693}{k_1} = \text{Constant}$$

Thus the time taken for completion of definite fraction of the first order reaction is independent of the initial concentration of reactant.

6.8 Pseudo-Order Reactions: *The reaction which appears to be bimolecular but infact it is first order is called pseudo unimolecular reaction.*

OR

'A reaction in which one of the reactants if present in a large excess shows a different order is known as Pseudo-order reaction.'

The reaction is in fact bimolecular but behaves as a first order reaction is known as Pseudo first order reaction. Pseudo-first order reaction may also be called Pseudo unimolecular reaction.

Example of Pseudo-Order Reactions:

i) Hydrolysis of methyl acetate in presence of mineral acid.

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

In above reaction water is taken in such a large excess so that its concentration does not change appreciably during the reaction and rate of reaction depends only on the concentration of methyl acetate so that it is Pseudo-unimolecular reaction.

ii) Inversion of cane sugar in the presence of mineral acid.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Actually above reaction is bimolecular as it involves two molecules of reactants but follows first order rate equation as water is present in large excess. Hence this is an example of Pseudo-unimolecular reaction.

Examples of First Order Reactions

Example 1: Decomposition of H_2O_2 - This reaction is supposed to take place in two steps as-

i) $H_2O_2 \longrightarrow H_2O + O$ (slow)
ii) $O + O \longrightarrow O_2$ (fast)

The rate of the reaction is only due to first step; hence is first order. The progress of the reaction can be followed in two ways -

a) By titrating with $KMnO_4$: In this method H_2O_2 is treated with standard solution of $KMnO_4$. Thus, withdraw equal volume of H_2O_2 at different time intervals and titrate with standard $KMnO_4$ solution. Thus volume of $KMnO_4$ solution 'V_t' used corresponds to the concentration of unreacted H_2O_2 i.e. (a-x) value at that instant. The volume of $KMnO_4$ solution 'V_o' required initially gives initial concentration of H_2O_2 i.e. 'a'. Thus the equation (13) becomes –

$$k_1 = \frac{2.303}{t}\log\left(\frac{V_0}{V_t}\right)$$

b) By measuring volume of O_2 gas: In this method progress of reaction is followed by measuring the volume of O_2 gas evolved at various time intervals. Thus, $V_t = x$, $V_\infty = a$

$$k_1 = \frac{2.303}{t}\log\left(\frac{V_\infty}{V_\infty - V_t}\right)$$

Problem 4: The decomposition of H_2O_2 was studied by titrating it at different intervals of time with potassium permanganate ($KMnO_4$). Calculate the velocity constant from the following data, if the reaction is of the first order.

t (min)	0	10	22	40
Vol. of $KMnO_4$ (dm^3)	25.0	20.0	15.5	9.6

Solution: Given that

$V_0 = a = 25$

We know that for decomposition of H_2O_2 by titrating with potassium permanganate ($KMnO_4$), rate law equation is-

$$k_1 = \frac{2.303}{t}\log\left(\frac{V_0}{V_t}\right)$$

i) When, t = 10 min, V_t = 20.0 ml

$$\therefore k_1' = \frac{2.303}{10}\log_{10}\left(\frac{25}{20}\right)$$

$$= 0.0223 \text{ min}^{-1}$$

ii) When, t = 22 min, V_t = 15.5 ml

$$\therefore k_2' = \frac{2.303}{22}\log_{10}\left(\frac{25}{15.5}\right)$$

$$= 0.0217 \text{ min}^{-1}$$

iii) When, t = 40 min, V_t = 9.6 ml

$$\therefore k_3' = \frac{2.303}{40}\log_{10}\left(\frac{25}{9.6}\right)$$

$$= 0.0239 \text{ min}^{-1}$$

$$\therefore k_1 = \frac{k_1' + k_2' + k_3'}{3} = \frac{0.0223 + 0.0217 + 0.0239}{3}$$

$$= 0.0226 \text{ min}^{-1}$$

Problem 5: The decomposition of H_2O_2 was studied by titrating it at different intervals of time with potassium permanganate ($KMnO_4$). Calculate the velocity constant from the following data, if the reaction is of the first order.

t (sec)	0	100	200
Vol. of $KMnO_4$ (dm^3)	22.8	13.80	8.28

Solution: Given that $V_0 = a = 22.8$

We know that for decomposition of H_2O_2 by titrating with potassium permanganate ($KMnO_4$), rate law equation is-

$$k_1 = \frac{2.303}{t}\log\left(\frac{V_0}{V_t}\right)$$

i) When, t = 100s, V_t = 20.0 ml

$$\therefore k_1' = \frac{2.303}{100}\log_{10}\left(\frac{22.8}{13.80}\right) = 5.021 \times 10^{-2}$$

ii) When, t = 200s, V_t = 15.5 ml

$$\therefore k_2' = \frac{2.303}{200}\log_{10}\left(\frac{22.8}{8.28}\right) = 5.065 \times 10^{-2}$$

Example 2: Hydrolysis of Methyl Acetate

The reaction is catalysed by mineral acid as-

$$CH_3COOCH_3 + H_2O \xrightarrow{H'} CH_3COOH + CH_3OH$$

This reaction involves two molecules, but the concentration of H_2O does not change appreciably. Hence the reaction is *Pseudo uniorder reaction or Pseudo first order reaction.* Acetic acid produced during the reaction is titrated with standard alkali solution. The mineral acid is used as catalyst also reacts with the alkali solution. Equals volumes of reaction mixture are withdrawn at different time intervals & titrated with standard solution of NaOH. If V_0 is the volume of alkali required at time, t = 0, it will correspond to the concentration of mineral acid & V_t volume correspond to the acetic acid formed & mineral acid. Hence,

$$x = (V_t - V_0)\ \text{ml} \quad \& \quad a = (V_\infty - V_0)\ \text{ml}$$

$$(a - x) = (V_\infty - V_0) - (V_t - V_0) = (V_\infty - V_t)\ \text{ml}$$

Thus, the equation (13) becomes-

$$\therefore k_1 = \frac{2.303}{t}\log_{10}\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

Problem 6: Following data was obtained in the hydrolysis of ethyl acetate at 25°C in presence of 0.35 N hydrochloric acid which was used as a catalyst.

Time (seconds) →	0	1200	4500	7140	∞
ml. of alkali used →	24.36	25.85	29.32	31.42	47.15

From this data, show that hydrolysis of methyl acetate is a first order reaction.

Solution: Given that

$V_0 = a = 24.36$ and $V_\infty = 47.15$

We know that for acid hydrolysis of methyl acetate rate law equation is-

$$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{V_\infty - V_0}{V_\infty - Vt}\right)$$

i) At, t = 1200 s, $k_1 = \frac{2.303}{1200}\log_{10}\left(\frac{47.15 - 24.36}{47.15 - 25.85}\right) = 5.64 \times 10^{-5} s^{-1}$

ii) At, t = 4500 s, $k_1 = \frac{2.303}{4500}\log_{10}\left(\frac{47.15 - 24.36}{47.15 - 29.32}\right) = 5.46 \times 10^{-5} s^{-1}$

iii) At, t = 7140 s, $k_1 = \frac{2.303}{7140}\log_{10}\left(\frac{47.15 - 24.36}{47.15 - 31.42}\right) = 5.46 \times 10^{-5} s^{-1}$

Since, k_1 is nearly constant, this reaction follows first order kinetics.

Problem 7: Following data was obtained in the hydrolysis of methyl acetate at 25°C in presence of 0.1N hydrochloric acid which was used as a catalyst.

Time in Sec	0	75	119	183	∞
Volume alkali Added (dm3)	19.24	24.20	26.60	29.32	42.03

From this data, show that hydrolysis of methyl acetate is a first order reaction.

Solution: Given that

$$V_0 = a = 19.24 \text{ and } V_\infty = 42.03$$

We know that for acid hydrolysis of methyl acetate rate law equation is-

$$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

i) At, t = 75s, $k_1 = \frac{2.303}{75}\log_{10}\left(\frac{42.03-19.24}{42.03-24.20}\right) = 0.00315 \text{ sec}^{-1}$

ii) At, t = 119 s, $k_1 = \frac{2.303}{119}\log_{10}\left(\frac{42.03-19.24}{42.03-26.60}\right) = 0.00321 \text{ sec}^{-1}$

iii) At, t = 183 s, $k_1 = \frac{2.303}{183}\log_{10}\left(\frac{42.03-19.24}{42.03-29.32}\right) = 0.00310 \text{ sec}^{-1}$

Since, k_1 is nearly constant, this reaction follows first order kinetics.

