



SG GOVT. DEGREE COLLEGE : PILER

(Re-Accredited by NAAC with 'B' grade)

DEPT. OF CHEMISTRY

MINIMUM STUDY MATERIAL

Sem-1, chemistry paper -1

2021 - 22

Dr. M. Sudhakar Reddy

Principal

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Lecturer

THREE-YEAR B.Sc. (B.Sc Chemistry)

SEMESTER – I

Subject: Chemistry

Course I (Inorganic & Physical Chemistry)

Semester-wise Syllabus under CBCS (w. e. f. 2020-21)

INORGANIC CHEMISTRY**UNIT-I****Chemistry of p-block elements.**

Group 13: Preparation & structure of Diborane, Borazine

Group 14: Preparation, classification and uses of silicones

Group 15: Preparation & structures of Phosphonitrilic halides $(\text{PNCl}_2)_n$ where $n=3, 4$

Group 16: Oxides and Oxoacids of Sulphur (structures only)

Group 17: Pseudohalogens, Structures of Interhalogen compounds.

UNIT-II**1. Chemistry of d-block elements.**

Characteristics of d-block elements with special reference to electronic configuration, variable valence, magnetic properties, catalytic properties and ability to form complexes. Stability of various oxidation states.

2. Chemistry of f-block elements

Chemistry of lanthanides - electronic structure, oxidation states, lanthanide contraction, consequences of lanthanide contraction, magnetic properties. Chemistry of actinides – electronic configuration, oxidation states, actinide contraction, comparison of lanthanides and actinides.

3. Theories of bonding in metals

Valence bond theory and Free electron theory, explanation of thermal and electrical conductivity of metals based on these theories, Band theory- formation of bands, explanation of conductors, semiconductors and insulators

PHYSICAL CHEMISTRY**UNIT-III****Solid state**

Symmetry in crystals. Law of constancy of interfacial angles. The law of rationality of indices. The law of symmetry. Miller indices, Definition of lattice point, space lattice, unit cell.

Bravais lattices and crystal systems. X-ray diffraction and crystal structure. Bragg's law. Powder method. Defects in crystals. Stoichiometric and nonstoichiometric defects.

UNIT-IV**1. Gaseous state**

Vander Waal's equation of state. Andrew's isotherms of carbon dioxide, continuity of state. Critical phenomena. Relationship between critical constants and vander Waal's constants. Law of corresponding states. Joule- Thomson effect. Inversion temperature.

2. Liquid state

Liquid crystals, mesomorphic state. Differences between liquid crystal and solid/liquid. Classification of liquid crystals into Smectic and Nematic. Application of liquid crystals as LCD devices.

UNIT-V**1. Solutions**

Azeotropes-HCl-H₂O system and ethanol-water system. Partially miscible liquids-phenol- water system. Critical solution temperature (CST), Effect of impurity on consolute temperature. Immiscible liquids and steam distillation. Nernst distribution law. Calculation of the partition coefficient. Applications of distribution law.

2. Ionic equilibrium

Ionic product, common ion effect, solubility and solubility product. Calculations based on solubility product.

3. Dilute solutions Colligative properties-RLVP, Osmotic pressure, Elevation in boiling point and depression in freezing point. Experimental methods for the determination of molar mass of a non-volatile solute using osmotic pressure, Elevation in boiling point and depression in freezing point. Abnormal colligative properties. Van't Hoff factor.

MODEL PAPER
FIRST YEAR B.Sc., DEGREE EXAMINATION
SEMESTER-I
CHEMISTRY Course-I: INORGANIC & PHYSICAL CHEMISTRY

Time: 3 hours

Maximum Marks: 75

PART- A

5 X 5 = 25 Marks

Note : Answer any **FIVE** of the following questions. Each one carries **FIVE** marks

1. Explain the preparation & structures of Phosphonitrilic compounds.
2. Explain in brief, catalytic properties & stability of various oxidation states of d-block elements.
3. Write short note on Bravais lattices and crystal systems.
4. What are Smectic & Nematic liquid Crystals? Explain.
5. Write account on Common ion effect & Solubility product.
6. Describe Andrew's isotherms of carbon dioxide.
7. Explain Actinide Contraction.
8. Explain the structure of Borazine.

PART- B

5 X 10 = 50 Marks

Note : Answer **ALL** the questions. Each one carries **TEN** marks

9. (a) Explain Classification, Preparations & uses of Silicones
(or)
(b) (i) What are Pseudohalogens.
(ii) Explain the Structures of any one AX₃& AX₅ interhalogen compounds.
10. (a) What is Lanthanide Contraction? Explain the Consequences of Lanthanide Contraction.
(or)
(b) (i) Explain the magnetic properties of d- block elements.
(ii) Explain about Conductors, Semi-Conductors& Insulators using Band Theory.
11. (a) Write an essay on Crystal defects.
(or)
(b) What is Bragg's Law. Explain the determination of structure of a crystal by powder method.
12. (a) Derive the relationship between Critical constants & Vanderwaal constants
(or)
(b) (i) Write any 5 differences between liquid crystals & liquids, solids
(ii) Write the applications of Liquid crystals.
13. (a) Explain Nernst distribution Law. Explain its applications
(or)
(b). What are colligative properties. Write experimental methods for determination of molar mass of a non-volatile solute by using Elevation in boiling point & depression in freezing point.

IMPORTANT QUESTIONS FOR UNIVERSITY EXAMS - 2022**SHORT NOTES****UNIT - I**

1. Preparation & structures of Phosphonitrilic halides.
2. Structures of Sulphur Oxoacids
3. Pseudohalogens
4. Preparation & structure of Diborane.
5. Preparation & structure of Borazine

UNIT - II

1. Lanthanide contraction, consequences
2. d-block elements – a. Variable valence,
b. Magnetic properties,
c. Catalytic properties
d. Ability to form complexes.
3. Comparison of lanthanides and actinides.

UNIT - III

1. Miller indices, Bravais lattices – Crystal systems.
2. Law of Constancy of Interfacial angles and The law of Rationality of indices.
3. Lattice point, Space lattice, Unit Cell.

UNIT - IV

1. Andrew's isotherms of carbon dioxide.
2. Joule- Thomson effect. Inversion temperature.
3. Application of liquid crystals as LCD devices.

UNIT - V

1. Nernst distribution law - Applications
2. Effect of impurity on consolute temperature
3. Common ion effect
4. Solubility product.
5. Abnormal colligative properties. Van't Hoff factor.

LONG ANSWER QUESTIONS**UNIT - I**

1. Preparation, classification and uses of silicones
2. Structures of Interhalogen compounds.

UNIT - II

1. Valence bond theory and Free electron theory
2. Band theory- conductors, semiconductors and insulators.

UNIT - III

1. X-ray diffraction, Bragg's law - Crystal structure - Powder method.
2. Defects in crystals. Stoichiometric and non-stoichiometric defects.

UNIT - IV

1. What are Ideal solutions. Reasons for deviation of real gases from ideal behaviour – Vander Waal's corrections - Vander Waal's equation derivation.
2. What are critical constants? Relation between Critical constants and Vander Waal's equation.
3. Liquid crystals - Classification - Application

UNIT - V

1. Azeotropes-HCl-H₂O system and Ethanol-Water system.
2. Partially miscible liquids – Critical solution temperature (CST) - Phenol - Water system.
3. What are colligative properties. Write experimental methods for determination of molar mass of a non-volatile solute by using
 - a. Elevation in boiling point
 - b. Depression in freezing point.
 - c. Osmotic Pressure.

***** ALL THE BEST *****

K. Ram Babu, Lecturer in Chemistry

UNIT-I

BORANES

The binary compounds of boron and hydrogen are called boranes. There are several types of boranes. Based on molecular formula boranes are classified mainly into two types.

They are

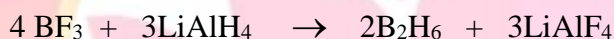
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|-----------------------------|----------------------------------|
| 1. Boranes : B_nH_{n+4} | 2. Hydroboranes : B_nH_{n+6} . |
| B_2H_6 : Diborane | B_4H_{10} : Tetra borane |
| B_5H_9 : Pentaborane -9 | B_5H_{11} : Penta borane -11 |
| B_6H_{10} : Hexaborane-10 | B_6H_{12} : Hexaborane - 12 |

- Between these two series of boranes B_nH_{n+4} type of boranes are known to be relatively more stable than B_nH_{n+6} type.
- Boranes are known to be electron deficient compounds. Among the boranes, diborane(B_2H_6) is the simplest and widely studied borane.

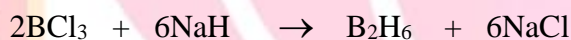
DIBORANE (B_2H_6)**Preparation methods**

Diborane is prepared

- By the reduction of boron trifluoride with $LiAlH_4$ in the presence of ether medium.



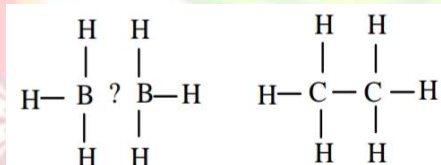
- By the reduction of borontrichloride with sodiumhydride



- By the reduction of sodium borohydride with iodine in the presence of ether.

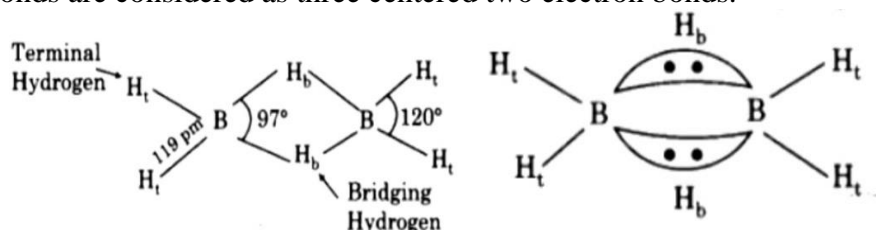
**Structure of diborane**

Diborane molecular formula is B_2H_6 . Diborane is an electron deficient compound. It has only 12 valence electrons (6 from two boron atoms and 6 from six hydrogen atoms) against 14 electrons actually required for forming covalent bonds with all the atoms. If Diborane has to have ethane like structure 14 electrons are necessary. So it cannot have the ethane like structure.

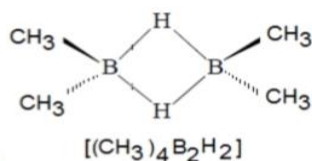


Diborane B_2H_6 Ethane C_2H_6

- In order to explain the bonding with the available 12 valence electrons the following bridge structure was proposed for diborane, in confirmation with the results of electron diffraction and IR spectroscopic experiments.
- Diborane is a non-planar molecule. In this two BH_2 groups lie in one plane and the two bridging hydrogen atoms are perpendicular to the plane of the molecule. This structure has four terminal hydrogens and two bridged hydrogens.
- The four B-H bonds are considered as two centered two electron bonds (normal covalent bonds). The two B-H-B bonds are considered as three centered two electron bonds.

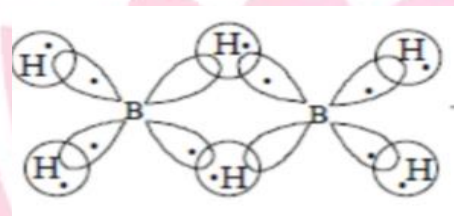


4. Diborane on methylation forms tetra methyl diborane ($B_2H_2(CH_3)_4$). This reaction supported the presence of two bridged hydrogens and four terminal hydrogens in diborane

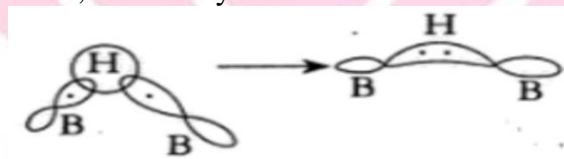


Molecular Orbital Structure of Diborane

1. In diborane both the boron atoms are in the sp^3 hybridised state. Each boron therefore forms 4 sp^3 hybrid orbitals, out of which three of them contain one electron each and one sp^3 hybrid orbital is vacant.
2. The four sp^3 hybrid orbitals of two borons overlap axially with 1s orbitals of four hydrogen atoms and form 4 sp^3 -s sigma bonds, i.e., B-H bonds.
3. sp^3 hybrid orbital of one boron atom having one electron and vacant sp^3 hybrid orbital of other boron atom overlap with 1s orbital of hydrogen atom and forms two sp^3 -s- sp^3 bridged molecular orbital bond (B-H-B bond).



4. These two B-H-B bonding molecular orbitals are three centred two electrons bond. (3C-2e bond) and resemble the shape of banana, hence they are also called banana bond (or) 'tau' bond.



Uses of Diborane

Diborane is used

1. As a rocket fuel
2. For the preparation of high energy fuels and propellants
3. As a reducing agent in organic chemistry
4. As a catalyst in polymerization reactions
5. In the preparation of alcohols, ketones, carboxylic acids through hydroboration reaction.
6. For the preparation of metallic borohydrides like $LiBH_4$, $NaBH_4$, $Al(BH_4)_3$ etc.
7. For the preparation of higher boranes.

BORAZOLE (or) **BORAZINE** ($B_3N_3H_6$)

Triborinetriamine is known as Borazine (or) Borazole.

1. Its molecular formula $B_3N_3H_6$
2. It is also called as Inorganic Benzene, because it is isoelectronic and identical structure with Benzene.
3. Borazine is a colourless liquid, with characteristic aromatic smell.
4. It is thermally a very stable compound.

Preparation methods

Borazole is prepared by the following methods.

1. From diborane and ammonia

The preparation of borazine from diborane and ammonia involves two steps.

Step : 1 Reaction of diborane with excess of ammonia at a low temperature of $-120^\circ C$ to form an addition compound $B_2H_6 \cdot 2NH_3$, also called diammoniate of diborane.

Step : 2 Heating of diammoniate of diborane to $200^\circ C$ to get borazine.



2. Borazine is prepared by the reduction of chloroborazine with sodiumborohydride. The chloroborazine required for this reaction can be obtained by the reaction of boron trichloride and ammonium chloride at $140^\circ C$

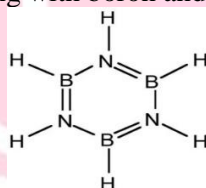


Chloroborazine

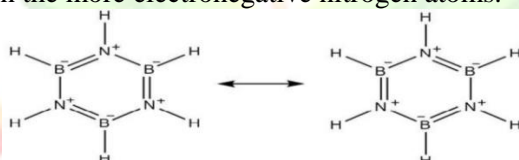
3. Borazine is obtained by the reaction of Ammoniumchloride with $LiBH_4$ in vacuum at $230^\circ C$

**Structure of Borazine**

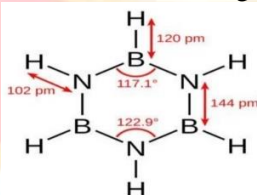
1. The structure of borazine is identical and isoelectronic to that of benzene. Like benzene it has a planar hexagonal structure containing six membered ring with boron and nitrogen atoms in alternate positions.



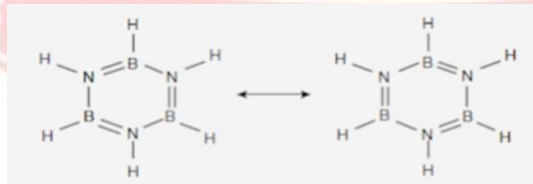
2. In borazine both Boron and Nitrogen atoms are in sp^2 hybridised state.
3. So it has six delocalised 'p' electrons. Unlike in benzene the B-N bonds are polar and hence the 'p' electron density is more localised on the more electronegative nitrogen atoms.