Example 3: Inversion of Cane-Sugar- The inversion or hydrolysis of cane sugar takes place in presence of mineral acid as follows

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Cane sugar (dextro-ratatory) | glucose (dextro-ratatory) | fructose (laevo-ratatory)

Actually above reaction is bimolecular as it involves two molecules of reactants but follows first order rate equation as water is present in large excess. Hence this is an example of ***Pseudo-unimolecular reaction.***

The initial solution of sucrose is dextro-ratatory but on hydrolysis in presence of hydrochloric acid, it gives glucose (dextro-ratatory) and fructose (laevo-ratatory) in equal amounts the laevo-rotation of fructose is -92^0 while dxtro-rotation of glucose is $+52.5^0$. The mixture, therefore on whole, is laevo-ratatory. For this reason the reaction is known as inversion of cane sugar. The progress of the reaction can be followed by measuring the change in angle of ration by means of polarimeter. Change in angle of rotation is directly proportional to the change of concentration of sugar (x) to glucose and fructose. The angle of rotation of plane polarized light decreses with time.The total change in angle of rotation produced at the end of reaction gives the initial concentration 'a'

Let, r_0 be the initial rotation
r_∞ be the final rotation
r_t be the rotation at time t

Then,

$a \ \alpha \ (r_0 - r_\infty)$ → Initial concentration of cane sugar

$x \ \alpha \ (r_0 - r_t)$ → The concentration of sugar at time t

$$\therefore (a - x) \propto (r_0 - r_\infty) - (r_0 - r_t)$$

OR $(a - x) \propto (r_t - r_\infty)$

Substituting these values in equation (13), we get,

$$k_1 = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

OR $$k_1 = \frac{2.303}{t}\log\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right)$$

Problem 8: A 20% solution of cane sugar is inverted by 0.5 N HCl at 25°C. The angle of rotation of cane sugar at various time intervals are given below

Time (seconds) →	0	72	368	460	680	∞
Rotation (degrees) →	+ 24.1	+21.4	+12.4	+10	+5.5	-10.7

From this data, show that inversion of cane sugar is a first order reaction.

Solution: Given that

$$r_0 = 24.1 \text{ and } r_\infty = -10.7$$

We know that for inversion of cane sugar rate law equation is-

$$k_1 = \frac{2.303}{t}\log\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right)$$

Also, $r_0 - r_\infty = 24.1 - (-10.7) = 24.1 + 10.7 = 34.8$

i) At, $t = 72$ s, $k_1 = \frac{2.303}{72}\log_{10}\left(\frac{34.8}{21.4-(-10.7)}\right) = 1.12 \times 10^{-3}\,s^{-1}$

ii) At, $t = 368$ s, $k_1 = \frac{2.303}{368}\log_{10}\left(\frac{34.8}{12.4-(-10.7)}\right) = 1.11 \times 10^{-3}\,s^{-1}$

iii) At, $t = 460$ s, $k_1 = \frac{2.303}{460}\log_{10}\left(\frac{34.8}{10-(-10.7)}\right) = 1.13 \times 10^{-3}\,s^{-1}$

iv) At, $t = 680$ s, $k_1 = \frac{2.303}{680}\log_{10}\left(\frac{34.8}{5.5-(-10.7)}\right) = 1.12 \times 10^{-3}\,s^{-1}$

Since, k_1 is nearly constant, this reaction follows first order kinetics.

Problem 9: From the following data for the decomposition of ammonium nitrite in aqueous solution, show that the reaction is of the first order.

Time (Minutes)	10	15	20	15	∞
Volume of N_2 (c.c.)	6.25	9.00	11.40	13.65	35.05

Solution:

For this reaction

$$k_1 = \frac{1}{t}\ln\frac{V_\infty}{V_\infty - V_t};\ V_\infty = 35.05 = a$$

The values of k_1 at different times are obtained as follows:

Time	$V_\infty - V_t$	$\frac{1}{t}\ln\frac{V_\infty}{V_\infty - V_t} = k_1$
10 min.	$35.05 - 6.25 = 28.80$	$\frac{1}{10}\ln\frac{35.05}{28.80} = 0.01976\ \text{min}^{-1}$
15 min.	$35.05 - 9.00 = 26.05$	$\frac{1}{15}\ln\frac{35.05}{26.05} = 0.01976\ \text{min}^{-1}$
20 min.	$35.05 - 11.40 = 23.65$	$\frac{1}{20}\ln\frac{35.05}{23.65} = 0.01964\ \text{min}^{-1}$
10 min.	$35.05 - 13.65 = 21.40$	$\frac{1}{25}\ln\frac{35.05}{21.40} = 0.01971\ \text{min}^{-1}$

A constant value of k_1 shows that the reaction is of the first order.

Problem 10: The rate constant for a first-order reaction is $1.54 \times 10^{-3}\ s^{-1}$. Calculate its half-life time.

Solution:

We have, $$t_{1/2} = \frac{0.693}{k_1} = \frac{0.693}{1.54 \times 10^{-3} s^{-1}} = 450\ s$$

Problem 11: The half-life of the homogeneous gaseous reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ which obeys first-order kinetics, is 8-0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?

Solution:

We get, $$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{8.0\text{min}} = 0.087\ \text{min}^{-1}$$

For a first-order reaction,

$$k_1 = \frac{1}{t}\ln\frac{a}{a-x}$$

$$t = \frac{1}{k_1}\ln\frac{a}{a-x} = \frac{1}{0.087\text{min}^{-1}}\ln\frac{100}{1} = 52.93\ \text{min}$$

Problem 12: In an enzyme solution, sucrose undergoes fermentation. If 0.1 M solution of sucrose is reduced to 0.05 M in 10 hours and to 0.025 M in 20 hours, what is the order of the reaction and what is the rate constant?

Solution: Since on doubling the time from 10 hours to 20 hours, fractional reduction of sucrose concentration is also doubled, the reaction must be of the first order.

Since for a first-order reaction, $t_{1/2} = \frac{0.693}{k_1}$,

Hence, $$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \times 60 \times 60 s} = 1.9 \times 10^{-5} s^{-1}$$

6.9 Second Order Reactions

When the rate of the reaction is depend on the change in initial concentration of two reactants, the reaction is said to be of second order.

Such a reaction in general is represented in two ways

$$2A \rightarrow \text{Product}$$

OR

$$A + B \rightarrow \text{Product}$$

Case 1: Two reactants with equal initial concentration. Consider any one of above reaction

$$2A \rightarrow \text{Product}$$

At time, t= 0 a o

t = t, (a - x) x

Suppose 'a' mole dm^{-3} be the initial concentration of reactant 'A' and 'x' mol dm^{-3} be the concentration of product after time, 't'. The rate of the reaction is given as-

$$r = \frac{dx}{dt} \alpha (a - x)^2$$

i.e.

$$\frac{dx}{dt} = k_2 (a - x)^2 \qquad \text{..........(15)}$$

Where, k_2 is second order rate constant (or velocity constant) of second order reaction.

Equation (15) can be written as-

$$\frac{dx}{(a - x)^2} = k_2 dt$$

Integrating above equation, we get

$$\int \frac{dx}{(a - x)^2} = \int k_2 dt$$

$$\frac{1}{(a - x)} = k_2 t + C \qquad \text{..........(16)}$$

Where 'C' is integration constant which can be evaluated from initial condition of reaction as at t = 0, x= 0.

$$\therefore \frac{1}{a} = C \qquad \text{..........(17)}$$

From equations (16) and (17) we get,

$$\frac{1}{(a - x)} = k_2 t + \frac{1}{a}$$

$$k_2 t = \frac{1}{(a - x)} - \frac{1}{a}$$

$$k_2 t = \frac{x}{a(a - x)}$$

$$k_2 = \frac{1}{t} \frac{x}{a(a - x)} \qquad \text{..........(18)}$$

This equation (18) is known as kinetic equation (or integrated rate law) of second order reaction.