4. The bond angle in borazine is 120° . All B-N bond lengths 1.44 \AA .



5. The resonance structures of borazine

**Uses of borazine**

Borazine is used

1. As a starting material for the synthesis of ceramic materials.
2. In the preparation of hexagonal boron nitride thin films.

SILICONES

Organo silicon polymers which are containing -Si-O-Si- (or) -O-Si-O- linkages are known as silicones.

1. These are also known as 'Polysiloxanes'.
2. The repeating unit in Silicones are $--R_2SiO--$
Where R = Organic groups.
3. Silicones can be represented by the general formula $(R_2SiO)_n$. R may be alkyl (CH_3 , C_2H_5 etc.) or aryl (C_6H_5 etc.) groups.
4. The silicones can be obtained in the form of oils, viscous liquids, resins, greases, rubber like solids etc.
5. Now a days silicones are gaining much importance in view of their special and desirable properties.
6. They are very stable even at high temperatures.

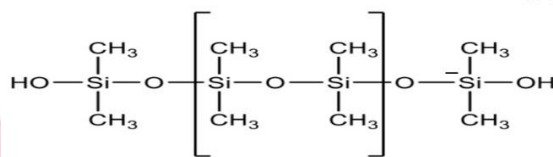
Classification

Silicones can be classified into three types based on structure.

1. Linear silicones,
2. Cyclic silicones, and
3. Cross linked silicones.

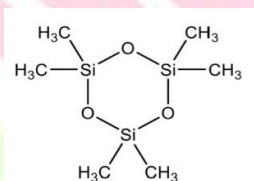
1. Linear silicones

Hydrolysis of dialkyl dichloro silane gives rise to straight chain polymers. Since an active -OH group is left at each end of the chain. Polymerization continues and the chain length increases.



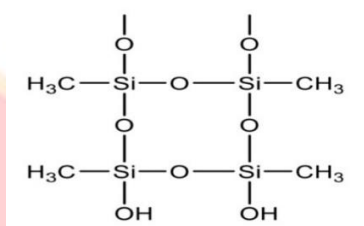
2. Cyclic silicones

These are formed by the elimination of H_2O molecule from terminal -OH groups of the linear silicone.



3. Cross - linked silicones

Hydrolysis of alkyl trichlorosilanes followed by polymerization forms cross linked silicones.



Types of silicones

Silicones are four types

- 1) Silicone Oils,
- 2) Silicone Rubbers,
- 3) Silicone Greases
- 4) Silicone Resins.

1. Silicone oils:

- a. Straight chain polymers of 20 to 500 units are used as silicone oils.
- b. The boiling point and viscosity increases with chain length.
- c. These fluids are water repellent because of the organic side groups.
- d. These are prepared mainly by hydrolysing dichloro dimethyl silane $((CH_3)_2SiCl_2)$.
- e. These are non - toxic and have a low surface tension.
- f. Silicones with some phenyl groups are better lubricants.

2. Silicone rubbers:

- Silicone rubbers are made of long straight chain polymers between 6,000 - 6,00,000.
- These are prepared by hydrolysis of dimethyl dichloro silane with KOH.
- They retain their elasticity from -90°C to 250°C .
- These are good electrical insulators.
- They may be vulcanized to give hard rubber.
- On heating in air to $350 - 400^{\circ}\text{C}$, silicones are rapidly oxidized and cross - links are formed.

3. Silicone greases:

- Several types of greases are made from mixtures of silicone fluids and fillers such as silica, lithium soap and carbon black.

Ex: For insulating and water repellent greases, silicone fillers are used and the fluid may be dimethyl copolymerised with methyl phenyl (or) methyl trifluoropropyl silicone.

4. Silicone resins:

- Silicone resins are rigid polymers and extensively cross linked.
- If the hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ is carried out in presence of CH_3SiCl_3 , extensive cross -linking accompanies polymerisation. This results in rigid polymers known as silicone resins.

Preparation methods

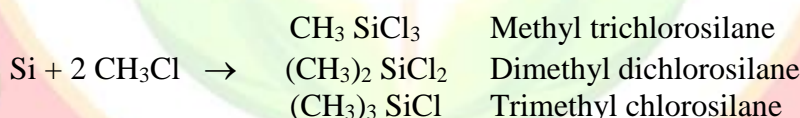
The preparation of any silicone involves three stages.

- Preparation of alkyl or aryl substituted chlorosilanes.
- Hydrolysis of chlorosilanes.
- Polymerization of silanols.

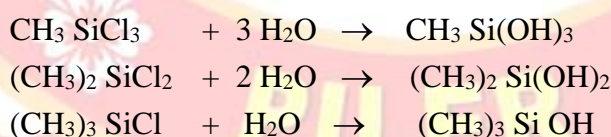
1. Preparation of alkyl chlorosilanes

A mixture of methyl chlorosilanes are formed by heating methyl chloride with silicon in the presence of copper catalyst at 300°C . The above silanes can be separated by careful fractionation.

Ex:

**2. Hydrolysis of alkyl Chlorosilanes**

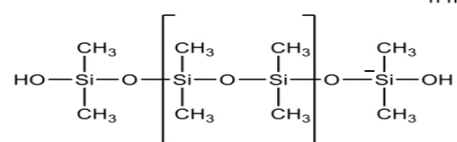
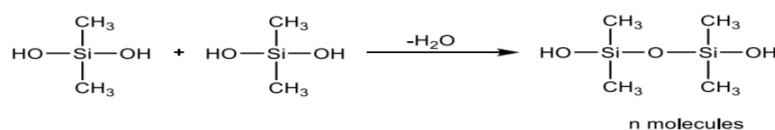
Hydrolysis of alkyl chlorosilanes form the respective Silanols.

**3. Polymerization of Silanols**

Depending on the nature of the silanols, linear, cyclic or two dimensional cross linked silicones are formed.

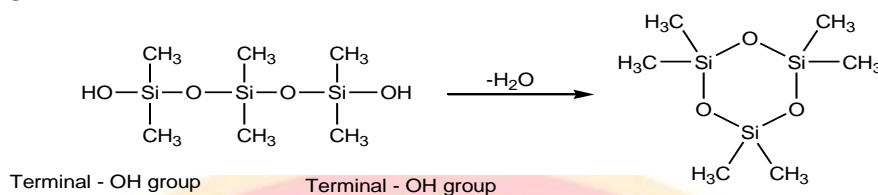
a. Preparation of linear silicones

Condensation Polymerization of two or more dialkyl silane diols give a linear silicone

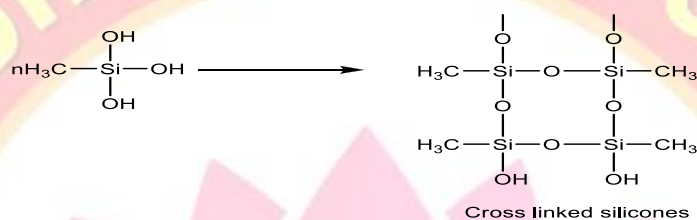


b. Preparation of cyclic silicones

These are formed by the elimination of H₂O molecule from terminal -OH groups of the linear silicone.

**c. Preparation of cross-linked silicones**

Condensation polymerization of many molecules of alkyl silane triol give a cross-linked two dimensional silicone

**Uses of Silicones**

Silicones have wide variety of applications based on their characteristic properties.

1. Silicone oils are used as dielectric insulating media, heat transfer media and hydraulic fluids.
2. Silicon oils are also used as anti foam agents in textile industry, due to they have low Surface tension.
3. Silicone oils are added to cooking oils to prevent frothing, since they are non-toxic.
4. Silicone greases are used in car polishes, lubricants and in lipsticks.
5. Silicone rubbers are used in cable insulations, electric tapes, gaskets, medical tubings, static and rotatory tubes.
6. Silicone rubbers are also used to make moulds for dentures.
7. Silicone resins are used as laminates for printing circuit boards.
8. Silicone resins are used in the manufacture of paints and enamels.
9. Silicone resins are used as non-stick coatings for pans and for making moulds for cars and bread.

PHOSPHAZINES (or) PHOSPHONITRILIC COMPOUNDS

Phosphazenes are cyclic or acyclic polymers of Phosphorus and Nitrogen.

1. These are represented by the formula $(PNX_2)_n$ Where X= F, Cl, Br, SCN, OCH₃, OC₂H₅ etc
2. They possess $---N=PX_2---$ as repeating unit.
3. They are polymers and have π and σ bonds like aromatic compounds.
4. In these polymers nitrogen is trivalent and phosphorous is pentavalent.
5. Among Phosphonitrilic compounds, Phosphonitrilic halides are industrially important compound

Ex: Phosphonitrilic Chloride $(PNCl_2)_n$

Phosphonitrilic Chloride

The general formula is $(PNCl_2)_n$. Where 'n' may be 3 or 4. These are trimeric and tetrameric.

Trimeric Phosphonitrilic chloride

- 1) Important compound is Hexachlorocyclotriphosphazene.
- 2) Its molecular formula is $(NPCl_2)_3$

Preparation:

- 1) Hexachlorocyclotriphosphazene is prepared by the action of PCl_5 on NH_3



- 2) It can also be prepared by heating PCl_5 with solid NH_4Cl at 145° to 160° C



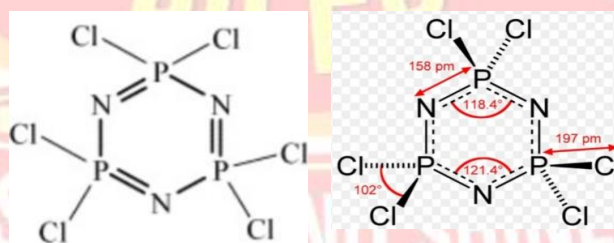
In this method a mixture of $(PNCl_2)_n$ are formed which are separated by distillation.

Structure

- a) In this N is in sp^2 hybridization.
P is in sp^3 hybridization.
- b) Delocalization involves 'P' orbital of Nitrogen and 'd'-orbital of phosphorus. Delocalisation similar to benzene or graphite.
- c) Phosphazenes have planar rings in which 'P' and 'N' are alternatively arranged have equivalent P-N and P=N bonds. Coordinate bond is formed between a filled sp^2 orbital on 'N' atom and the empty $3d_{x^2-y^2}$ orbital on phosphorus.

Their bond lengths P-N : 158 ppm, p-Cl : 197 ppm.

Bond angles : N-P-N : $118^{\circ}.4^1$, P-N-P : $121^{\circ}.4^1$



PSEUDOHALOGENS - PSEUDOHALIDES

The univalent anions with two or more atoms of which one is nitrogen atom and which are similar to those of the halide ions (F^- , Cl^- , Br^- and I^-) are called pseudohalide ions or pseudohalides.

The molecules formed by the dimerisation of these pseudohalides and which resemble the halogens (F_2 , Cl_2 , Br_2 and I_2) in properties are called pseudohalogens or halogenoids.

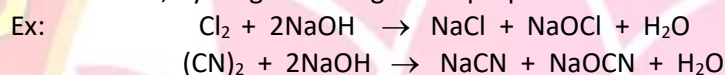
Ex :

Pseudohalide ion	Formula	Pseudohalogen	Formula
Cyanide	CN^-	Cyanogen	$(CN)_2$
Thiocyanide	SCN^-	Thiocyanogen	$(SCN)_2$
Selenocyanide	$SeCN^-$	Selenocyanogen	$(SeCN)_2$
Cyanate	OCN^-	Oxycyanogen	$(OCN)_2$
Azide ion	N_3^-		

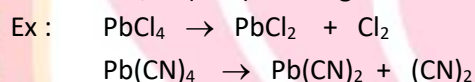
Similarities between pseudohalogens and halogens

Ex:

- Like Cl_2 , Br_2 and I_2 , Cyanogen undergoes disproportionation reaction in the presence of alkali.



- Similar to $PbCl_4$, $Pb(SCN)_4$ undergo thermal decomposition.



- Similar to Chlorine, $(SCN)_2$ undergo addition with unsaturated hydrocarbons.

USES OF PSEUDOHALOGENS

- Cyanogen is used as a poisonous gas in warfare and in organic synthesis.
- Thiocyanogen is used as an oxidising agent.
- Azides are used as organic intermediates.
- Lead azide is used as a detonator.

CYANIDE ION

Among the pseudohalides the best known pseudo halide is cyanide ion. It resembles the halide ions Cl^- , Br^- and I^- in the following aspects.

- It forms hydrocyanic acid, HCN similar to hydrogen halides HCl, HBr and HI.
- It gets oxidized to form the dimer called cyanogen, $(CN)_2$ similar to F_2 , Cl_2 , Br_2 and I_2 .
- It forms insoluble salts with Ag^+ , Pb^{2+} , Hg^+ similar to halides of these cations.
- $AgCN$ is insoluble in water similar to $AgCl$, $AgBr$ and AgI .
- It forms soluble salts such as ($NaCN$, KCN etc) with alkali metals, similar to $NaCl$, $NaBr$ etc.
- Similar to Interhalogen compounds (ClF , ClF_3 , BrF_5 etc.) it forms Pseudointerhalogen compounds such as $ClCN$, $BrCN$ etc.
- It forms complexes such as $[Cu(CN)_4]^{2-}$, $[Co(CN)_6]^{3-}$, $[Zn(CN)_4]^{2-}$ similar to halide complexes $[CuCl_4]^{2-}$, $[CoCl_6]^{3-}$, $[ZnCl_4]^{2-}$.

Like halides, cyanide can act as bridging group,

INTERHALOGEN COMPOUNDS

The binary compounds which are formed when two different halogens react with each other are called interhalogen compounds.

- These compounds are formed due to difference in their atomic sizes and electronegativity values.
- All the interhalogen compounds can be divided into four types.
 - AX type
 - AX₃ type
 - AX₅ type
 - AX₇ type
- In these compounds 'A' is the larger halogen and 'X' is the smaller halogen.
- As the ratio between radii of 'A' and 'X' increases, the number of atoms per molecule increases.

Ex: IF₇ has a maximum of eight atoms since the ratio of radii between Iodine and Fluorine is maximum.

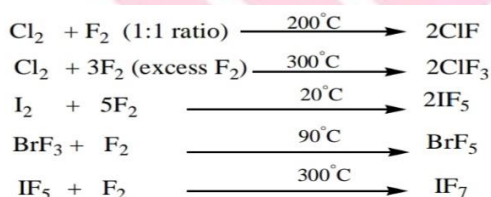
Ex :

AX	AX ₃	AX ₅	AX ₇
ClF	ClF ₃	ClF ₅	IF ₇
BrF	BrF ₃	BrF ₅	
BrCl	(ICl ₃) ₂	IF ₅	
ICl	(IF ₃)*		
IBr			
(IF)*			

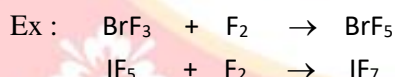
Preparation Methods

- Interhalogen compounds are generally prepared by the reaction of two different halogens under suitable conditions.

Ex :



- Interhalogen compounds are prepared by the reaction of lower interhalogen compounds with halogens under suitable conditions.



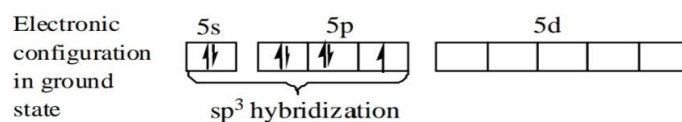
Structures of Inter halogen Compounds

AX Type of Interhalogen compounds

Ex: ClF, BrF, BrCl, IF, ICl, IBr.

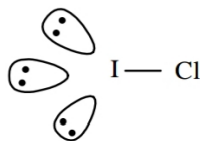
- In AX A is the central atom, and undergoes sp³ hybridization.
The outer most electronic configuration of 'A' is : ns² np⁵ nd⁰
The outer most electronic configuration of 'B' is : ns² np⁵ nd⁰
- Out of four sp³ hybrid orbitals, three of them contain one lone pair of electrons each and the fourth sp³ hybrid orbital contains one electron.

Ex : ICl



- The sp^3 hybrid orbital having one electron overlaps axially with $2p_z$ orbital of 'B' atom having one electron and forms sp^3-p sigma bond.
- Due to the repulsions between lone pairs and bond pairs shape is deviated from tetrahedral to linear.

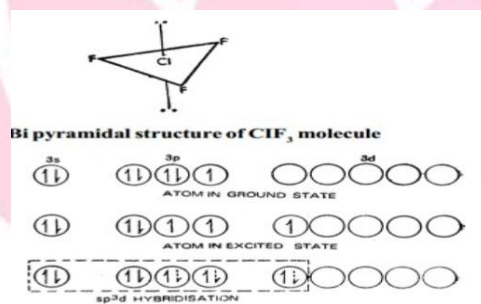
Ex : ICl



AX₃ Type of interhalogen compounds

Ex: ClF₃, BrF₃, IF₃

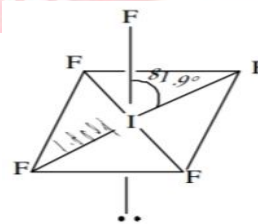
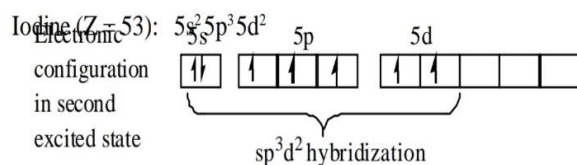
- In AX₃ 'A' is the central atom, in its first excited state undergoes sp^3d hybridization.
The outer most electronic configuration of 'A' is : $ns^2 np^5 nd^0$
First excited state electronic configuration is : $ns^2 np^4 nd^1$
The outer most electronic configuration of 'B' is : $ns^2 np^5 nd^0$
- Out of five sp^3d hybrid orbitals, two of them contain one lone pair of electrons each and the remaining three sp^3d hybrid orbital contains one electron.
- The sp^3d hybrid orbital having one electron overlaps axially with $2p_z$ orbital of 'B' atom having one electron and forms three sp^3d-p sigma bonds.
- Due to the repulsions between lone pairs and bond pairs shape is deviated from trigonal bipyramidal to bent T-shape with the bond angle of $87^\circ 40'$.



AX₅ Type of interhalogen compounds

Ex: ClF₅, BrF₅ and IF₅

- In AX₅ 'A' is the central atom, in its second excited state undergoes sp^3d^2 hybridization.
The outer most electronic configuration of 'A' is : $ns^2 np^5 nd^0$
Second excited state electronic configuration is : $ns^2 np^3 nd^2$
The outer most electronic configuration of 'B' is : $ns^2 np^5 nd^0$
- Out of six sp^3d^2 hybrid orbitals, one of them contain one lone pair of electrons and the remaining five sp^3d^2 hybrid orbitals contains one electron each.
- The sp^3d^2 hybrid orbital having one electron overlaps axially with $2p_z$ orbital of 'B' atom having one electron and forms five sp^3d^2-p sigma bonds.
- Due to the repulsions between lone pairs and bond pairs shape is deviated from octahedral to square pyramidal.

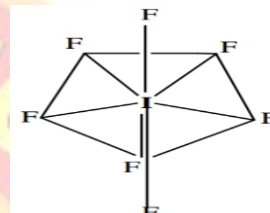
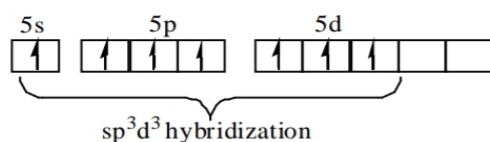
Ex : ICl₅

AX₇ Type of Interhalogen compounds

- In AX₇ 'A' is the central atom, in its third excited state undergoes sp³d³ hybridization.
The outer most electronic configuration of 'A' is : ns² np⁵ nd⁰
Second excited state electronic configuration is : ns¹ np³ nd³
The outer most electronic configuration of 'B' is : ns² np⁵ nd⁰
- All the seven sp³d³ hybrid orbitals are contains one electron each.
- The seven sp³d³ hybrid orbitals having one electron overlaps axially with 2p_z orbital of 'B' atom having one electron and forms seven sp³d³ – p sigma bonds.
- Shape is Pentagonal bipyramidal with the two bond angle of 90° and five bond angle of 72°.

Ex: IF₇Iodine (Z = 53): 5s¹5p³5d³

Electronic configuration in third excited state

**Uses of Interhalogen compounds.**

They are used as

- as non-aqueous solvents.
- as good fluorinating agents. BrF₃ and ClF₃ are used for the production of UF₆ in the enrichment of U²³⁵, U⁺³
- for the estimation of iodine number, solution of ICl in glacial acetic acid is used. Iodine number is a measure for the unsaturation of oils and fats.
- ClF₃, BrF₅ are used as oxidizers for propellants.
- BrF₃, ClF₃, ICl₃ are used in the preparation of polyhalides.

UNIT-II

1. d-BLOCK ELEMENTS (or) TRANSITION ELEMENTSELECTRONIC CONFIGURATION.

The elements in which the differentiating electron enters in to (n-1)d orbital are called d-block elements.

1. The d-block elements are also called as transition elements as they lie in between s-block and p-block, showing transitional properties between s-block and p-block.
2. The elements or its cation with an incomplete (n-1)d-subshell are called transition elements.

Electronic configuration:

General electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{1-2}$.

The d-block elements are divided in to four series namely

1. 3d series : Scandium (Z=21) to Zinc (Z=30)
2. 4d series : Yttrium (Z=39) to Cadmium (Z=48)
3. 5d series : Lanthanum (Z=57) to Mercury (Z=80)
4. 6d series : Actinium (Z=89) to Copernicium (Z=112)

The electronic configuration of 3d series

Element	Atomic number(Z)	Symbol	Electronic configuration
Scandium	21	Sc	(Ar)3d ¹ 4s ²
Titanium	22	Ti	(Ar)3d ² 4s ²
Vanadium	23	V	(Ar)3d ³ 4s ²
Chromium*	24	Cr	(Ar)3d ⁵ 4s ¹
Manganese	25	Mn	(Ar)3d ⁵ 4s ²
Iron	26	Fe	(Ar)3d ⁶ 4s ²
Cobalt	27	Co	(Ar)3d ⁷ 4s ²
Nickel	28	Ni	(Ar)3d ⁸ 4s ²
Copper*	29	Cu	(Ar)3d ¹⁰ 4s ¹
Zinc	30	Zn	(Ar)3d ¹⁰ 4s ²

The electronic configuration of 4d series

Element	Atomic number(Z)	Symbol	Electronic configuration
Yttrium	39	Y	(Kr)4d ¹ 5s ²
Zirconium	40	Zr	(Kr)4d ² 5s ²
Niobium	41	Nb	(Kr)4d ⁴ 5s ¹
Molybdenum*	42	Mo	(Kr)4d ⁵ 5s ¹
Technetium	43	Tc	(Kr)4d ⁵ 5s ²
Ruthenium	44	Ru	(Kr)4d ⁷ 5s ¹
Rhodium	45	Rh	(Kr)4d ⁸ 5s ¹
Palladium	46	Pd	(Kr)4d ¹⁰ 5s ⁰
Silver*	47	Ag	(Kr)4d ¹⁰ 5s ¹
Cadmium	48	Cd	(Kr)4d ¹⁰ 5s ²

The electronic configuration of 5d series

Element	Atomic number(Z)	Symbol	Electronic configuration
Lanthanum	57	La	(Xe)5d ¹ 6s ²
Hafnium	72	Hf	(Xe)5d ² 6s ²
Tantalum	73	Ta	(Xe)5d ³ 6s ²
Tungston	74	W	(Xe)5d ⁴ 6s ²
Rhenium	75	Re	(Xe)5d ⁵ 6s ²
Osmium	76	Os	(Xe)5d ⁶ 6s ²
Iridium	77	Ir	(Xe)5d ⁷ 6s ²
Platinum	78	Pt	(Xe)5d ⁹ 6s ¹
Gold*	79	Au	(Xe)5d ¹⁰ 6s ¹
Mercury	80	Hg	(Xe)5d ¹⁰ 6s ²

The electronic configuration of 6d series

Element	Atomic number(Z)	Symbol	Electronic configuration
Actinium	89	Ac	(Rn)6d ¹ 7s ²
Rutherfordium	104	Rf	(Rn)6d ² 7s ²
Dubnium	105	Db	(Rn)6d ³ 7s ²
Seaborgium	106	Sg	(Rn)6d ⁴ 7s ²
Bohrium	107	Bh	(Rn)6d ⁵ 7s ²
Hassium	108	Hs	(Rn)6d ⁶ 7s ²
Meitnerium	109	Mt	(Rn)6d ⁷ 7s ²
Darmstadtium*	110	Ds	(Rn)6d ⁹ 7s ¹
Roentgenium	111	Rg	(Rn)6d ⁹ 7s ²
Copernicium	112	Cn	(Rn)6d ¹⁰ 7s ²

Anomalous configurations of certain d-block elements

Series	Element	Atomic number(Z)	Electronic configuration as per Aufbau rule	Anomalous configuration
3d	Cr	24	[Ar] 3d ⁴ 5s ²	[Ar] 3d ⁵ 5s ¹
	Cu	29	[Ar] 3d ⁹ 5s ²	[Ar] 3d ¹⁰ 5s ¹
4d	Mo	42	[Kr] 4d ⁴ 5s ²	[Kr] 4d ⁵ 5s ¹
	Ag	47	[Kr] 4d ⁹ 5s ²	[Kr] 4d ¹⁰ 5s ¹
5d	Au	79	[Xe] 5d ⁹ 6s ²	[Xe] 5d ¹⁰ 6s ¹
6d	Ds	110	[Rn] 6d ⁸ 7s ²	[Rn] 6d ⁹ 7s ¹

The irregularities associated with the electronic configuration of these elements can be attributed to

1. Half-filled and completely filled subshells give more stability to the atom.
2. The electron-electron repulsions and nucleus electron attractions.

VARIABLE OXIDATION STATES

Transition elements are exhibiting two or more oxidation states called variable oxidation states. This is due to the involvement of both 'ns' and unpaired '(n-1)d' electrons in bond formation, it is due to the slight difference of energy between 'ns' and '(n-1)d' sub levels.

1. If 'ns' electrons alone involve in bond formation, they exhibit a common oxidation state of +2.
2. In addition to ns electrons if unpaired (n-1)d electrons involve in bond formation, the number of oxidation states gradually increases up to group 7 elements. There onwards the number of oxidation states gradually decreases due to decrease in number of unpaired (n-1)d electrons and successive increase of nuclear charge, leading to high ionization enthalpy values.
3. The various oxidation states possible for 3d, 4d and 5d series of elements

The oxidation states of 3d-series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
(+2)	(+2)	+2	(+1)	+2	+2	+2	+2	+1	+2
+3	+3	+3	+2	(+3)	+3	+3	(+3)	+2	
	+4	+4	+3	+4	+4	(+4)	(+4)		
	+5	(+4)	+5	(+5)	(+5)				
			+5	(+6)	(+6)				
			+6	+7					

4. Lower oxidation states are known as 'Ous' states and the compounds with ionic nature, Higher oxidation states are known as 'ic' states and the compounds with covalent nature.

Ex: Cu^+ = Cuprous Cu^{+2} = Cupric

Fe^{+2} = Ferrous Fe^{+3} = Ferric

5. In 3d series 'Mn' exhibits highest oxidation state of +7 ,
4d series 'Ru' exhibits highest oxidation state of +8
4d series 'Ru' exhibits highest oxidation state of +8
5d series 'Os' exhibits highest oxidation state of +8.
6. Several of these elements exhibit zero or low oxidation states in metal complexes.
Ex : $\text{Ni}(\text{CO})_4$
7. The stability of these oxidation states can be explained in terms of the stable electronic configurations. However, in aqueous solution Cu^{2+} is more stable than Cu^+ in terms of hydration energies.
8. From 3d series of elements to 5d series of elements the stability of lower oxidation states decreases and that of higher oxidation states increases.

CATALYTIC PROPERTIES

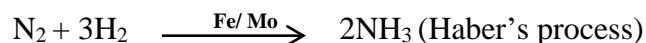
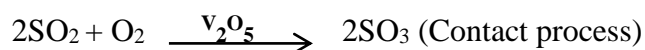
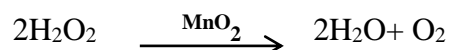
A catalyst is a substance which alters the rate of a reaction without being consumed in the reaction. There are two types of catalysis, heterogeneous catalysis and homogeneous catalysis.

1. **Homogeneous catalysis:** Reactants and catalyst exist in same phase.
2. **Heterogeneous catalysis:** Reactants and catalyst exist in different phase.

A number of transition metals and their compounds are used as catalyst in both heterogeneous and homogeneous catalysis. The heterogeneous catalyst provides an active surface on which the reaction occurs in a new pathway of lower activation energy.

Reason:-The catalytic activity of d-block elements are due to

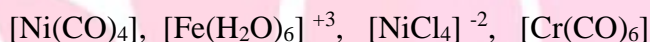
1. Presence of vacant d-orbitals in metal ions
2. Transition metals shows variable oxidation states
3. Transition metals forms complexes easily

Ex:

COMPLEX FORMATION

Transition metal ions have great tendency to form complex compounds. The neutral molecules or negatively charged ions, which donate a lone pair of electrons to the transition metal ion, are called **ligands**.

A complex is formed by transitional metal ion with ligands, the bonds between metal ion and ligands are coordinate covalent bonds. Hence the complexes are also called **coordination compounds**. The ligands like CO, NO etc. form complexes only when the transition metal ions are in zero or lower oxidation states. The ligands like F⁻, Cl⁻, NH₃, H₂O etc. form complexes with the transition metal ions in higher oxidation states.

Ex:**Reason:-**

1. The transition metal ions are very small in size.
2. The transition metal ions possess high positive charge.
3. The transition metal ions possess vacant d and p-orbitals to accept electron pair from ligands to form coordinate covalent bond.

Stability of complexes:-

Ligands like CO, NO form stable complexes. The transition metal ions with highest oxidation state form more stable complexes than metal ions with lower oxidation state.

2. f - block Elements

DISTINGUISH BETWEEN LANTHANIDES AND ACTINIDES

Lanthanides	Actinides
The additional electron enters 4f orbital.	The additional electron enters 5f orbital.
Due to large energy difference between 4f and 5d sub levels, their chemistry is fairly similar.	Due to very small difference between 5f and 6d sub- levels, there is a variability in chemistry of these elements.
Binding energies of 4f-orbitals are higher.	Binding energies of 5f orbitals are lower.
4 f-electrons have greater shielding effect.	5 f- Electron have poor shielding effect.
Maximum oxidation state exhibited by lanthanides is +4 e.g. Ce ⁴⁺	Due to lower binding energies they show higher oxidation states such as +4,+5, +6,and +7.
They do not form complexes easily.	They have much tendency to form complexes.
They do not form oxocations	They form oxocations such as UO ₂ ⁺² , UO ⁺ etc.
Except promethium, they are non-radioactive.	All of them are radioactive.
Most of their ions are colourless.	Most of their ions are coloured.
Their compounds are less basic	Their compounds are more basic

LANTHANIDE CONTRACTION - CONSEQUENCES

Lanthanide series comprises elements from Lanthanum (Z=57) to Lutetium (Z=71). The name lanthanides is derived from lanthanum

In lanthanides as we move across from Lanthanum (La) to Lutetium (Lu), there is a regular decrease in size of the atoms or ions with increase in atomic number. This decrease in size is known as lanthanide contraction.