Case II: Two reactants with different initial concentration.

i.e.		A	+	B	→	Product
At time,	$t=0$	a		b		o
	$t=t,$	(a - x)		(b-x)		x

Suppose 'a' & 'b' are the initial concentrations in mol/dm^3 of A & B respectively. Let x mol/dm^3 of A & B, have reacted in time t. Then concentration of A & B after time t will be (a-x) & (b-x) mol/dm^3 respectively. The rate law equation is

$$r=\frac{dx}{dt}\alpha(a-x)(b-x)$$

i.e. $$\frac{dx}{dt}=k_2(a-x)(b-x) \qquad \text{..........(19)}$$

Where, k_2 is second order rate constant (or velocity constant) of second order reaction. Equation (19) can be written as-

$$\frac{dx}{(a-x)(b-x)}=k_2dt \qquad \text{..........(20)}$$

By using partial fraction, we can write,

$$\frac{1}{(a-x)(b-x)}=\frac{1}{(a-b)}\left(\frac{1}{b-x}-\frac{1}{a-x}\right)$$

Thus equation (20) becomes –

$$\frac{1}{(a-b)}\left(\frac{1}{b-x}-\frac{1}{a-x}\right)dx=k_2dt$$

i.e. $$\frac{1}{(a-b)}\left(\frac{dx}{b-x}-\frac{dx}{a-x}\right)=k_2dt$$

Integrating, $$\frac{1}{(a-b)}\left[\int\frac{dx}{b-x}-\int\frac{dx}{a-x}\right]=k_2dt$$

$$\frac{1}{(a-b)}[-\ln(b-x)-(-\ln(a-x)]=k_2t+C$$

$$\frac{1}{(a-b)}[\ln(a-x)-\ln(b-x)]=k_2t+C$$

$$\frac{1}{(a-b)}\left[\ln\frac{(a-x)}{(b-x)}\right]=k_2t+C \qquad \text{..........(21)}$$

Where, C is integration constant & evaluated as-

At, $t=0$, $x=0$

$$\therefore\frac{1}{(a-b)}[-\ln b-(-\ln(a)]=C$$

OR $$\frac{1}{(a-b)}[\ln a-\ln b]=C$$

OR $$\frac{1}{(a-b)}\ln\frac{a}{b}=C \qquad \text{..........(22)}$$

Hence equation (21) becomes-

$$\frac{1}{(a-b)}\ln\frac{(a-x)}{(b-x)}=k_2t+\frac{1}{(a-b)}\ln\frac{a}{b}$$

$$\frac{1}{(a-b)}\ln\frac{(a-x)}{(b-x)}-\frac{1}{(a-b)}\ln\frac{a}{b}=k_2t$$

$$\frac{1}{(a-b)}\left[\ln\frac{(a-x)}{(b-x)}-\ln\frac{a}{b}\right]=k_2t$$

$$\frac{1}{(a-b)}\ln\left(\frac{b(a-x)}{a(b-x)}\right)=k_2t$$

$$\therefore k_2=\frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}$$

$$k_2=\frac{2.303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)} \qquad \cdots\cdots\cdots(23)$$

Equation (23) is kinetic equation (or integrated rate law) for second order reaction with different initial concentration.

Characteristics of second order reaction

i) Unit of second order reaction

We know that rate law for the second order reaction is

$$k_2=\frac{1}{t}\frac{x}{a(a-x)}$$

$$k_2=\frac{1}{\text{sec}}\frac{\text{moldm}^{-3}}{\text{moldm}^{-3}.\text{moldm}^{-3}}$$

$$k_2=\frac{1}{\text{sec}}\frac{1}{\text{moldm}^{-3}}$$

$$k_2=\text{dm}^3\text{mol}^{-1}\,\text{sec}^{-1}$$

ii) Half life

Half life of reaction is the time required to complete half of the reaction. It is represented by $t_{1/2}$.

The second order rate law equation

$$k_2=\frac{1}{t}\frac{x}{a(a-x)}$$

Thus, when $t=t_{1/2}$, $x=\frac{a}{2}$

Substitute these values in above equation, we get

$$k_2=\frac{1}{t_{1/2}}\frac{\frac{a}{2}}{a\left(a-\frac{a}{2}\right)}$$

OR $$k_2 = \frac{1}{t_{1/2}} \frac{\frac{a}{2}}{a \times \frac{a}{2}}$$

OR $$k_2 = \frac{1}{t_{1/2}} \frac{1}{a}$$

OR $$t_{1/2} = \frac{1}{k_2} \frac{1}{a}$$

OR $$t_{1/2} \propto \frac{1}{a}$$

Thus the time required for completion of definite fraction of the second order reaction is inversely proportional to initial concentration of reactant.

iii) Graphical representation

We have, $k_2 = \frac{1}{t} \frac{x}{a(a-x)}$ OR $k_2 t = \frac{1}{(a-x)} - \frac{1}{a}$ OR $\frac{1}{(a-x)} = k_2 t + \frac{1}{a}$

This is in the form of $y = mx + C$

Thus when the graph is plotted between, $\frac{1}{(a-x)}$ and time 't' we get a straight line, not passing through origin having slope, k_2 and intercept $\frac{1}{a}$ as shown in Figure 5.

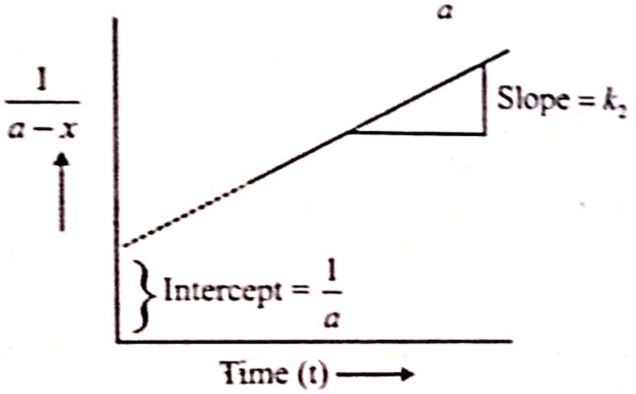


Fig. 6.5 : Plot of $\frac{1}{(a-x)}$ versus time 't'

iv) The second order rate constant (k_2) depends on initial concentration of the reactants

Let the reaction is started with new initial concentration m times the original concentration. Then initial concentration will be ma, the concentration after time t will be 'm (a-x)' & that of the product will be mx.

We have, $k_2 = \frac{1}{t} \frac{x}{a(a-x)}$

The new equation with new concentration will be,

$$k_2' = \frac{1}{t}\frac{\text{mx}}{\text{ma.m}(\text{a-x})}$$

$$= \frac{1}{m}\left(\frac{1}{t}\frac{x}{a(a-x)}\right)$$

$$\therefore k_2' = \frac{1}{m}k_2$$

Hence the new value of velocity constant is $\frac{1}{m}$ times the original value.

v) When one of the reactants is present in large excess, a second order reaction behaves as first order.

For the reaction of type, A + B → P, we have the rate equation as-

$$k_2 = \frac{2.303}{(a-b)t}\log\frac{\text{b}(\text{a}-\text{x})}{\text{a}(\text{b}-\text{x})}$$

Let 'A' is in the large excess compared to B. Then, $a >> b$. So that $a - x \approx a$ and $a - b \approx a$

$$\therefore k_2 = \frac{2.303}{ta}\log\frac{\text{b.a}}{\text{a}(\text{b}-\text{x})}$$

$$k_2' = k_2 a = \frac{2.303}{t}\log\frac{\text{b}}{(\text{b}-\text{x})}$$

$$\therefore k_2' = k_1 \qquad \left\{Since, k_1 = \frac{2.303}{t}\log\left(\frac{\text{b}}{(\text{b}-\text{x})}\right)\right\}$$

Examples of Second Order Reaction

Example 1: Saponification of ethyl acetate (Hydrolysis of ethyl acetate by an alkali) with equal initial concentration of ester and alkali. The reaction can be written as-

$$\underset{\text{Ethyl Acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{Sodium Acetate}}{CH_3COONa} + \underset{\text{Ethyl Alcohol}}{C_2H_5OH}$$