Cause of Lanthanide contraction

The lanthanide contraction is due to imperfect shielding of one 4f electron by another in the same sub-shell. The reason for imperfect shielding of f-electrons is due to very much diffused shape of f-orbitals. Thus as atomic number increase from La to Lu, the nuclear charge increases, while no comparable increase in shielding effect of f-electrons. This causes a contraction in the size of 4f-subshell and consequently the lanthanide contraction.

Consequences of lanthanide contraction

1. Anomalous behaviour of post-lanthanides

The elements after lanthanides are called post-lanthanide elements. The sizes of third transition series elements are expected to be larger than second transition series elements, but because of lanthanide contraction, the sizes of the atoms of second and third transition series are almost equal.

Ex : The pair of elements Zr / Hf, Nb / Ta. etc are almost identical in size. Due to similar size of the two elements of each pair, they have almost same chemical properties and hence they occur together in nature and are difficult to separate.

2. Basicity:

Larger the size of an ion, greater the tendency to lose electrons and greater is the basicity.

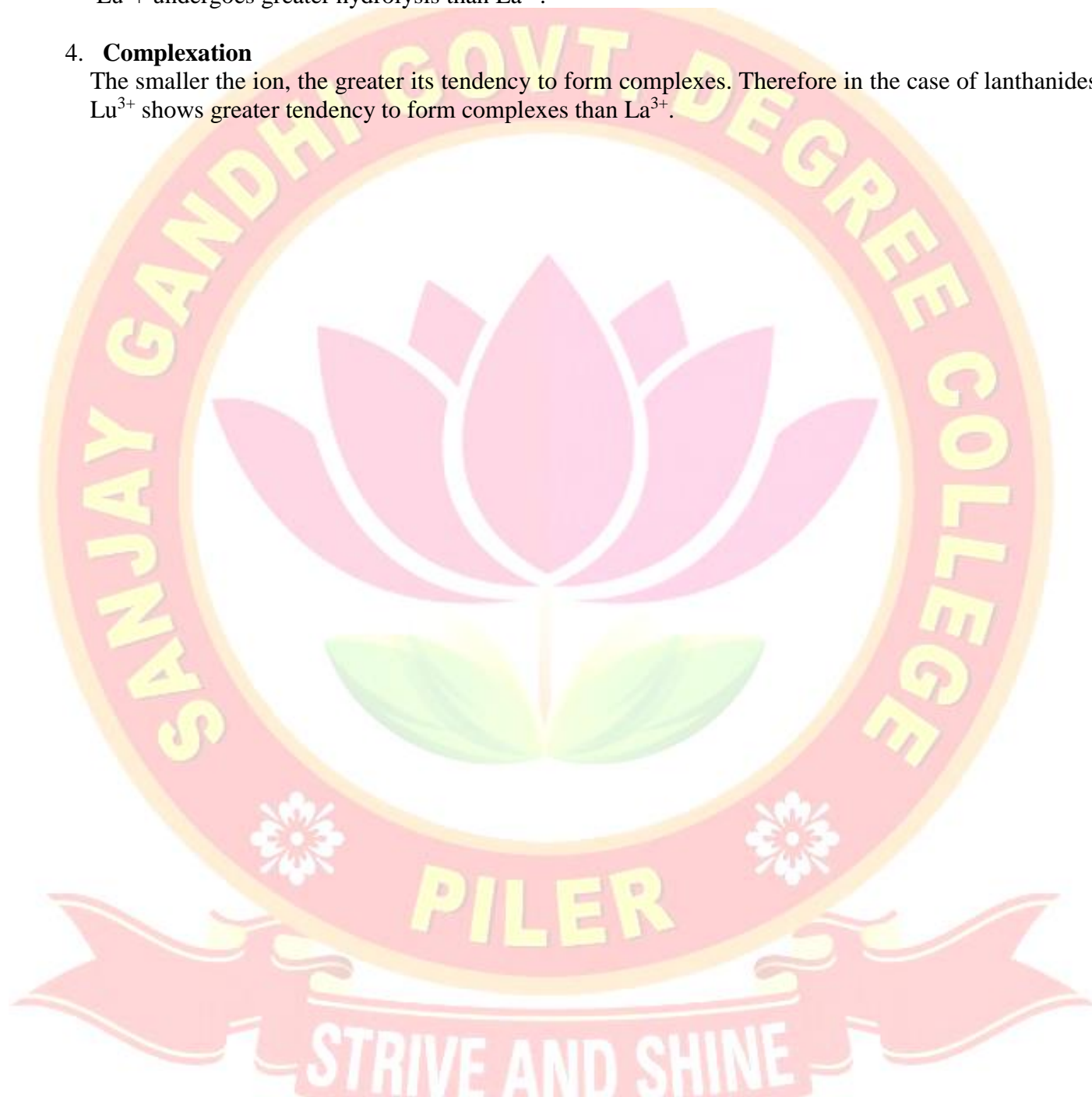
Ex : Due to lanthanide contraction the size decreases from La^{3+} to Lu^{3+} . So basicity decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$.

3. Hydrolysis

The smaller the ion, the greater its tendency towards hydrolysis. Therefore in the case of lanthanides Lu^{3+} undergoes greater hydrolysis than La^{3+} .

4. Complexation

The smaller the ion, the greater its tendency to form complexes. Therefore in the case of lanthanides Lu^{3+} shows greater tendency to form complexes than La^{3+} .



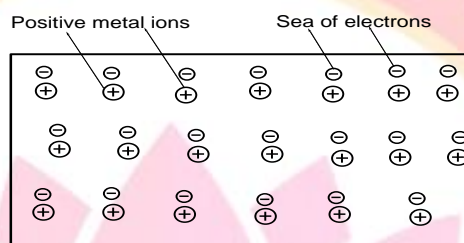
3. BONDING IN METALS

FREE ELECTRON THEORY OF METALS

This theory was proposed by Drude and Lorentz.

Postulates

1. Due to low ionization energies of metals, the metal atoms lose one or more of their valence electrons and form positive ions.
2. The lost electrons move freely and randomly throughout the volume of the metal.
3. Metal is regarded as “**an assembly of positive ions immersed in a sea of mobile electrons.**”
4. The electrostatic attraction between the electron cloud and metal ions is called the **metallic bond**. It holds the metal ions close and gives a stable structure of metal.



Explanation of metallic properties:

- Thermal and electrical conductivity:** Metals are good conductors of heat and electricity. The presence of mobile valence electrons explains the high thermal and electrical conductivity of metals. The free electrons allow the flow of heat and electric current.
- Ductility and malleability:** Metals are ductile (can be drawn into wires) and malleable (can be made into sheets). The non-directional nature of the metallic bond explains the ductility and malleability of metals.
- Lustre:** When light falls on the metal surface, the mobile electrons absorb the light and get excited. The emitted light gets reflected on metal surface and shows lustre.
- Hardness and high melting point:** Smaller the size of metal ion and greater the number of valence electrons, Greater the strength of the metallic bond, Harder is the metal and higher is the melting point.
- Hardness and brittleness due to impurities:** The presence of impurities like carbon or sulphur in a metal increases its hardness and brittleness. This is because the impurities form directional bonds with the metal and decrease the mobility of the metal atoms, resulting in the increased hardness. If stress is applied the directional bonds may break which results in the brittleness of the metal.

Limitations:

1. It fails to explain why some metals like silver have greater electrical conductivity than other metals.
2. It fails to explain about semiconductors.
3. It fails to explain the high specific heats of metals.

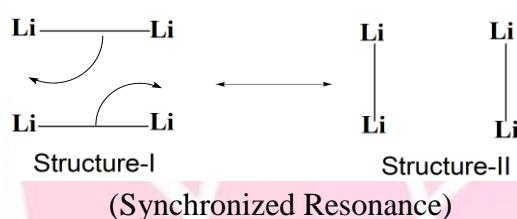
VALENCE BOND THEORY OF METALS

VBT is proposed by Pauling.

Postulates

1. In a metal, each atom is held to 8 or 12 more atoms.
2. Consider Lithium metal which crystallizes in body centered cubic structure with coordination number 8. Each Lithium atom must form eight covalent bonds with eighty nearest neighbour Li atoms. However only nine electrons are available for bond formation between nine Li atoms.
3. Pauling suggested that, **“The Covalent bond between the Li atoms are not localized but they are highly delocalized. Each covalent bond between two Li atoms is reasonable between various atoms in the metal.”**

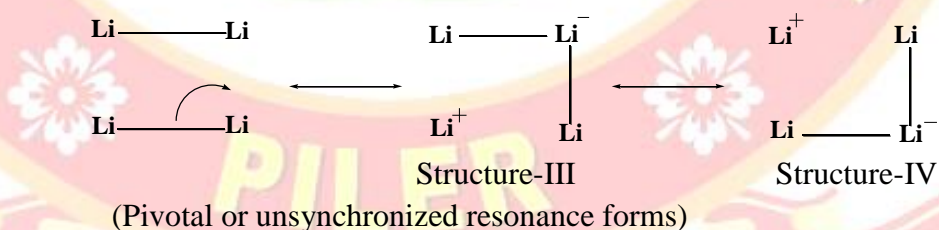
Consider four Li atoms,



The non-ionic resonance forms (I&II) are obtained when a covalent bond between two ‘Li’ shifts, the other bond between two other ‘Li’ shifts simultaneously. This is called **“Synchronized resonance”**.

Thus all the ‘Li’ atoms come close but the valence electrons remain free because of their delocalization.

4. The Ionic resonance forms (III&IV) are obtained when a bond between two ‘Li’ shift to a new place without simultaneous shifting of the other bond. This resonance is called **“Pivotal resonance”** or **“Unsynchronized resonance”**.



Explanation of metallic properties:

1. **Thermal and electrical conductivity:** The mobile (free) electrons in the unsynchronized resonating structures are responsible for high electrical conductivity and Thermal conductivity of metals.
2. **Ductility and malleability:** The metal ions may change their position, without changing the internal environments. i.e., the shape is changed without breaking the crystal. This explains high Malleability and ductility of metals.

Limitations:

1. It fails to explain thermal and electrical conductivity, ductility and malleability on a quantitative scale.
2. It fails to explain metallic character in liquid state or in solution.

CONDUCTORS

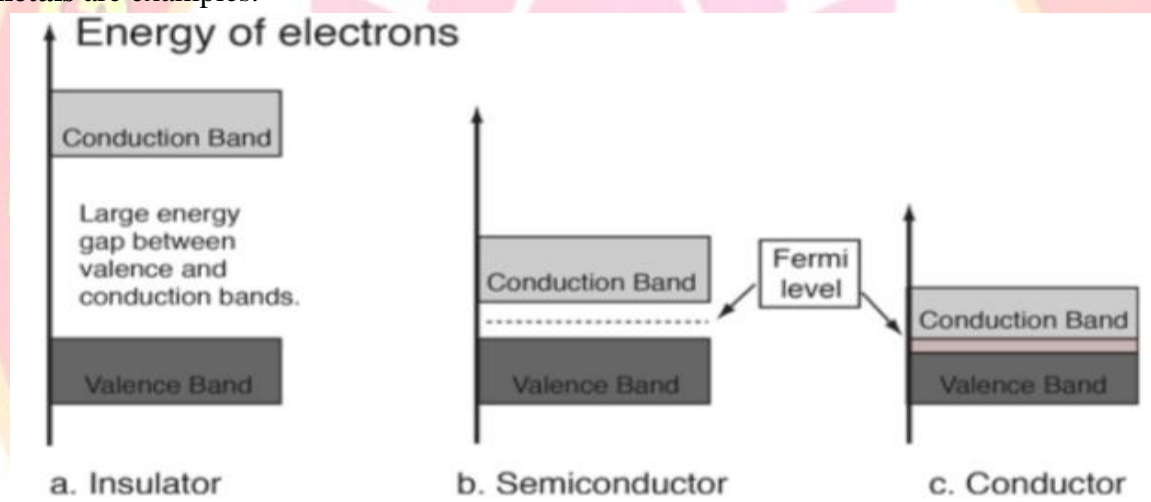
The molecular orbitals are formed by combination of individual atomic orbitals cover the entire metal. The closely spaced energy levels are called a "Band". The band consisting of valence electrons is called "**Valence Band**". The next band of higher energy to valence band is called "**Conduction band**".

Ex: 'Be' atom, The 2s AO's form a band of MO's (Valence band) and 2p AO's form a band of MO's (Conduction band). The valence electrons would fill the 2s band of MO's. The upper part of 2s band overlaps with lower part of 2p band.

In a conductor (metal), an increase in temperature does not increase the number of conducting electrons but increases collisions between conducting electrons and hence the electrical conductivity of conductors (metals) decreases with an increase in temperature.

Insulators:

If the valence band is completely filled and also it is separated from the empty conduction band by a large energy gap, then thermal energy is also not sufficient to cause excitation of electrons from valence band to conduction band and thus do not conduct electricity. These are called "insulators". All **non-metals** are examples.



SEMI - CONDUCTORS

Semi conductor is a crystal with a narrow energy gap between the filled valence band and conduction band.

1. In Semi-conductors, the valence band is completely filled and the conduction band is separated by a small energy gap, then the thermal energy is sufficient to cause excitation of electrons from filled valence band to empty conduction band.
2. With increase in temperature, the number of electrons excited to conduction band increases and hence the electrical conductivity of semi conductors increases with an increase in temperature.

Ex : Silicon and Germanium

3. Semiconductors are used in transistors.

Types of Semi-Conductors:

Semiconductors are of two types

- a. Intrinsic semiconductors, and
- b. Extrinsic semiconductors

a. **Intrinsic semiconductors:**

A semiconductor which is obtained by heating an insulator is called intrinsic semiconductor.

In these, valence band is completely filled and the conduction band is separated by a small energy gap, but increase in temperature causes excitation of electrons from filled valence band to empty conduction band, hence they become conductors.

b. **Extrinsic semiconductors:**

A semiconductor which is obtained by adding suitable impurity to insulator is called extrinsic semiconductor. When small impurities are added to insulators, it decreases the energy gap between valence band and conduction band by acting as bridge. The process of adding impurities is known as doping. Doping can be done with an impurity. These semi-conductors are insulators at absolute zero temperature and which is electron rich or electron deficient. Based on this extrinsic semiconductors are of two types.

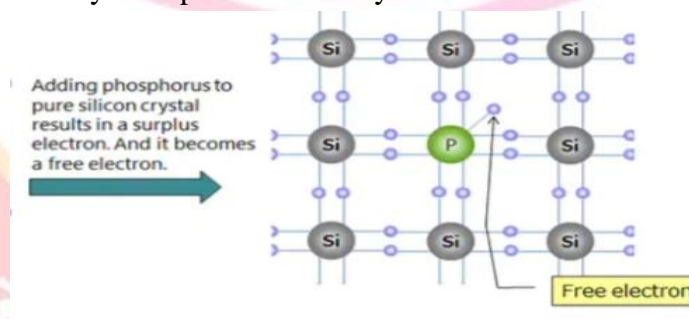
1. n- type semiconductor, and
2. p- type semiconductor.