As the rate of reaction depends on concentration of both the reactants, the reaction is of second order. The progress of reaction is studied by titrating same volume of the reaction mixture against standard acid solution at regular time intervals. The volume of acid required for titration corresponds to unreacted alkali or ester (a - x) and volume required initially will give initial concentration of reactant as 'a'. Thus,

$$a \equiv V_0$$

$$a - x \equiv V_t$$

OR $a-(a-x) \equiv V_0 - V_t$

OR $x \equiv V_0 - V_t$

Hence the rate equation second order reaction, $k_2 = \frac{1}{t}\frac{x}{a(a-x)}$ becomes

$$k_2 = \frac{1}{t}\frac{V_0 - V_t}{V_0[V_0 - (V_0 - V_t)]} \qquad \text{OR} \qquad k_2 = \frac{1}{t}\frac{V_0 - V_t}{V_0 \times V_t}$$

Examples of Second Order Reaction

Example 1: Saponification of ethyl acetate (Hydrolysis of ethyl acetate by an alkali) with equal initial concentration of ester and alkali. The reaction can be written as-

$$\underset{\text{Ethyl Acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{Sodium Acetate}}{CH_3COONa} + \underset{\text{Ethyl Alcohol}}{C_2H_5OH}$$

As the rate of reaction depends on concentration of both the reactants, the reaction is of second order. The progress of reaction is studied by titrating same volume of the reaction mixture against standard acid solution at regular time intervals. The volume of acid required for titration corresponds to unreacted alkali or ester (a - x) and volume required initially will give initial concentration of reactant as 'a'. Thus,

$$a \equiv V_0$$

$$a - x \equiv V_t$$

OR $$a-(a-x) \equiv V_0 - V_t$$

OR $$x \equiv V_0 - V_t$$

Hence the rate equation second order reaction,

$$k_2 = \frac{1}{t}\frac{x}{a(a-x)} \text{ becomes } k_2 = \frac{1}{t}\frac{V_0 - V_t}{V_0[V_0-(V_0-V_t)]}$$

OR $$k_2 = \frac{1}{t}\frac{V_0 - V_t}{V_0 \times V_t}$$

Problem 13: In the hydrolysis of ethyl acetate using equal concentration of ester and NaOH, the following results were obtained.

Show that the reaction follows second order kinetics.

Time (min)	0	5	15	25
Vol. of HCl (ml)	16.0	10.24	6.13	4.32

Show that the reaction follows second order kinetics.

Solution: Given that

$$V_0 = 16 \text{ ml}$$

We know that for basic hydrolysis of ethyl acetate, rate law equation is-

$$k_2 = \frac{1}{t}\frac{V_0 - V_t}{V_0 \times V_t}$$

∴ At, t = 5 min, $k_2 = \frac{1}{5} \times \frac{(16-10.24)}{16 \times 10.24} = 0.0070 \text{ ml}^{-1}\text{min}^{-1}$

At, t = 15 min, $k_2 = \frac{1}{15} \times \frac{(16-6.13)}{16 \times 6.13} = 0.0067 \text{ ml}^{-1}\text{min}^{-1}$

At, t = 25 min, $k_2 = \frac{1}{25} \times \frac{(16-4.32)}{16 \times 4.32} = 0.0067 \text{ ml}^{-1}\text{min}^{-1}$

Since values of k_2 are nearly the same, the reaction follows second order, kinetics.

Problem 14: In the hydrolysis of ethyl acetate using equal concentration of
and NaOH, the following results were obtained.
Show that the reaction follows second order kinetics.

Time (Sec)	0	4.88	10.06	23.65	∞
ml of acid added	47.63	38.90	32.62	22.58	11.84

Solution: We know that

$$k_2 = \frac{1}{t}\frac{x}{a(a-x)}$$

Time	a	a-x	$x = a-(a-x)$	$k_2 = \frac{1}{t}\frac{x}{a(a-x)}$
4.88	47.63	38.90	47.63-38.90=8.72	0.000962
10.06	47.63	32.62	47.63-32.62 = 15.02	0.000960
23.65	47.63	22.58	47.63-22.58 = 25.06	0.000983

The value of k_2 is constant the reaction is of the second order.

Example 2: Thermal decomposition of acetaldehyde

The reaction is represented as-

$$CH_3CHO_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$$

Thus the kinetics of the reaction can be studied by the increase in pressure of the gaseous reaction mixture. Let initial pressure of acetaldehyde is P_i& suppose after time 't' its pressure decreases by 'x', which gives CH_4 & CO. Thus at time 't', pressure of CH_4& CO will be 'x'. Thus total pressure P of reaction mixture will be-

$$P = (P_i - x) + x + x$$

OR $$P = P_i + x$$

OR $$x = P - Pi$$

Now, $a \equiv Pi \qquad a - x \equiv P_i - x$

Hence, the rate equation of second order reaction,

$$k_2 = \frac{1}{t}\frac{x}{a(a-x)} \text{ becomes } k_2 = \frac{1}{t}\frac{x}{Pi(Pi-x)}$$

Problem 15: The thermal decomposition of acetaldehyde was studied at 518°C with following result.

Time (sec)	42	73	105	170
$x=(P-P_i)$ mm	34	54	74	114

If initial pressure is 363 mm, show that the reaction follows second order kinetics.

Solution:

Given that, $P_i = 363$ mm

We know that for thermal decomposition of acetaldehyde

$$k_2 = \frac{1}{t}\frac{x}{Pi(Pi-x)}$$

Thus, at t = 42 sec., $k_2 = \frac{1}{42}\frac{34}{363(363-34)} = 6.80\times10^{-6}$ mm of $Hg^{-1}s^{-1}$

at t = 73 sec., $k_2 = \frac{1}{73}\frac{54}{363(363-54)} = 6.6\times10^{-6}$ mm of $Hg^{-1}s^{-1}$

at t = 105 sec., $k_2 = \frac{1}{105}\frac{74}{363(363-74)} = 6.70\times10^{-6}$ mm of $Hg^{-1}s^{-1}$

at t = 170 sec., $k_2 = \frac{1}{170}\frac{114}{363(363-114)} = 7.40\times10^{-6}$ mm of $Hg^{-1}s^{-1}$

As the values of k_2 are nearly same, the reaction follows second order kinetics.

Problem 16: The $t_{1/2}$ of a reaction is halved as the initial concentration of the reactant is doubled. What is the order of reaction?

Solution:

In general we know that, $t_{1/2} \alpha 1/a_0^{n-1}$

In the present case, $\frac{1}{2}t_{1/2} = \frac{1}{(2a_0)^{n-1}}$

Hence, $$\frac{t_{\frac{1}{2}}}{\frac{1}{2}t_{1/2}} = \frac{1/a_0^{n-1}}{1/(2a_0)^{n-1}}$$

OR $2 = 2^{n-1}$ OR $2^1 = 2^{n-1}$

So that,

$$n-1=1 \quad \text{OR } n=2$$

The reaction is of the **second order.**

Problem 17: The $t_{1/2}$ of a reaction is doubled as the initial concentration of the reactant is doubled. What is the order of the reaction?

Solution: Proceeding as in the last example,

$$\frac{t_{\frac{1}{2}}}{2t_{1/2}} = \frac{1/a_0^{n-1}}{1/(2a_0)^{n-1}}$$

OR $½ = 2^{n-1}$ OR $2^{-1} = 2^{n-1}$ OR $n-1=-1$

So that, $n=0$

The reaction is of the zero order.

6.10 Methods of Determination of Order of Reaction

From the chemical equation it is not possible to calculate order of reaction. The mechanism of the reaction can only be determined after determining the order of reaction. To determine the order of reaction, following methods are conveniently used

Integration Method

In this method the reaction is carried actually with known initial concentration 'a' of the reactants. The amount of reactants consumed 'x' after different time intervals't' are determined. Then these values of a, x and t are substituted in first, second & third order rate equations. The equation which gives the satisfactory constant values of velocity constant (k) gives the order of the reaction. This method is referred as hit & trial method and used for the simple reactions.

Van't Hoff's Differential Method: Vant Hoff in 1884 suggested that the rate of the equation of nth order is proportional to the nth power of concentration.

$$\therefore -\frac{dc}{dt} \propto C^n$$

OR

$$-\frac{dc}{dt} = k\,C^n \qquad \text{..........(24)}$$

Where, 'C' is the concentration of reacting substance.

Taking log to both side of equation (24) & simplifying we get,

$$\log\left(-\frac{dc}{dt}\right) = log k + n\log C \qquad \text{..........(25)}$$

Suppose, we start with two experiments having initial concentration C_1& C_2. Then, equation (25) becomes-

$$\log\left(-\frac{dc_1}{dt}\right) = log k + n\log C_1 \qquad \text{..........(26)}$$

$$\log\left(-\frac{dc_2}{dt}\right) = log k + n\log C_2 \qquad \text{..........(27)}$$

Taking equation (26) - (27), we get

$$\log\left(-\frac{dc_1}{dt}\right) - \log\left(-\frac{dc_2}{dt}\right) = n\left(\log C_1 - \log C_2\right)$$

$$\therefore n = \frac{\log\left(-\frac{dc_1}{dt}\right) - \log\left(-\frac{dc_2}{dt}\right)}{\left(\log C_1 - \log C_2\right)} \qquad \text{..........(28)}$$

Using equation (28), the order i.e. value of 'n' can be known from $\left(\frac{dc_1}{dt}\right)$ & $\left(\frac{dc_2}{dt}\right)$ values. These values can be measured by plotting 'C' against't'. The slope of the curve gives the value of $\frac{dC}{dt}$.

Equifractional Change Method or Half Life Method: This method is also known as equifractional change method. It has been proved that half life of zero order reaction is proportional to initial concentration of reactant. Half life of first order reaction is independent of initial concentration of the reactant & inversely proportional to initial concentration for second order &so on. If 't' is the time required for completion of half of the reaction i.e. half life of nth order reaction, then in general we can write,

$$t \propto \frac{1}{a^{n-1}} \qquad \text{..........(29)}$$

Let, t_1 & t_2 are the times of half life or equifractional change when initial concentrations are a_1 & a_2 respectively. Then equation (29) becomes,

$$t_1 \propto \frac{1}{a_1^{(n-1)}} \qquad \text{..........(30)}$$

& $$t_2 \propto \frac{1}{a_2^{(n-1)}} \qquad \text{..........(31)}$$

From equation (30) & (31) we get,

$$\frac{t_2}{t_1} = \frac{a_1^{(n-1)}}{a_2{}^{(n-1)}}$$

$$= \left(\frac{a_1}{a_2}\right)^{(n-1)} \qquad \text{..........(32)}$$

Taking logarithm to both sides of equation (32) and simplifying, we get,

$$\log\left(\frac{t_2}{t_1}\right) = (n-1)\log\left(\frac{a_1}{a_2}\right)$$

OR $$(n-1) = \frac{\log\left(\frac{t_2}{t_1}\right)}{\log\left(\frac{a_1}{a_2}\right)}$$

OR $$(n-1) = \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2}$$

OR $$n = 1 + \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2} \qquad \text{..........(33)}$$

From this equation (33) we can determine the order of reaction 'n'by knowing the a_1, a_2, $t_1$andt_2.

Graphical Method

If amount of reactant decomposed (x) is plotted against time t then slope of the graph gives value of $\frac{dx}{dt}$. We can easily determine $\frac{dx}{dt}$ at any time from the graph shown in figure 6(A) by drawing tangent at the point i.e.

$$\tan\theta = \frac{dx}{dt} = \frac{AB}{BC}$$

Number of such $\frac{dx}{dt}$ values are determined at different points.

We know, if 'a' is the initial concentration & 'x' is the amount of reactant decomposed in time 't' then,

$$\frac{dx}{dt} = k(a-x) \text{ for first order reaction}$$

$$\frac{dx}{dt} = k(a-x)^2 \text{ for second order reaction}$$

$$\frac{dx}{dt} = k(a-x)^3 \text{ for third order reaction}$$

Thus, if the plot of $\frac{dx}{dt}$ against (a-x) is straight line, then the reaction is first order. If the plot of $\frac{dx}{dt}$ against $(a-x)^2$ is a straight line then the reaction is of second order. If the plot $\frac{dx}{dt}$ against $(a-x)^3$ is a straight line, then the reaction if of third order reaction as shown in figure 6(B).

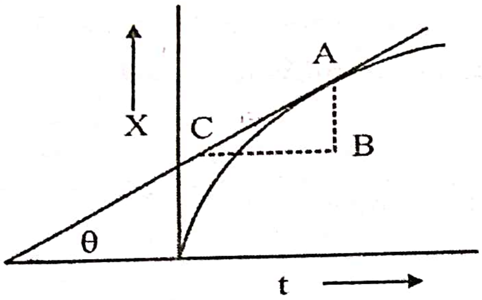


Fig. 6.6 (A)

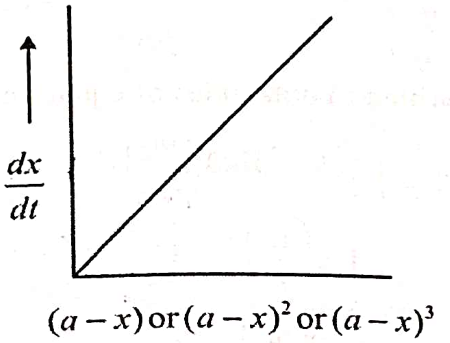


Fig. 6.6 (B)

Ostwald's Isolation Method: In this method all the reactants except one are taken in large excess, so that their concentrations remain constant throughout this change. Thus the order of the reaction is determined with respect to that isolated reactant which is not taken in large excess. The experiment is repeated by isolating each reactant in turn. The total order of the reaction will be given by the sum of the order of reaction with respect to different reactants.

Let the reaction as- $n_1 A + n_2 B + n_3 C \longrightarrow$ product

$$\text{rate} = \frac{dx}{dt} = kC_A^{n_1} . C_B^{n_2} . C_C^{n_3}$$

In the first experiment, the reactants B and C are taken in large excess and the order of reaction is determined with respect to A, which gives order = n_1. Then, take A and C in large excess and the order of reaction is determined with respect to B, which gives order = n_2. Now, take A and B in large excess and the order of reaction is determined with respect to C, which gives order = n_3.

Total order of reaction = $n_1 + n_2 + n_3$.

Problem 18: In Hambly's experiment following results were obtained.

Time (sec)	0	72	157	312
(a-x) mol/dm^3	0.0916	0.0656	0.0512	0.0348

Find the order of reaction.

Solution: Given that at $t = 0, (a-x) \equiv a = 0.0916$, as the concentration at various time intervals $(a-x)$ are given we use integration method,

Thus, for first order reaction, the values of rate constant k_1 are given by using equation (13)

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$\text{At, } t = 72 \text{ min, } k_1 = \frac{2.303}{72}\log\frac{0.0916}{0.0656} = 0.00462 \text{ min}^{-1}$$

$$\text{At, } t = 157 \text{ min, } k_1 = \frac{2.303}{157}\log\frac{0.0916}{0.0512} = 0.00370 \text{ min}^{-1}$$

$$\text{At, } t = 312 \text{ min, } k_1 = \frac{2.303}{312}\log\frac{0.0916}{0.0348} \approx 0.00308 \text{ min}^{-1}$$

As k_1 values are not constant the reaction is not first order.

Now, for second order reaction, the values of rate constant k_2 are given by using equation (18),

$$k_2 = \frac{1}{t}\frac{x}{a\times(a-x)} \text{ dm}^3\text{mol}^{-1}$$

$$\text{At, } t = 72 \text{ min, } k_2 = \frac{1}{72}\times\frac{0.026}{0.0916\times0.0656} = 0.0601 \text{ dm}^3\text{mol}^{-1}\text{min}^{-1}$$

$$\text{At, } t = 157 \text{ min, } k_2 = \frac{1}{157}\times\frac{0.0568}{0.0916\times0.0512} = 0.0548 \text{ dm}^3\text{mol}^{-1}\text{min}^{-1}$$

$$\text{At, } t = 312 \text{ min, } k_2 = \frac{1}{312}\times\times\frac{0.0568}{0.0916\times0.0348} = 0.0571 \text{ dm}^3\text{mol}^{-1}\text{min}^{-1}$$

As k_2 values are nearly constant, the reaction is of second order.

Problem 19: The study of decomposition of phosphine gave the following data-

Pressure (mm)	**707**	**79**	**37.5**
Half life period (sec)	**84**	**84**	**84**

What is the order of reaction?

Solution: We know that for first order reaction the half life time is independent of initial concentration (pressure). Hence, this reaction is first order.