1. **n- type semiconductor**

The extrinsic semiconductor, Doping can be done with an impurity, which is electron rich are called n- type semiconductor.

Ex:

Silicon and Germanium have four valence electrons each. So each atom forms four covalent bonds with its neighbours. When doped with P or As, having five valence electrons, they occupy some of the lattice points in Silicon or Germanium crystal. Out of five valence electrons four are involved in the formation of four covalent bonds with the four neighbouring Si or Ge atoms. The fifth electron which is extra becomes delocalised. These delocalised electrons are responsible for the increase of conductivity of doped Si or Ge crystals.

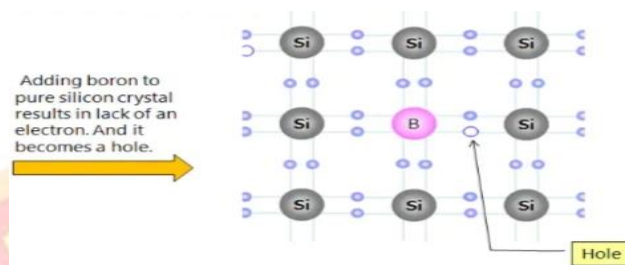
2. **p- type semiconductor**

The extrinsic semiconductor, Doping can be done with an impurity, which is electron deficient are called p- type semiconductor.

Ex :

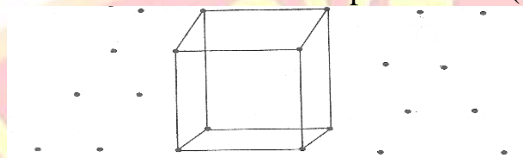
Silicon and Germanium have four valence electrons each. So each atom forms four covalent bonds with its neighbours. When doped with 'B' or 'Al' having three valence electrons, they occupy some of the lattice points in Silicon or Germanium crystal. The three valence electrons are involved in the formation of three covalent bonds with the three neighbouring Si or Ge atoms. The place where the fourth valence electron is missing is called an electron vacancy or electron hole.

An electron from a neighbouring atom can come and fill the electron hole. In doing so it leaves an electron hole at its original position. It gives an impression that electron hole is moving in the direction opposite to that of the electron that filled it.

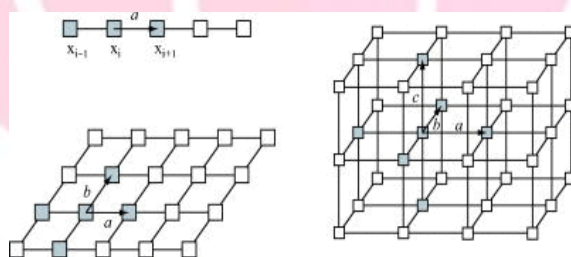


PHYSICAL CHEMISTRY**UNIT – III
SOLID STATE****1) SPACE LATTICE (OR) CRYSTAL LATTICE (OR) LATTICE**

The regular pattern of points which describe the three dimensional arrangement of particles (atoms, molecules, ions) in a crystal structure is called the Space lattice (or) Crystal lattice.

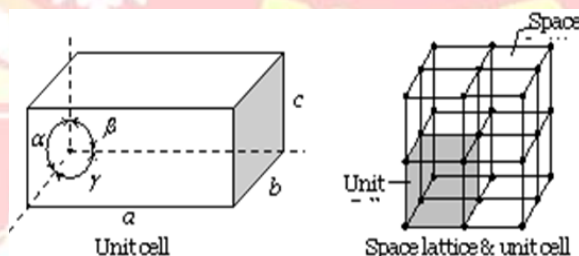


- 1) The sites which are occupied by constituent particles are called Lattice sites (or) Lattice points.
- 2) Each lattice point in the space lattice has the same environment.
- 3) It is classified into three types.
 - a) One dimensional lattice : In this exists a set of points arranged at equal distances along.
 - b) Two dimensional lattice : In this specify two basis vectors (a and b) and angle between them.
 - c) Three dimensional lattice : In this specify three basis vectors (a,b and c) and angle between them.

**UNIT CELL**

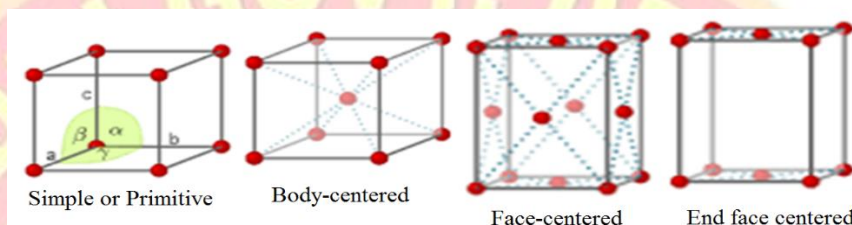
The smallest repeating unit in space lattice is called Unit cell.

1. This on repeating a number of times results in the formation of the crystal structure.
2. It possesses all the structural properties of the given crystal.



3. These are classified into two main types
 - a) Primitive or Simple Unit cells :
In this type constituent particles are located only at the corners.
 - b) Non-Primitive Unit cells :
In this type constituent particles are located not only at the corners but also at some other positions like face- centres, body – centres etc.
These are three types

- 1) Body – centred Unit cell:
In this type constituent particles are located at the corners as well as in the body centre of Unit cell.
- 2) Face – centred Unit cell:
In this type constituent particles are located at the corners as well as at the centre of each face of the Unit cell.
- 3) End – centred Unit cell:
In this type constituent particles are located at the corners and at centres of any two opposite faces the Unit cell.
It is not found in cubic system, it is found in orthorhombic system.



LAWS OF CRYSTALLOGRAPHY

Crystallography is the branch of science which deals with the Geometry, properties and structure of crystals and crystalline substances.

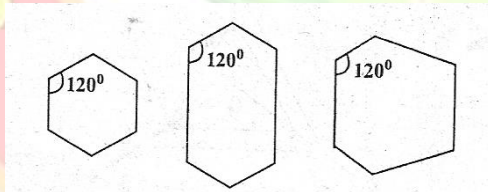
There are Four fundamental laws of crystallography.

1) LAW OF CONSTANCY OF ANGLES (OR) STENO'S LAW

Crystals are bounded by plane surfaces called faces. The angle between any two faces is called interfacial angle.

“The interfacial angle remains constant throughout in spite of the different sizes and shapes of the crystals of the same substance is called Law of Constancy of Interfacial angles”.

- 1) It was made by STENSEN in 1669.
- 2) It describing the geometric properties of crystal.



A = Section of an ideal Quartz crystal

B, C = Different possible shapes of the quartz crystal system.

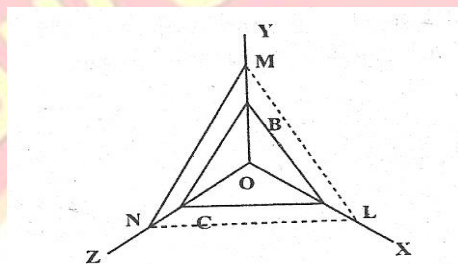
- 3) The instrument used for this is known as GONIOMETER, and they operate either by contact or through reflection of light beams from the face.

2) LAW OF RATIONAL OF INDICES. (OR) HAUY'S LAW

This law states that the ratio between the intercepts on the axis for the different faces of the crystal can always be expressed by rational number.

- 1) It was made by HAUY in 1784.
- 2) For describing the geometry of a crystal usually three non-co-planar co-ordinate axes are chosen. These are known as Crystallographic axes. These may coincide or be parallel to the edges between the principal phases of the crystal.

Ex :



Let OX, OY & OZ be three crystallographic axes and ABC be the unit cell, LMN be the plane of the crystal. The unit intercepts for OA, OB & OC a, b & c respectively.

For the plane LMN the intercepts will be OL, OM, ON (2a; 4b, 3c). Thus the intercepts for the plane LMN are in the ratio 2a:4b:3c. Simple whole number ratio (2:4:3) are known as Weiss indices. It may be noted that it is not necessary that the Weiss indices always be simple integral number, they may be fractions or infinity.

3) THE LAW OF SYMMETRY

According to this law ,

“The crystals of the same substance possess the same elements of symmetry.”

Symmetry Elements :

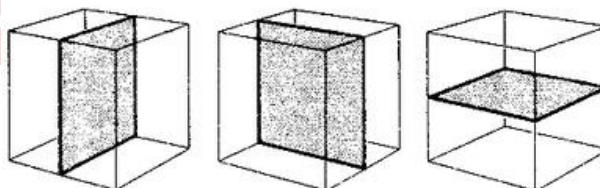
It may be defined as a geometrical entity such as a axis, a plane, or a point with respect to which one or more symmetry operations may be carried out.

1) PLANE OF SYMMETRY :

It is an imaginary plane which divides the crystal into two parts such that one is mirror image to the other. Cubic crystal consists of two types of planes.

a) Rectangular (or) Facial planes of symmetry :

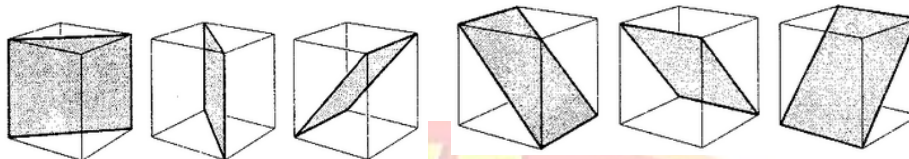
The plane which passes through the opposite faces of the crystal is known as Rectangular planes of symmetry. Total number of such planes are THREE.



b) Diagonal planes of symmetry :

The plane which passes through the opposite edges of the crystal is known as Diagonal planes of symmetry. Total number of such planes are SIX.

Total number of planes of symmetry in a cubic crystal : $3 + 6 = 9$



LINE (OR) AXIS OF SYMMETRY :

It is an imaginary line which passes through the crystal about which the crystal may be rotated such that it gives same appearance more than once during the complete rotation of 360° . Cubic crystal has three types of axis of symmetry.

a) Four fold axis of symmetry

It is an imaginary line , which passes through the centres of two opposite faces of a cube. If the cube is rotated about this line to give the same appearance four times in its complete rotation.

Total number of four fold axis of symmetry in a cubic crystal : 3

b) Three fold axis of symmetry

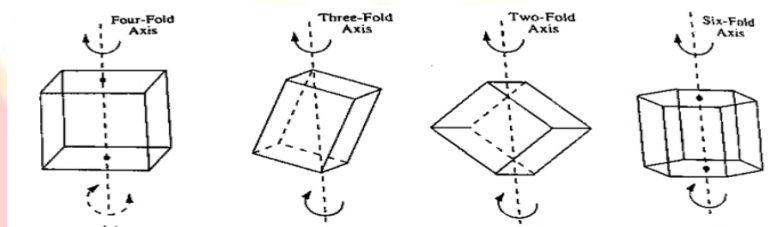
It is an imaginary line , which passes through the two opposite corners of a cube. If the cube is rotated about this line to give the same appearance three times in its complete rotation.

Total number of three fold axis of symmetry in a cubic crystal : 4

c) Two fold axis of symmetry

It is an imaginary line , which passes through the centres of two opposite edges of a cube. If the cube is rotated about this line to give the same appearance two times in its complete rotation.

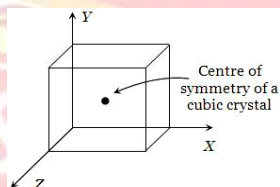
Total number of two fold axis of symmetry in a cubic crystal : 6



Total number of axis of symmetry in a cubic crystal : $3 + 4 + 6 = 13$

2) Centre of symmetry :

A point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side is known as Centre of symmetry.



Total number of centre of symmetry in a cubic crystal : 1

In a cubic crystal total number of elements of symmetry are

Total number of planes of symmetry in a cubic crystal : $3 + 6 = 9$

Total number of axis of symmetry in a cubic crystal : $3 + 4 + 6 = 13$

Total number of centre of symmetry in a cubic crystal : = 01

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BRAGG'S LAW - BRAGG'S EQUATION

In 1915 BRAGG,S devised a simple method for the study of crystals by X-rays.

BRAGG'S LAW :

When X-rays are incident on crystal face, they penetrate into the crystal and strike the atoms in different planes. From each of these planes X-rays are reflected.

BRAGG'S EQUATION :

Based on Bragg's law, an equation giving the relation between

- i) Wavelength, ii) Distance b/w the successive planes, and iii) The angle of incidence was derived, called Bragg's equation.

$$n\lambda = 2d \sin \theta$$

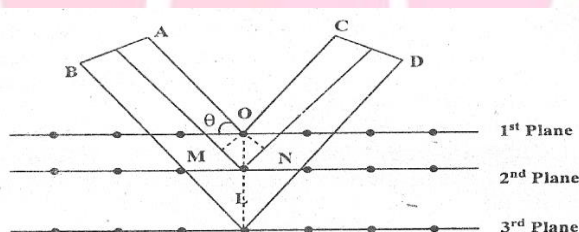
$n = 1,2,3,\dots$; $\lambda =$ Wavelength of X-rays ; $d =$ Distance b/w the successive planes

$\theta =$ The angle of incidence of x-rays

By knowing the Wavelength and the Angle of incidence, the distance b/w the successive planes can be determined.

Derivation of bragg's equation :

When X-rays incident on a crystal face they penetrate into the crystal and strike the atoms present in different planes. These are reflected like light rays reflected from a bundle of glass plates of equal thickness. In the figure horizontal lines represents the parallel planes of atoms in the crystal.



The distance between any two planes is 'd', suppose when a beam of x-rays falls on the crystal at an angle ' θ '. Some rays are reflected from the first plane with an angle ' θ ' and some reflected from successive planes.

Let the perpendiculars AB and CD drawn to the incident and reflected rays respectively these rays will be in phase with one another. The path difference of two rays are integral multiple, wave length of x-rays ($n\lambda$). The distance traveled by the 2nd ray is greater than the first one. To determine the difference OM & ON perpendiculars drawn to incident and reflected rays.

From the figure, it is clear that extra distance traveled by 2nd ray is LM+LN ... (1) from the triangles OLM & ONL.

$$\sin\theta = LM/OL \quad (\text{or}) \quad \sin\theta = LM/d \quad \dots\dots\dots(2)$$

$$\sin\theta = LN/OL \quad (\text{or}) \quad \sin\theta = LN/d \quad \dots\dots\dots(3)$$

$$\text{From (2) } LM = d \sin\theta$$

$$\text{From (3) } LN = d \sin\theta$$

From 2 and 3

$$\begin{aligned} LM+LN &= d \sin\theta + d \sin\theta \\ &= 2d \sin\theta \end{aligned}$$

Extra distance traveled by 2nd ray LM+NL is equal to integral multiple of wave length ' λ '

$$n\lambda = 2d \sin\theta$$

Uses:

1. It is used to study the internal structure of crystals.
2. By knowing ' λ ' and ' θ ', ' d ' can be calculated. .

DEFECTS IN CRYSTALS (OR) CRYSTAL IMPERFECTIONS**Ideal (or) Perfect Crystal :**

An ideal crystal is one which has the same unit cell containing the same lattice points across the whole crystal.

Crystal defects (or) Crystal imperfections :

Any departure from perfectly ordered arrangement of constituent particles in the crystals is called Crystal defects (or) Crystal imperfections.

- The defects may be Intrinsic (or) Extrinsic.
- Properties of ionic crystals are modified.
- The number of defects (n) per cm^3 are given by the relation

$$n = Ne^{-w/2RT}$$

N: Avogadro's number,
e : Base of natural logarithm
R : Gas constant
W : Energy required to produce defect
T : Absolute temp.