Problem 20: As a certain temperature, the half life periods for the catalytic decomposition of ammonia were found to be –

Pressure (mm)	**50**	**100**	**200**
Half life period (sec)	**3.52**	**1.82**	**1.00**

Find out the order of reaction?

Solution: We know that using half life the order of reaction can be determine by equation (33),

$$n = 1 + \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2}$$

Thus, i) For, $a_1 = 50, \quad t_1 = 3.52, \ \& \ a_2 = 100, \ t_2 = 1.82$

$$\therefore n = 1 + \frac{\log 1.82 - \log 3.52}{\log 50 - \log 100}$$

$$= 1.88 \approx 2.$$

ii) For, $a_1 = 100, \quad t_1 = 1.82, \ \& \ a_2 = 200, \ t_2 = 1.00$

$$\therefore n = 1 + \frac{\log 1.00 - \log 1.82}{\log 100 - \log 200}$$

$$= 1.95 \approx 2.$$

Thus the order is two

Problem 21: From the work of L.T. Reicher on action of bromine on fumaric acid, the following data was obtained.

I^{st} Expt.		II^{nd} Expt.	
t (min)	Concentration	t (min)	concentration
0	8.87	0	3.81
95	7.87	132	3.51

Find out the order.

Solution: For I^{st} Experiment

Let, mean concentration is $C_2 = \dfrac{8.87 + 7.87}{2} = 8.37$

$$\& \ \frac{-dc_1}{dt} = -\left(\frac{7.87 - 8.87}{95 - 0}\right) = 0.0106$$

For II^{nd} Experiment

Let, mean concentration is $C_2 = \dfrac{3.81 + 3.51}{2} = 3.66$

$$\& \ \frac{-dc_2}{dt} = -\left(\frac{3.51 - 3.81}{132 - 0}\right) = 0.00227$$

We know, $n = \dfrac{\log\frac{-dc_1}{dt} - \log\frac{-dc_2}{dt}}{\log C_1 - \log C_2}$ from equation (28)

$$= \frac{\log 0.0106 - \log 0.00227}{\log 8.37 - \log 3.66} = 1.62 \approx 2$$

Hence the reaction is second order.

6.11 Effect of Temperature on Reaction Rates:

It is observed that the velocity of a chemical reaction increases with rise in temperature. Reactions which are very slow at ordinary temperature, becomes fast or even explosive at higher temperature. With increase in temperature, the rates of all reaction do not increase to same extent. In homogeneous reactions, rate is doubled or tripled for each 10°C rise of temperature. This increase in the reaction rate with temperature is expressed in the form of temperature co-efficient. It is defined as- *'The ratio of rate constants of a reaction at two different temperatures separated by 10°C'*

Generally the two temperatures are taken as 25°C and 35°C.

$$\therefore \text{ Temperature Co-efficient } = \frac{k_{35^0 C}}{k_{25^0 C}}$$

OR $$\text{Temperature Co-efficient } = \frac{k_{(t+10)^0 C}}{k_{t^0 C}}$$

Where, $k_t \rightarrow$ Rate constant at t°C

$k_{(t+10)} \rightarrow$ Rate constant at (t + 10)°C

The increase in rate of reaction with temperature means that the reaction has a positive temperature coefficient. For homogeneous gaseous reaction, the value of temperature co-efficient is 2 to 3. Thus with 10°C rise of temperature, specific reaction rate becomes double or triple.

Example

i) The temperature coefficient for the dissociation of hydroiodic acid is 1.7

ii) The temperature coefficient for the reaction of metyl iodied with sodium ethaoxide is 2.9.

$$CH_3I + C_2H_5ONa \longrightarrow CH_3O\,C_2H_5 + NaI$$

6.12 Arrhenius Equation

To explain the increase in the rate of reaction with increase in temperature, Arrhenius (Nobel prize 1903) has put forward the following empirical equation.

$$k = Ae^{-\frac{Ea}{RT}} \qquad \text{..........} (34)$$

Where, A = Arrhenius constant (Frequency factor or pre-exponential factor)

R = Gas constant 8.314 J $K^{-1}mol^{-1}$

T = Temperature (K).

E_a=Energy of activation.

Taking logarithm on both sides of equation (34) we get,

$$\ln k = \ln\left(Ae^{-\frac{E_a}{RT}}\right)$$

OR $$\ln k = \ln A - \frac{E_a}{RT}$$

OR $$2.303\log_{10} k = 2.303\log_{10} A - \frac{E_a}{RT}$$

OR $$\log_{10} k = \log_{10} A - \frac{Ea}{2.303RT} \qquad \text{..........} (35)$$

OR $$\log_{10} k = \left(-\frac{E_a}{2.303R}\right)\frac{1}{T} + \log_{10} A$$

This in the form of $y = mx + C$

Thus plot of $\log_{10} k$ versus $\frac{1}{T}$ gives a straight line with slope $\frac{-E_a}{2.303R}$ and intercept $\log_{10} A$ Thus we determined the energy of activation of a reaction, from the slope of the line shown in figure 7.

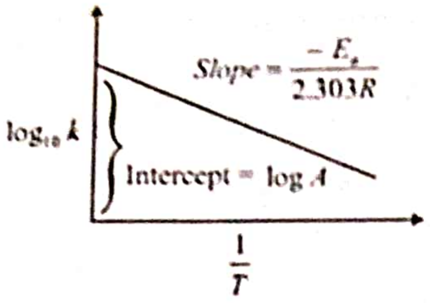


Fig. 6.7 : Plot of $\log_{10} k$ *versus* $\frac{1}{T}$

6.13 Concept of Activation Energy

According to collision theory, the rate of a reaction is proportional to the total number of collisions taking place between the reactant molecules. However, it is observed that all collisions are not effective. The collisions between only those molecules is effective or fruitful which possess certain minimum amount of energy known as threshold energy which is equal to or greater than the activation energy. Thus, before the reaction occurs, molecules must be activated i.e. they possess threshold energy.

'The activation energy is the minimum energy which the molecules must absorb to go into activated state, before the reaction can take place.'

Activated state and activation energy is shown in the energy profile diagram in Figure 8.

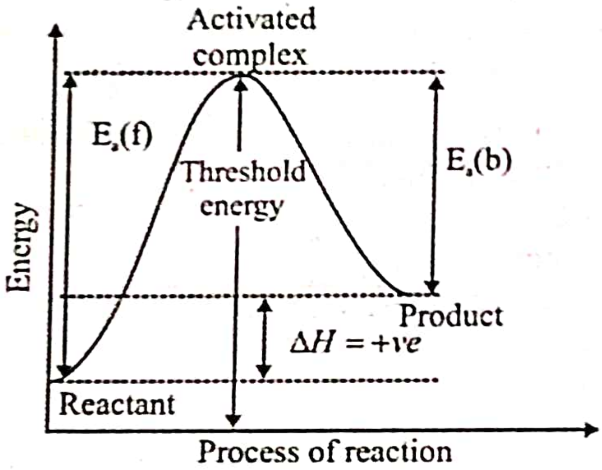


Fig. 6.8 : Plot of reaction rate versus energy

Thus there exists an energy barrier between reactants and products. If the reactant molecules can cross this energy barrier, they will convert into products. The reactant molecules can cross the energy barrier only when they possess the minimum energy which is equals to or greater than activation energy E_a.

Therefore, the activation energy can be defined as '*It is the minimum energy possess by reactant molecules which is equals to or greater than activation energy E_a required to cross the energy barrier and convert into products*'.

Determination of energy of activation by using Arrhenius equation at two different temperatures

We have logarithmic form of Arrhenius equation as-

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT} \qquad \text{.......... from equation (35)}$$

T_1 and T_2 are two temperatures at which constants are k_1 and k_2 then

$$\log_{10} k_1 = \log_{10} A - \frac{E_a}{2.303RT_1} \qquad \text{.......... (36)}$$

$$\log_{10} k_2 = \log_{10} A - \frac{E_a}{2.303RT_2} \qquad \text{.......... (37)}$$

Subtracting equation (36) from (37), we have

$$\log_{10} k_2 - \log_{10} k_1 = \left(\log_{10} A - \frac{E_a}{2.303RT_2}\right) - \left(\log_{10} A - \frac{E_a}{2.303RT_1}\right)$$

OR $$\log_{10} k_2 - \log_{10} k_1 = \left(\frac{E_a}{2.303RT_1} - \frac{E_a}{2.303RT_2}\right)$$

OR $$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

OR $$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \qquad \text{.......... (38)}$$

Problem 22: Trichloroacetic acid in aniline solvent decomposes to give chloroform & carbon dioxide. The rate constant for this first order reaction is $4.0 \times 10^{-5}\ min^{-1}$& at 25^0C&$8.0 \times 10^{-4}\ min^{-1}$ at 45^0C. Calculate the energy of activation for this reaction. (R= 8.314J $K^{-1}mol^{-1}$)

Solution: Given that

$k_1 = 4.0 \times 10^{-5}$, $\quad k_2 = 8.0 \times 10^{-4}$

$T_1 = 25 + 273$, $\quad T_1 = 45 + 273$

$= 298$ K $\quad = 318$ K

R = 8.314J $k^{-1}mol^{-1}$ $\quad E_a = ?$

We know that from equation (38)

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log \frac{8.0 \times 10^{-4}}{4.0 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{318 - 298}{318 \times 298}\right)$$

$\therefore E_a = 118.03$ $Jmol^{-1}$

Problem 23: Benzene diazomium chloride decomposes in presence of water according to first order Kinetics. If the velocity constant at 25^0C $2.8 \times 10^{-3}\ min^{-1}$& the activation energy is 49.74 k J mol^{-1}, find the velocity constant at 35^0C. (R= 8.314J $K^{-1}mol^{-1}$)

Solution:

Given that

$k_1 = 2.8 \times 10^{-3}$, $\quad k_2 = ?$

$T_1 = 25 + 273$, $T_2 = 35 + 273$

$= 298$ K $= 308$ K

R = 8.314J $k^{-1}mol^{-1}$ $E_a = 49.74$k J mol^{-1}

We know that from equation (38)

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\therefore \log\frac{k_2}{2.8\times10^{-3}} = \frac{49.74\times10^3}{2.303\times8.314}\left(\frac{308-298}{308\times298}\right)$$

$$\therefore k_2 = 5.37\times10^{-3}\ \text{min}^{-1}$$

Problem 24: The value of rate constant for the decomposition of nitrogen peroxide is 3.40 × 10^{-5} at 26 ^{0}C and 4.80 × 10^{-3} at 65^{0}C. Calculate the energy of activation for the Reaction. (R= 8.314J/K/Mole)

Solution:

T_1= 26+273 =298K T_2 = 65+273= 338K

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log_{10}\frac{4.80\times10^{-3}}{3.40\times10^{-5}} = \frac{E_a}{2.303\times8.314}\left(\frac{338-298}{298\times338}\right)$$

$$E_a = 103584\ Jmole^{-1}$$

Problem 25: The specific reaction rate of a reaction is 1×10^{-3} Min^{-1} at 299K and 2×10^{-3} Min^{-1} at 308^{0}K. Calculate the energy of activation. (R= 8.314J/K/Mole)

Solution :

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T}{T_1T_2}\right)$$

$$\log_{10}\frac{2\times10^{-3}}{1\times10^{-3}} = \frac{E_a}{2.303\times8.314}\left(\frac{308-299}{299\times308}\right)$$

$$E_a = 52.5986\ Jmole^{-1}$$

EXERCISE

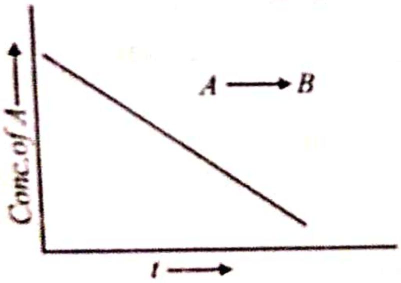
FILL IN THE BLANKS:

1. The rate of the reaction .... with the increase in the concentration of the reactants.
2. Higher the concentration of reactants greater is the possibility of and hence the ....
3. In the presence of catalyst the energy of activation is .... and hence greater numbers of molecules change over to products there by increasing the rate of the reaction.
4. The change in concentration of species per unit time gives the .... of the reaction.

5. The rate constant is equal to the rate of the reaction when concentration of reactants is ……….
6. Increase in surface area of reactant leads to more collisions per litre per second and hence the rate of the reaction is ……….
7. Acid hydrolysis of an ester is an example of ……….
8. Molecularity of a chemical reaction will never be equal to ……….

SHORT ANSWER QUESTIONS:

1. Define or explain the following terms:
   a) Rate of reaction
   b) Order of a reaction
   c) Molecularity of a reaction
   d) Rate constant
   e) Half-life of a reaction
   f) Arrhenius equation
2. State a condition under which a bimolecular reaction is kinetically a first order reaction.
3. Write the rate equation for the reaction 2A + B → C if the order of the reaction is zero.
4. How can you determine the rate law of the following reaction?
   $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$
5. For which type of reactions, order and molecularity have the same value?
6. In a reaction, if the concentration of reactant A is tripled, the rate of reaction becomes twenty-seven times. What is the order of the reaction?
7. Derive an expression to calculate the time required for completion of a zero order reaction.
8. For a reaction A + B → Products, the rate law is – Rate = k $[A][B]^{1/2}$. Can the reaction be an elementary reaction? Explain.
9. For a zero order reaction will the molecularity be equal to zero? Explain.
10. For a general reaction A ⟶ B, the plot of concentration of A vs time is given in Fig. Answer the following question on the basis of graph.



    a) What is the order of the reaction?
    b) What is the slope of the curve?
    c) What is the unit of the rate constant?
11. Why does the rate of a reaction increase with a rise in temperature?
12. Why does the rate of any reaction generally decrease during the course of the reaction?
13. Why can't the molecularity of any reaction be equal to zero?

DESCRIPTIVE QUESTIONS:

1. Define 'energy of activation of a reaction. How does it vary with a rise in temperature?
2. State and explain Arrhenius equation. How can we determine the activation energy of a reaction using this equation?
3. Define Half-life period ($t_{1/2}$) of a chemical reaction. Also obtain the expression for half-life period.
   a) Define half-life period of a chemical reaction. Write equation of $t_{1/2}$ for a first order reaction.
   b) A first order reaction is 75% complete in 60 minutes. Find the half-life of this reaction.
4. What is the effect of temperature on the rate constant of reaction? How can this temperature effect on rate constant be represented quantitatively.
5. What do you mean by zero order reaction? How the value of rate constant is determined? What is the relation between rate constant and half-life period?
6. What are the factors on which the rate of reaction depends? Discuss each factor in brief.
7. Define order and molecularity of reaction. Derive a general expression for specific rate constant of first order reaction.
8. Derive mathematical expression for the rate constant of a reaction ($A+B \rightarrow$ Products) of the second order.
9. How is the order of the reaction determined by Differential method and Half-life method?
10. Derive the rate equation for First order Reaction?
11. Describe graphical method for the determination of order of the reaction.
12. Show that a second order reaction behaves like first order reaction when one of the reactant is taken in large excess.
13. Explain van't Hofff differential method for the determination of order of reaction.
14. Describe half change or equifractional change method for the determination of order of reaction.
15. Explain the factors affecting on the rate of reaction
16. Describe the effect of temperature on the rate of reaction

    50% completion of first order reaction takes place in 16 minutes. What is the fraction that would react in 32 minutes?

    In a second order reaction half life period is 60 min, when the initial concentration is 0.02 mol dm^{-3}. Calculate the value of specific reaction rate.
17. For a given reaction at 25^0C, rate constant double when temperature is increased by 10^0 C.
18. Calculate the energy of activation for this reaction.

    (Given, $R=8.314\ J\ K^{-1}\ mol^{-1}$)

19. The rate constant of first order reaction is 6.93 min^{-1}. Calculate the half life period for this reaction.

20. For the given reaction at 25^0 C, the rate constant doubled when temperature is increased by 10^0 C. Calculate the energy of activation in a reaction ($R=8.314\ J\ K^{-1}\ mol^{-1}$).