- There are mainly two types.
 - Electronic defects , and
 - Atomic defects.

1. Electronic defects :

This type of defects arises due to irregular arrangement of electrons in the crystal structure.

2. Atomic (or) Point defects :

This type of defects arises due to deviations in regular arrangement of the constituent particles (atoms, ions) in the crystal structure.

For ionic crystal these are THREE types

- Defects in Stoichiometric crystals,
- Defects in Non-Stoichiometric crystals, and
- Impurity defects.

A) DEFECTS IN STOICHIOMETRIC CRYSTALS

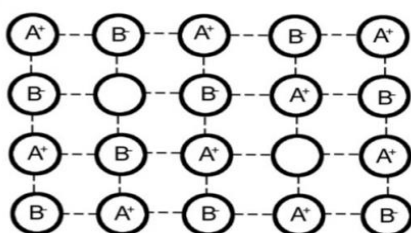
The defects which are arises without altering the stoichiometry of the crystal are called Stoichiometric crystals.

- These are depends on temperature. Increasing the temperature increases defects, hence these are called THEMODYNAMIC DEFECTS.
- These are of two types
 - SCHOTTKY DEFECTS , and
 - FRENKEL DEFECTS.

1. SCHOTTKY DEFECTS

- Equal number of positive and negative ions escapes from the lattice.
- The stoichiometry remains constant
- The crystal is electrically neutral.
- Volume of the crystal increases.
- This type of defect arises in strong ionic compounds which have high coordination number and the size of two +ve and -ve ions are almost same.

Ex: NaCl, CsCl, KCl, etc

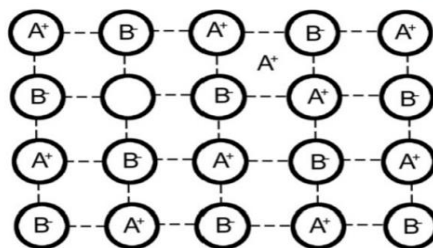


Consequences of Schottky defects.

- 1) Density of crystalline solid decreases.
- 2) Lattice energy of crystalline solid decreases.
- 3) Stability of crystalline solid decreases.
- 4) Entropy of crystalline solid increases.

2. FRENKEL DEFECTS (or) VACANCY DEFECT (or) INTERSTITIAL DEFECT (or) DISLOCATION DEFECT

- a) A cation displaces from its original lattice site to the interstitial position.
- b) The stoichiometry remains constant
- c) The crystal is electrically neutral.
- d) Volume of the crystal does not change.
- e) This type of defect arises in ionic compounds which have low coordination number and the size of +ve ion is smaller than -ve ion.
 - . Ex: AgCl, AgBr, ZnS..... etc

**Consequences of Frenkel defects.**

- 1) Density of crystalline solid not changed.
- 2) Lattice energy of crystalline solid decreases.
- 3) Stability of crystalline solid decreases.
- 4) Entropy of crystalline solid increases.

B) NON - STOICHIOMETRIC DEFECTS:

Non stoichiometric compounds are those in which the number of positive and negative ions are not in the ratio indicated by their chemical formula.

Ex : $\text{Fe}_{0.95}\text{O}$, $\text{Cu}_{1.97}\text{S}$,etc

The crystal defect which bring change in overall chemical composition are called non-stoichiometric defects.

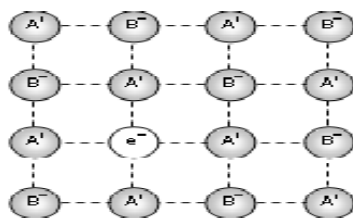
- a) Due to the presence of few extra electrons in interstitial position these are act as semiconductors.
- b) Non-stoichiometric defects are of two types:
 - 1) Metal excess defects , and
 - 2) Metal deficiency defects.

1) Metal excess defects :

In this type , metal ions (or) cations are in excess. These are may develop on account of the following two ways .

A) Anion vacancies :

A -ve ion may be missing from its lattice site leaving behind a vacancy or hole. This vacancy is occupied by an extra electron to maintain electrical neutrality.



- It is somewhat similar to Schottky defect.
- This hole is called 'F' centre or colour centre.
- Colour of the crystal depends upon the number of 'F' centres. Greater the number of 'F' centres, more is the intensity of colour.

Ex : NaCl with excess Na⁺ = Yellow

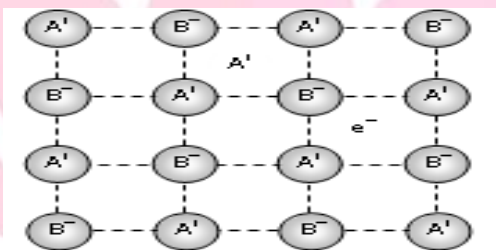
KCl with excess K⁺ = Violet

B) Excess positive ion in the interstitial position:

This type of defect arises due to the presence of positive ion in the interstitial position. The electrical neutrality is maintained by the presence of equal number of electrons in the interstitial position.

- It is somewhat similar to Frenkel defect.
- The number of cations are greater than the number of anions.

Ex: Heated ZnO is yellow, due to the loss of 'O'.

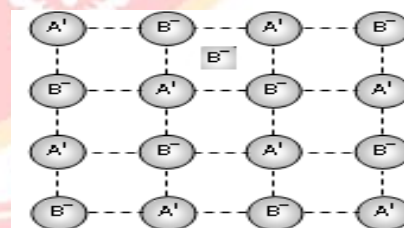
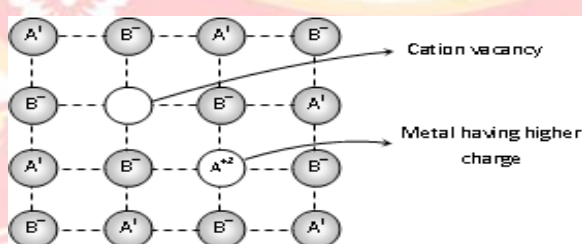


2) Metal deficiency defects.

In this type the cation missing from its lattice (or) an extra anion occupy the interstitial position and the electrical neutrality is maintained by the presence of a bivalent cation.

- The number of metal ions are less than anions.
- This defect occurs when metal shows variable valency.

Ex: FeO, FeS, NiOetc with metal deficiency defects are semiconductors of p-type.



C) IMPURITY DEFECTS.

A defect in an ionic solid can be introduced by adding foreign ions. If the impurity ions have a different oxidation state than that of the host ion, vacancies are created.

Ex: To the molten NaCl containing a little CaCl₂ as impurity is allowed to cool, some lattice sites will be occupied by Ca⁺² ion.

POWDER METHOD - STRUCTURE OF CRYSTAL

It was devised independently by DEBYE, SCHERRER, and HULL in 1961. In this method as little as 1mg of the material is sufficient for the study. It was completely based on X-ray diffraction.

Procedure :**A) Experimental main features are outline below**

- 1) The source of X-rays which can be made approximately monochromatic.
- 2) Allow the X-ray beam to fall on the powdered specimen 'P' through the slits 'S₁' and 'S₂' to get a narrow pencil of X-rays.
- 3) Fine powder 'P' stuck on a hair by means of gum is suspended vertically in the axis of a cylindrical camera. This enables sharp lines to be obtained on the photographic film which is bent in the form of a circular arc surrounding the powder crystal.
- 4) The X-rays after falling on the powder pass out of the camera through a cut in the film so as to minimize the fogging produced by the scattering of the direct beam.
- 5) On a photographic plate the observed pattern consists of traces.

B) Theory and calculation :

When a monochromatic beam of X-rays is allowed to fall on the powder of a crystal, then

- a) There will be some particles out of the random orientation of small crystals in the fine powder, which lie with a given set of lattice planes for reflection to occur
- b) While another fraction of the grains will have another set of planes in the correct position for the reflection to occur and so on.
- c) Also, reflections are possible in the different orders for each set.

All the like orientations of the grains due to reflection for each set of Planes and for each order will constitute a diffraction cone whose intersection with a photographic plate gives rise to a trace.

The crystal structure can be obtained from the arrangement of the traces and their relative intensities.

If the angle of incidence is 'θ', then the angle of reflection will be '2θ'. If the film radius is 'r', the circumference $2\pi r$ corresponds to a scattering angle of 360° . Then we can write

$$\frac{1}{2} \pi r = 2\theta/360^\circ \quad (\text{or}) \quad \theta = 360^\circ \times \frac{1}{4} \pi r$$

From the above equation, the value of 'θ' can be calculated and substituting this value in the Bragg's equation, the value of 'd' can be calculated.

$$n\lambda = 2d \sin\theta$$

Applications :

- 1) This method is most useful for Cubic crystals.
- 2) This method also used for determining the complex structure of metals and alloys.
- 3) This method helps to distinguish between the allotropic modifications of the same substance.
- 4) The structure of rubber was fully revealed by this method.

MILLER INDICES

- Miller indices of a plane are the reciprocals of the intercepts of that plane on the three crystallographic axes.
- They are the symbolic representation for the orientation of a plane (face) in a crystal with set of integers (hkl).

$$h = \frac{a}{\text{intercept of the plane along } x\text{-axis}}$$

$$k = \frac{b}{\text{intercept of the plane along } y\text{-axis}}$$

$$l = \frac{c}{\text{intercept of the plane along } z\text{-axis}}$$

- Miller indices (hkl) of a plane are obtained by taking reciprocals of the Weiss indices and multiplying by least common multiple to obtain integers. The miller indices of the plane LMN are (332).
- The distance between parallel planes in crystal are designated as d_{hkl} .

$$\text{For cubic system, } d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

CRYSTAL SYSTEMS - BRAVAIS LATTICES**Crystal systems:**

Based on the unit cell parameters (a,b,c) and (α,β,γ), Bravais showed there are seven different types of unit cells. These are called crystal systems.

Bravais Lattices :

Bravais showed from geometrical considerations that there can be only 14 different space lattices. These 14 types of lattices are known as Bravais Lattices.

$$7 \text{ Crystal systems} + 4 \text{ Unit cells} = 14 \text{ Bravais lattices}$$

Crystal system	Bravais Lattices	Parameters of unit cell		Examples
		Axial distances	Axial angles	
Cubic	Simple, Face centred, Body centred.	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$	NaCl, diamond
Tetragonal	Simple, Body centred	$a=b \neq c$	$\alpha=\beta=\gamma=90^\circ$	SnO ₂
Orthorhombic	Simple, Face centred, Body centred, End face centred	$a \neq b \neq c$	$\alpha=\beta=\gamma=90^\circ$	Rhombic sulphur
Monoclinic	Simple, End face centred	$a \neq b \neq c$	$\alpha=\gamma=90^\circ, \beta \neq 90^\circ$	Monoclinic sulphur
Triclinic	Simple	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇
Hexagonal	Simple	$a=b \neq c$	$\alpha=\beta=90^\circ, \gamma=120^\circ$	Graphite
Rhombohedral	Simple	$a=b=c$	$\alpha=\beta=\gamma \neq 90^\circ$	Quartz
Total=7	Total=14			

UNIT - IV**A) GASEOUS STATE****van der Waal's EQUATION OF STATE**

A number of equations of state have been given to describe the P-V-T relationship in real gases. In 1873 van der Waal's gave his famous equation of state for a non-ideal gas.

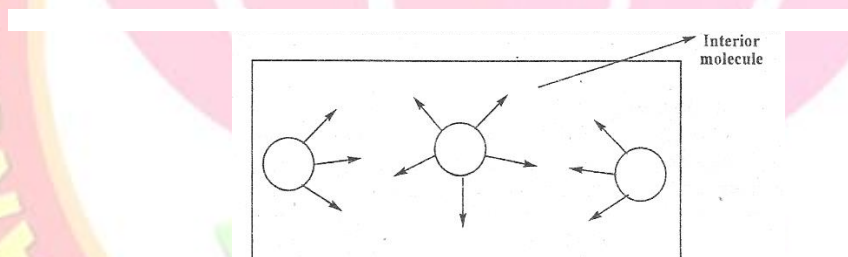
He modified the ideal gas equation by postulating that the gas molecules were not mass points but behaved like rigid spheres having a certain diameter and that there existed intermolecular forces of attraction between them. The following two correction terms introduced by van der Waal's

Volume Correction:

In the ideal gas equation 'V' is the Volume of the vessel in which gas is taken. This is the volume available for the movement of gas molecules. But the available volume for the gas molecules is less than the volume of the vessel because some space 'b' is occupied by the gas molecules. Hence the volume available for the gas molecules is (V-b) this is known as corrected volume.

Pressure Correction:

Let us consider the gas enclosed in a vessel. In this vessel the interior gas molecules are equally attracted by the other molecules from all sides. Hence net force of attraction exerted on such molecule is zero. The molecules nearer to the walls of the container are attracted by the interior molecules as showing fig.



Because of the backward pulling of the molecules the observed pressure is less than the actual pressure. To get the actual pressure, the pressure decreased due to pulling should be added to the observed pressure.

The decrease in pressure depends upon two factors.

- (i) The density of the interior (pulling) molecules.
- (ii) The density of the molecules striking the walls.

Correction factor $P \propto d \cdot d_1$ where d, d_1 is the density of interior and striking molecules. But $d \propto 1/V$

$$P \propto \frac{1}{V^2}$$

(or)

$$P = \frac{a}{V^2}$$

Where 'a' is a constant, known as van der Waal's constant.

The corrected pressure is equal to $\left[P + \frac{a}{V^2} \right]$.

By substituting corrected pressure and volume the ideal gas equation (PV=RT)

$$\left[P + \frac{a}{V^2} \right] (V-b) = RT$$

Where 'a' and 'b' are Van der waal's constants.

For 'n' moles of a gas the Van der waal's equation become

$$\left[P + \frac{an^2}{V^2} \right] (V - nb) = nRT$$

Significance of van der Waal's constants :

The constants 'a' and 'b' in van der Waal's equation of state are known as van der Waal's constants. Characteristic features are

- 1) The values of these constants are different for different gases.
- 2) They are assumed to be temperature independent although they are not totally independent.
- 3) Values of 'a' and 'b' depends on the units for expressing pressure and volume.

CRITICAL CONSTANTS

Critical temperature (T_c), critical pressure (P_c) and critical volume (V_c) are called critical constants.

Critical temp (T_c):

It may be defined as the temperature above which a gas can't be converted into liquid how so ever high pressure may be applied the critical temperature is represented by T_c . We know that gases can be liquefied by the application of pressure. It is possible only up to a certain range of temperature. Above which a gas can't be liquefied even at high pressure also.

Ex : The T_c of Carbon monoxide is 31.1°C

Critical Pressure (P_c):

It may be defined as the pressure required to liquefy the gas at the critical temperature.

Ex : The P_c of Carbon monoxide is 72.9 atmosphere at 31.1°C .

Critical Volume (V_c):

The volume occupied by 1 mole of a gas at its critical temperature and critical pressure is called critical volume V_c .

Ex : The V_c of Carbon monoxide is 95.6 c.c at 31.1°C . and 72.9 atms.