SELECT THE PROPER ANSWER FROM GIVEN ALTERNATIVE:

1. Which of the following includes all the aims of kinetics?
   i) to measure the rate of a reaction
   ii) to be able to predict the rate of a reaction
   iii) to be to establish the mechanism by which a reaction occurs
   iv) to be able to control a reaction
   a) (i), (ii) and (iii)   b) (i) and (ii)
   c) (i) and (iii)   d) (i), (ii) , (iii) and (iv)
2. Reaction rates can change with
   a) temperature   b) Addition of the catalyst
   c) reactant concentrations   d) all of these
3. Reaction rates generally
   a) are constant throughout a reaction
   b) are smallest at the beginning and increase with time
   c) are greatest at the beginning of a reaction and decrease with time
   d) no such generalisations can be made
4. Consider the reaction in which nitric oxide is oxidized to nitrogen dioxide, $2NO_{(g)} + O_{(g)} \rightarrow 2NO_{2(g)}$, for which the rate law is = k $[NO]^2[O]$. This reaction takes plast sealed vessel and the partial pressure of nitric oxide is doubled, what effect would this have on the r reaction?
   a) the reaction rate would triple   b) the reaction rate would double
   c) reaction rate would quadruple
   d) there would be no effect on the reaction rate
5. Which three factors affect the rate of a chemical reaction
   a) temperature, pressure and humanity
   b) temperature, reactant concentration and catalyst
   c) temperature, reactant concentration and pressure
   d) temperature, product concentration and container value
6. For first order reaction the rate constant, k, has the unit(s)
   a) $l\ mol^{-1}$ b) $time^{-1}$ c) $(mol/l)^{-1}\ time^{-1}$ d) time mol l^{-1}
7. What are the units of the rate constant for reaction in solution that has an overall reaction order of two?
   a) $M^{-1}\ S^{-1}$ b) M^{-1} c) s^{-1} d) $M\ s^{-1}$

26. Which One of the following is incorrect for the reaction A→B ?
    a) the half life of a second-order reaction inversely proportional to the initial concentration
    b) the half life is the time for one half of the reactant to be consumed
    c) the second order rate constant can be found by plotting $1/[A]^2$ versus time, where [A] is the concentration of reactant
    d) the initial rates for a second order reaction depends on the concentration of the reactant squared

27 Consider the reaction in which ammonia is synthesized from nitrogen and hydrogen gases : $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ How is the rate of formation of ammonia related to the rate of consumption of hydrogen ?
    a) the rate of formation of ammonia is half of the rate of consumption of hydrogen
    b) the rate of formation of ammonia is twice the rate of consumption of hydrogen
    c) the rate of formation of ammonia is equal to the rate of consumption of hydrogen
    d) the rate of formation of ammonia is two third the rate of consumption of hydrogen

28. Which concentration plot is linear for the first-order reaction? (A is one of the reactant).
    a) [A]versus time
    b) square root of [A]versus time
    c) In [A] versus time
    d) $[A]^2$ versus time

29. A reaction in which all reactions are in the same phase is called
    a) elementary b) bimolecular c) homogeneous d) heterogeneous

30. As temperature increases, the reaction rate ……
    a) decreases then increases
    b) decreases
    c) increases
    d) stays the same

31. For the reaction $2NO_2 + O_2 \rightarrow N_2O_3 + O_2$ the following observations are made: doubling the concentration $[NO_2]$of doubles the rate, and doubling the concentration of $[O_3]$ doubling rate. What is the rate law for the reaction ?
    a) rate = k $[NO_2]$
    b) rate = k $[NO_2]^2 [O_3]$
    c) rate = k $[NO_2]^2 [O_3]^2$
    d) rate = k $[NO_2] [O]_3$

32. The half life of a first-order process
    a) depends on the react and concentration raised to the first power
    b) is inversely proportional to the square of the reactant concentration
    c) is inversely proportion to the reactant concentration
    d) is totally independent of the react and concentration

33. The rate constant of zero-order reactions has the unit
    a) s^{-1} b) mol L^{-1} s^{-1} c) L^2 mol^{-2} s^{-1} d) L mol^{-1} s^{-1}

34. When the rate of the reaction is equal to the rate constant, the order of the reaction is
    a) zero order b) first order c) second order d) third order

35. For a second-order reaction, what is the unit of the rate of the reaction?
    a) s^{-1} b) mol $L^{-1}s^{-1}$ c) mol^{-1} L s^{-1} d) mol^{-2} L^2 s^{-1}

36. Which of the following observations is incorrect about the order of a reaction?
    a) Order of a reaction is always a whole number
    b) The stoichiometric coefficient of the reactants doesn't affect the order
    c) Order of reaction is the sum of power to express the rate of reaction to the concentration terms of the reactants.
    d) Order can only be assessed experimentally

37. The acid hydrolysis of ethyl acetate follows the ....?
    a) Second order   b) Unimolecular
    c) Pseudo-unimolecular   d) Third order

38. Which among the following is a false statement?
    a) Rate of zero order reaction is independent of initial concentration of reactant.
    b) Half life of a third order reaction is inversely proportional to square of initial concentration of the reactant.
    c) Molecularity of a reaction may be zero or fraction.
    d) For a first order reaction, t1/2=0.693K

39. The rate of a certain hypothetical reaction A + B + C → products is given by $r = -d[A]dt = K[A]^{1/2}[B]^{1/3}[C]^{1/4}$. The order of the reaction is
    a) 13/11   b) 13/14   c) 12/13   d) 13/12

40. For a chemical reaction A→B, it is found that the rate of reaction doubles when the concentration of A is increased four times. The order of reaction is
    a) Two   b) One   c) Half   d) Zero

41. For the reaction A + H_2O → products, find the rate of the reaction when [A] = 0.75 M, k= 0.02.
    a) 0.077 s^{-1} b) 0.085 s^{-1} c) 0.015 s^{-1} d) 0.026 s^{-1}

42. What is the rate law for acid hydrolysis of an ester such as $CH_3COOC_2H_5$ in aqueous solution?
    a) k $[CH_3COOC_2H_5]$ b) k $[CH_3COOC_2H_5]$ $[H_2O]$
    c) k $[CH_3COOC_2H_5]^2$ d) k

43. How many times will the rate of the elementary reaction 3X + Y → X_2Y change if the concentration of the substance X is doubled and that of Y is halved?
    a) $r_2 = 4.5r_1$
    b) $r_2 = 5r_1$
    c) $r_2 = 2r_1$
    d) $r_2 = 4r_1$

Hint: $r = k[X]^3[B]$ ....rate law equation

Write $r = k[X][B]$

i) $8r = k[2X]^3[B]$

ii) $r/2 = k[X]^3[B/2]$

iii) Overall 8r/2r = 4r

44. For a zero order reaction, the rate of reaction is independent of ....
    a) Temperature   b) Nature of reactants
    c) Concentration of reactants   d) Effect of catalyst

45. The half-life period of zero order reaction is directly proportional to the
   a) Rate constant b) Initial concentration of reactants
   c) Final concentration of reactants d) Concentration of products

46. For a first order reaction, the half life period is independent of the ....
   a) Initial concentration of the reactants b) Final concentration of the reactants
   c) Rate constant d) Concentration of products

47. The half life period of n^{th} order reaction varies inversely to ....th power of the initial concentration of the reactants.
   a) n b) 2n c) (n+1) d) (n-1)

48. What will be the fraction of molecules having energy equal to or greater than activation energy, Ea?
   a) K b) A c) $Ae^{-Ea/RT}$ d) $e^{-Ea/RT}$
   d) $e^{-Ea/RT}$

49. Arrhenius equation shows the variation of .... with temperature?
   a) Reaction rate b) Rate constant
   c) Energy of activation d) Frequency factor

50. Which of the following statements about the catalyst is true?
   a) A catalyst accelerates the rate of reaction by bringing down the activation energy.
   b) A catalyst does not participate in reaction mechanism.
   c) A catalyst makes the reaction feasible by making ΔG more negative.
   d) A catalyst makes equilibrium constant more favorable for forward reaction.

ANSWERS OF MCQ:

1 - d	11 - d	21 - a	31 - d	41 - c
2 - d	12 - c	22 - c	32 - d	42 - a
3 - d	13 - d	23 - b	33 - b	43 - d
4 - c	14 - a	24 - c	34 - a	44 - c
5 - b	15 - b	25 - a	35 - c	45 - b
6 - b	16 - d	26 - c	36 - a	46 - a
7 - a	17 - a	27 - d	37 - c	47 - d
8 - c	18 - d	28 - c	38 - c	48 - d
9 - a	19 - a	29 - c	39 - d	49 - b
10 - d	20 - d	30 - c	40 - c	50 - a

****