RELATION BETWEEN CRITICAL CONSTANTS AND VAN DER WAAL'S EQUATION

The relationship between critical constants and van der Waal's constants can be derived

Van der waal corrected equation for 1 mole gas is

$$\left[P + \frac{a}{V^2} \right] (V - b) = RT \quad \dots\dots\dots (1)$$

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

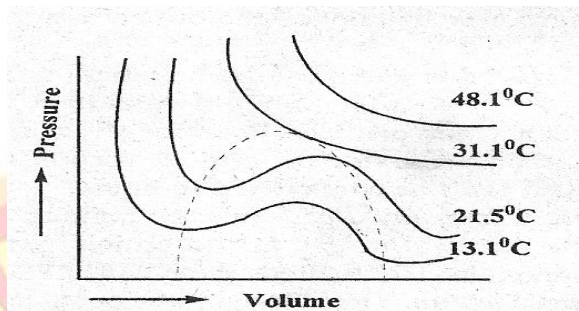
Multiplying both sides by V^2/P

$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} = RTV^2/P$$

$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - RTV^2/P = 0$$

$$V^3 - V^2 [b + RT/P] + \frac{aV}{P} - \frac{ab}{P} = 0 \quad \dots\dots\dots (2)$$

It is third order (cubic) equation in terms of 'V'. It may have three real roots or one real two imaginary roots at the given values of pressure and temperature. But in the isotherms (Pressure volume curves) of carbon monoxide at different temperature only two values of 'V' are observed as shown in figure.



From the graph it is clear that the theoretical and experimental isotherms are similar below 'T_c' except 'V' has three values in accordance with van der Waal's equation. But at critical temperature there is only one value of 'V'. It means 'V' becomes 'V_c' at 'T_c'.

$$\begin{aligned}
 V &= V_c \text{ or } V - V_c = 0 \\
 (V - V_c)^3 &= 0 \\
 V^3 - V_c^3 - 3V^2V_c - 3VV_c^2 &= 0 \\
 V^3 - V_c^3 - 3VV_c(V - V_c) &= 0 \\
 V^3 - V_c^3 - 3V^2V_c + 3VV_c^2 &\dots\dots\dots(3)
 \end{aligned}$$

van der waal's equation at T_c & P_c.

By substituting T_c and P_c instead of T & P.

$$V^3 - V^2 [b + RT_c/P_c] + aV/P_c - ab/P_c = 0 \dots\dots\dots(4)$$

At critical point the above two equations (3 & 4) must be identical so the coefficients of equal powers of V must be equal.

V² coefficients

$$3V_c = b + (RT_c/P_c) \dots\dots\dots(5)$$

V Coefficients

$$a/P_c = 3V_c^2 \dots\dots\dots(6)$$

$$V_c^3 = ab/P_c \dots\dots\dots(7)$$

By dividing equation 7 by equation 6

$$\begin{aligned}
 V_c^3 / 3V_c^2 &= (ab/P_c) (P_c/a) \\
 V_c/3 &= b \text{ or } V_c = 3b \dots\dots\dots(8)
 \end{aligned}$$

By substituting V_c value in eq. 6

$$\begin{aligned}
 a/P_c &= 3(3b)^2 \\
 P_c &= a/27b^2 \dots\dots\dots(9)
 \end{aligned}$$

Substituting V_c and P_c values in eq. 5

$$T_c = 8a/27Rb \dots\dots\dots(10)$$

Putting the value of b = V_c/3 in eq. 5 we get

$$RT_c/P_cV_c = 8/3 \text{ (constant)}$$

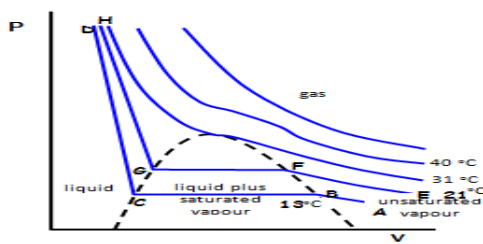
Thus, knowing the values of 'P_c', 'T_c' the values of critical constants 'a' and 'b' can be calculated. The calculated values of 'a' and 'b' fairly agree with the experimental values near the critical point and show departures away from the critical point.

Andrew's Isotherms of Carbon dioxide

At any constant temperature when pressure is increased volume is decreased and vice versa. Such P-V curves at constant temperature are known as isotherms.

Ex

Andrew's isotherms of CO₂ at different temperatures are shown in the figure.



Consider first the isotherm at the temperature 13.1°C. The point A represents Carbon dioxide in the gaseous state occupying a certain volume under a certain pressure. On increasing the pressure its volume decreases as is indicated by the curve AB. At B, liquefaction of gas commences and thereafter a rapid decrease in the volume takes place at the same pressure, since more and more of the gas is converted into the liquid state. At C, the gas becomes completely liquefied. After 'C' the increase of pressure produces only a very small decrease in volume. This is shown by a steep line CD which is almost vertical. Thus, along the curve AB, carbon dioxide exist as gas. Along BC, it exists in equilibrium between gaseous and liquid state. Along CD it exists entirely as a liquid.

The isotherm at 21.5°C shows similar behaviour. The isotherm at 21.5°C shows that the volume increases due to increase in the temperature. Therefore more pressure is applied to decrease the volume. This effect makes liquefaction to commence at higher pressure compared to the previous isotherm at 13.1°C.

At still higher temperature, the horizontal portion of the curve becomes shorter and shorter until at 31.1°C it reduces to a point. The temperature 31.1°C is regarded as the critical temperature of CO₂. At this temperature, the gas turns into liquid. Above 31.1°C the isotherm is continuous. CO₂ cannot be liquefied above 31.1°C no matter how high the pressure may be.

LAW OF CORRESPONDING STATES

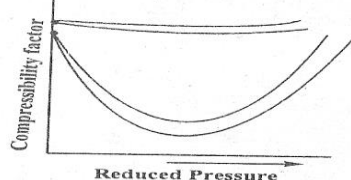
In 1881 Van der waal developed a law known as Van der waal 's reduced equation of state (or) Law of corresponding states.

“If two or more gases have the same reduced temperature and pressure then their reduced volumes are equal.”

This is called law of corresponding states, and the substances are said to be in corresponding states.

Importance of the law:

Substances which are in corresponding states shows similar properties. It is useful to study the relation between physical property and chemical constitution. The validity of the law is illustrated by a plot of compressibility factor verses reduced pressure.



This shows that all gases in corresponding states deviate, almost equally from ideal behavior. This law simplifies the treatment of non ideal gases. It has been found that boiling point of a liquid in absolute degrees is approximately two thirds of its critical temperature various liquids are nearly in corresponding states a their boiling points. Hence their properties can be studied at their boiling points.

Law of corresponding states (Reduced equation of state):

“If two or more gases have the same reduced temperature and pressure then their reduced volumes are equal.” This is called law of corresponding states the substances are said to be in corresponding states.

van der Waal’s expressed pressure, volume and temperature in terms of ratio of pressure and critical pressure, Temperature and critical temperature, volume and critical volume as given below.

$$\frac{P}{P_c} = \pi \quad (\text{or}) \quad P = P_c \pi \quad \dots\dots\dots(1)$$

$$\frac{V}{V_c} = \phi \quad (\text{or}) \quad V = V_c \phi \quad \dots\dots\dots(2)$$

$$\frac{T}{T_c} = \theta \quad (\text{or}) \quad T = T_c \theta \quad \dots\dots\dots(3)$$

Where π , ϕ and θ are called reduced pressure, reduced volume and reduced temperature respectively.

Substituting the value of P,V and T in Van der waals equations.

$$\left[P + \frac{a}{V^2} \right] (V-b) = RT \quad \text{for 1mole of gas}$$

$$\left[\pi P_c + \frac{a}{\phi^2 V_c^2} \right] (\phi V_c - b) = R \theta T_c \quad \dots\dots\dots(4)$$

We know that

$$P_c = \frac{a}{27b^2}, V_c = 3b \text{ and } T_c = \frac{8a}{27Rb}$$

Substituting above values in equation (4)

$$\left[\pi \frac{a}{27b^2} + \frac{a}{\phi^2 9b^2} \right] (\phi 3b - b) = R \theta \cdot \frac{8a}{27Rb} \quad \dots\dots\dots(5)$$

Dividing above equation with $\frac{a}{27b^2}$

$$\left[\pi \frac{a}{27b^2} * \frac{27b^2}{a} + \frac{a}{\phi^2 9b^2} * \frac{27b^2}{a} \right] b(3\phi - 1) = R \theta \cdot \frac{8a}{27Rb} * \frac{27b^2}{a}$$

$$\left[\pi + \frac{3}{\phi^2} \right] (3\phi - 1) = 8\theta \quad \dots\dots\dots(6)$$

It is called van der waal’s reduced equation of state.

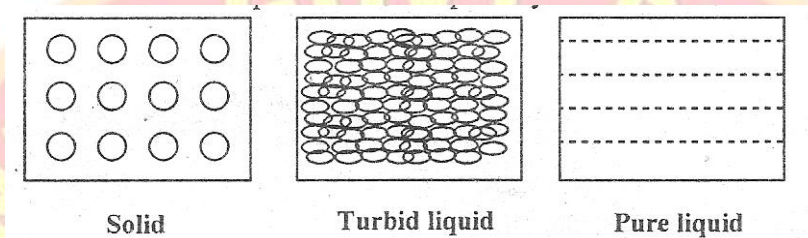
This equation is free of critical constants as well as the gas constant ‘R’. Thus, this general equation is applicable to all substances.

LIQUID CRYSTALS

Liquid crystal may be defined as intermediate state of matter between solid state (crystalline) and liquid state, exhibiting some properties of both.

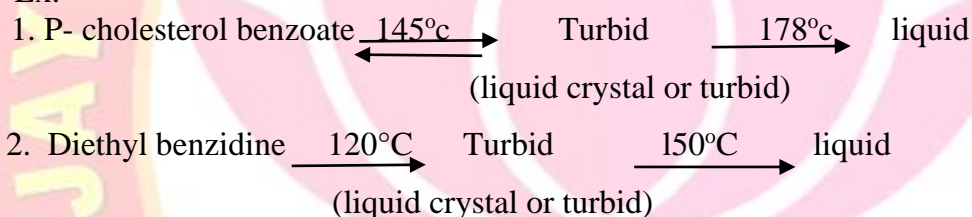
There are some solids which on heating fuse into a turbid liquid and at higher temp convert into clear liquid. On cooling the clear liquid converts into turbid liquid and then solid. The turbid liquid is called liquid crystal.

Ex: Cholesterol benzoate
Diethyl benzidine



- Liquid crystals are anisotropic in nature.
- The term liquid crystal is replaced by mesomorphic state or mesomorphic phase. (mesomorphic means intermediate in Greek).
- In mesomorphic state, the intermolecular attractions are less than that of crystalline solid state.

Ex:

**CLASSIFICATION OF LIQUID CRYSTALS**

On the basis of molecular arrangement these are classified into three types.

- Smectic liquid crystals (soap like)
- Nematic liquid crystals (thread like)
- Cholesteryl liquid crystals.

1) Smectic liquid crystals (Soap like) :

This type retained long range order gives smectic (soap like) phase.

Ex: n-Octyl p-azoxy cinnamate . Turbid temp = 94° M.P = 175°

Ethyl p-azoxy benzoate Turbid temp = 140° M.P = 249°

Properties

- Smectic liquid crystals do not flow as normal liquids since they have limited mobility.
- In the case of different sheets gliding over one another, they flow in layers.
- The flow of these crystals is non – Newtonian.
- The concept of viscosity does not apply to these liquid crystals.
- These crystals produce X-ray diffraction patterns only in one direction.
- This appears in a fan-like structure in polarized light.
- These are not affected by magnetic field because they are uniaxial.

2) Nematic liquid crystals (thread like)

Some liquid crystals on heating loses their layer structure but retains parallel alignment like thread are called Nematic crystals.

Ex: p-azoxy anisole Transition temp : 116° M.P : 135°
 p-methoxy cinnamic acid Transition temp : 170° M.P : 180°

Properties

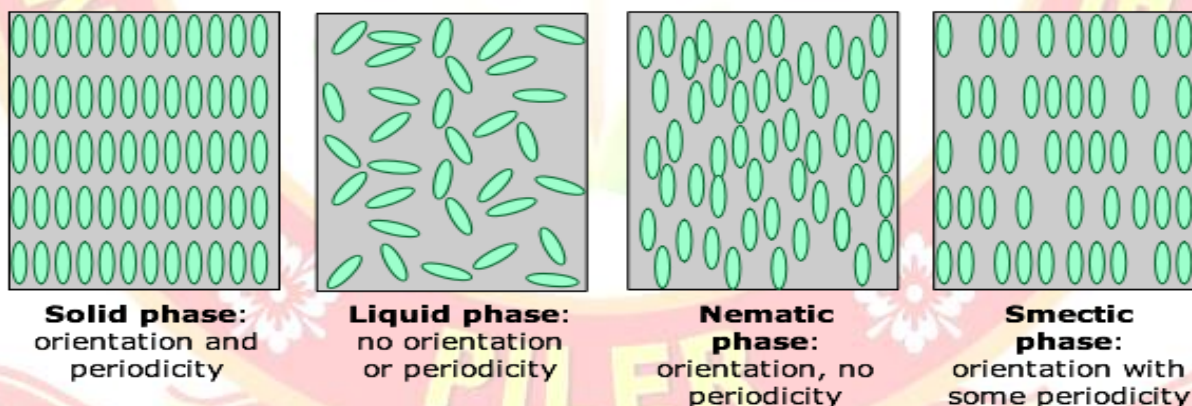
1. These liquid crystals flow quickly.
2. The flow of these crystals is Newtonian.
3. These are possess low anisotropic properties.
4. They exhibit normal flow behaviour of pure liquids.
6. The viscosity of these crystals is less when compared to pure liquids.
7. These are scatter the light and hence, they appear as translucent.
8. In polarized light nematic crystals exhibit thread like structure.

3) Chole steric liquid crystals:

Crystals having some nematic and some smectic characters, are called cholesteric liquid crystals.

Ex: Cholesteryl benzoate Turbid temp : 145°c MP : 178°c

1. The layers are slightly rotated to give a spiral (helical) structure.
2. These exhibits high optical rotation.
3. The pitch of the molecule decreases with the increase of temperature. This results change in the reflected light colour.

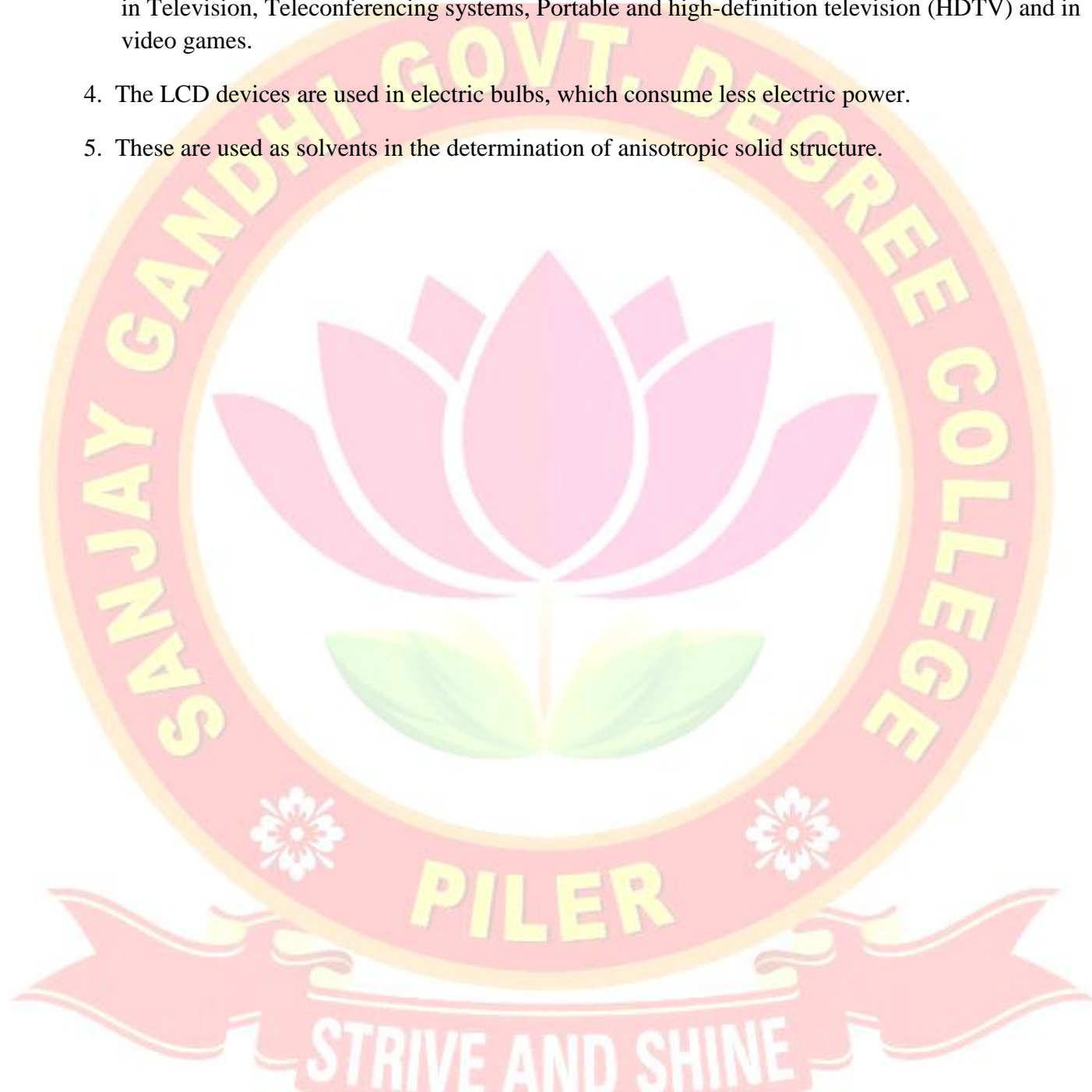


APPLICATIONS OF LIQUID CRYSTALS

1. Liquid crystals have been used in gas liquid chromatography because of their mechanical and electrical properties lying between crystalline solids and liquids.
2. These are used in digital displays like calculators, digital watches because they consume very little power.
3. These are used as solvents for the study of structures spectroscopically.
4. Cholesteric type crystals used for detecting, tuberos in the body.
5. These are also used as commercial lubricants.

APPLICATION OF LIQUID CRYSTALS AS LCD DEVICES

1. They are used as displays in digital wrist watches, calculators, panel meters and industrial products.
2. They can be used to record, store and display images which can be projected onto a large screen.
3. Liquid-crystal displays (LCDs) are used as displays in several areas, as Laptop computers, in Television, Teleconferencing systems, Portable and high-definition television (HDTV) and in video games.
4. The LCD devices are used in electric bulbs, which consume less electric power.
5. These are used as solvents in the determination of anisotropic solid structure.



UNIT - V**SOLUTION****TYPES OF SOLUTIONS****Solution:**

A solution is a homogeneous mixture of two or more substances.

The substance which is present in excess is called solvent while the other which is present in small amount is called solute.

Ex: Most of the gases are soluble in water as well as in other solvents.

Types of solutions:a) *Completely miscible liquids:*

The liquids which are completely soluble in each other are called miscible liquids. These include the polar and non polar solvents. .

Ex: C₂H₅OH and H₂O

Benzene and toluene are completely miscible (C₆H₆) -(C₆H₅ - CH₃)

b) *Partially miscible liquids:*

In this case a liquid is soluble in another liquid up to a certain extent. Then the resulting liquid separates into two layers each layer is a solution of one in another.

Ex:

Ether is slightly soluble in water

Phenol and water.

c) *Immiscible liquids:*

The two liquids which do not dissolve at all in each other are called immiscible liquids.

Ex: Benzene and water

Kerosene and water

Ideal solutions

The solutions which obey Raoult's law are called ideal solutions.

In the formation of an ideal solution no heat is evolved or absorbed. It means change in heat of the solution is zero ($\Delta H=0$) and change in the total volume of the solution is zero ($\Delta V=0$). It means the volume of the solution is the sum of the volumes of the components. The physical properties of the solution will be the average property of the pure components.

Ex :

Benzene and toluene

Carbon tetrachloride and Silicon tetra chloride

Non- ideal solutions

The solutions which do not obey Raoult's law are called non ideal solutions.

Ex:

Acetone and ethyl alcohol.

Water and sulphuric acid.

In this case there is a hydrogen bond between water and OH of sulphuric acid it means there is a strong interaction between these two. As a result the tendency of evaporation decreases. Hence the vapor pressure is less than ideal value. Some heat will be evolved in H₂O and H₂SO₄ mixture and total volume also decreases. In some cases the vapor pressure is greater than ideal value.

AZEOTROPIC MIXTURES

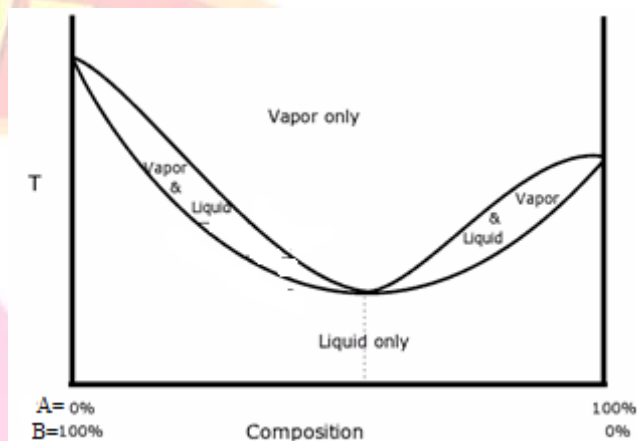
A mixture of two or more liquids which boils at a constant temperature without change in composition is known as azeotropic mixture. It means they behave like a pure chemical compound.

These are classified into two types

1. Maximum boiling point azeotropic mixture:
2. Minimum boiling point azeotropic mixture:

1. Minimum boiling azeotropes:

These azeotropes are formed from liquid mixtures which show positive deviations from ideal behaviour (Raoult's law). Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the highest and thus the boiling point is the lowest. Such azeotropes have boiling point lower than either of the pure components.

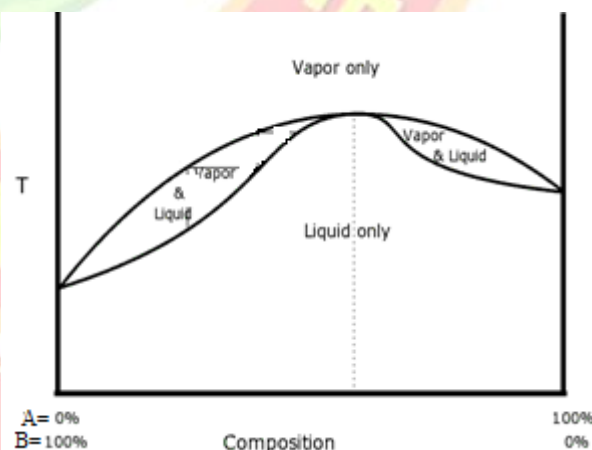


Ex: When **95.6%** of ethanol is mixed with **4.4%** of water, the mixture (azeotrope) boils at **78.1 °C** which is lower than the boiling point of ethanol (**78.4 °C**) and water (**100 °C**). Hence, 78.1 °C is the minimum temperature at which any ethanol + water solution can boil at atmospheric pressure.

Component A	B.P. (°C)	Component B	B.P. (°C)	Azeotrope	
				Mass % B	B.P. (°C)
Water	100	C ₂ H ₅ OH	78.4	95.59	78.1
Water	100	C ₆ H ₆	80.2	67.6	68.2

2. Maximum boiling azeotropes:

These azeotropes are formed from liquid mixtures which show negative deviations from ideal behaviour (Raoult's law). Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the lowest and thus the boiling point is the highest. Such azeotropes have boiling point higher than either of the pure components.



Ex: An aqueous solution containing **20.24 % of HCl** is an azeotropic mixture which boils at **110 °C**, which is higher than the boiling point of HCl (**-84 °C**) and water (**100 °C**) at atmospheric pressure.

Component A	B.P. (°C)	Component B	B.P. (°C)	Azeotrope	
				Mass % B	B.P. (°C)
Water	100	HCl	- 84	20.24	110
Water	100	HNO ₃	86	68	120.5

NERNST'S DISTRIBUTION LAW

This law explains the distribution of solute among the two immiscible liquids.

According to this law

“When a solute is distributed among the two immiscible liquids in such a way that at equilibrium the ratio of the concentration of the substance in the two layers is constant at given temperature.”

This ratio is independent on the amount of solvent and solute provided that the solute have the same molecular state in both the solvents.

If C_A and C_B are concentrations of a solute, X in the layers in A and B, then at constant temperature,

$$\frac{\text{Concentration of X in Solvent A}}{\text{Concentration of X in Solvent B}} = \frac{C_A}{C_B} = K_D = \text{constant}$$

where K_D = distribution coefficient or partition coefficient

The value of K_D depends only on the temperature of the system. It is independent of the amount of solute taken and also of the relative amounts of the two immiscible solvents.

Ex:

If I_2 is distributed between the immiscible solvents CCl_4 and H_2O , I_2 distributes itself between the CCl_4 and water layers in such a way that at equilibrium, the ratio of conc. of I_2 in two layers is constant.

$$\frac{C_1}{C_2} = K_D = \text{Constant}$$

Where, C_1 and C_2 are the concentrations of I_2 in the aqueous and organic layer respectively.

Limitations (Validity of the distribution law):

- The temperature is to be kept constant:**
The solubility of a solute changes with temperature. The change in solubility is not same in the two different solvents and hence K_D vary with temperature.
- The molecular state of the solute should be the same in both layers:**
When benzoic acid is added to water and benzene, the acid exists as single molecules in water. However in benzene, the benzoic acid exists as dimer. In this case, the law is valid only for concentration of single molecules in two solvents.
- The two solvents must be immiscible.
- The solution should be dilute.

Applications of Nernst's distribution law:

1. Determination of solubility of sparingly soluble solutes:

In case of *sparingly soluble solute*, the two solvents are saturated with the solute. The distribution law can be written as:

$$K_D = \frac{C_1}{C_2} = \frac{S_1}{S_2}$$

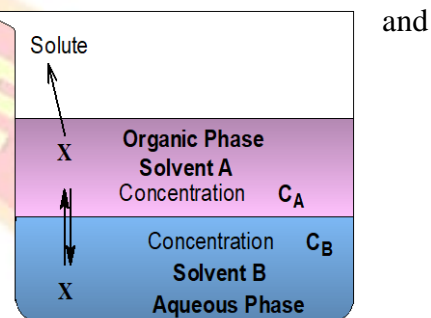
Knowing the value K_D and solubility of solute in one solvent, the solubility of solute in other solvent can be determined.

2. Study the association or dissociation of a solute in solvent:

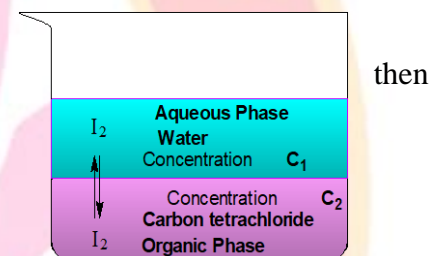
Distribution law helps in studying the extent of association or dissociation of a solute in solvent.

Association of solute: If a solute exists as single molecules in one phase and exists as associated in second phase, then the distribution coefficient is given by:

K. Ram Babu, Lecturer in Chemistry



Nernst's Distribution Law



$$K_D = \frac{C_1}{\sqrt[n]{C_2}} \quad \text{where, } n = \text{number of associated molecules}$$

Dissociation of solute: If a solute dissociates in one phase, then distribution coefficient is given by:

$$K_D = \frac{C_1}{C_2(1-\alpha)} \quad \text{where, } \alpha = \text{degree of dissociation of solute}$$

If degree of dissociation (α) of solute is known at one concentration, then its value at some other concentration can be calculated because K_D is constant

3. Solvent extraction:

This is the most important application of distribution law. This method is used to separate an organic compound from their aqueous solutions by means of organic solvent. The efficiency of the separation increases if

1. Distribution ratio is greater than 1 and
2. Multiple extractions are done.

Critical solution temperature (CST) (or) Consolute temperature

Partially miscible liquids :

Partially miscible liquids are those that do not mix in all proportions at all temperatures.

Critical solution temperature (or) consolute temperature

*The temperature at which two partially miscible liquids get completely miscible at all proportions is known as **critical solution temperature** or **consolute temperature**.*

- a) Above this temperature, all compositions of this liquid mixture are completely miscible.
- b) Depending upon the CST, the partially miscible systems are of three types.
 - (i) Upper critical solution temperature system,
 - (ii) Lower critical solution temperature system, and
 - (iii) Upper and lower critical solution temperature system

(i) Upper critical solution temperature system (UCST)

As the CST is the maximum temperature on temperature-composition curve, it is called as upper critical solution temperature.

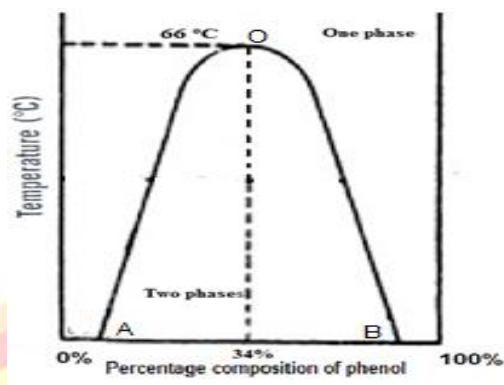
Ex : Phenol-Water system

1) Upper critical solution temperature (Phenol-Water system)

As the CST is the maximum temperature on temperature-composition curve, it is called as **upper critical solution temperature (UCST)**.

Ex : Phenol-Water system

- If a small quantity of phenol is added to water, the two liquids are miscible, but on further addition of phenol to water, we get two layers. The upper layer is water in phenol and the lower layer is phenol in water.
- The solubility curve of phenol in water is shown by AO and the solubility curve of water in phenol is shown by BO. When temperature is increased, the mutual solubility of two liquid increases.
- When temperature reaches **66°C**, the composition of two layers become identical (**34% phenol**) and two layers become completely miscible.



- The temperature at O (66°C), represents the temperature at or above which the phenol and water are miscible in all proportions. This is called critical solution temperature. As the CST is the maximum temperature on temperature-composition curve, it is called as **upper critical solution temperature (UCST)**.
- The dome shaped area represents two phases in equilibrium and outside the dome shaped curve only one phase is present.

EFFECT OF IMPURITY ON CST (or) CONSOLUTE TEMPERATURE

Critical solution temperature is markedly affected by the presence of impurities in the system.

1. If an impurity is added to the partially miscible liquid mixture, mutual solubilities of the component liquids in the mixture are affected.
2. The mutual solubilities of the liquids also depend on the nature and quantity of the impurity.
3. If the added impurity is soluble in only one of the two liquids, then mutual solubilities of the two liquids decrease and the added impurity raises the consolute temperature.

Ex: 1. KCl is added to the phenol-water system, then its consolute temperature rises. This is because KCl is soluble in water but not in phenol.

2. Naphthalene is added to the phenol-water system, here also the consolute temperature is increased. This is because of the solubility of naphthalene phenol but not in water.

4. Impurity is soluble in both the liquids, then the consolute temperature is decreased. The impurity increases the mutual solubility of the liquids by distributing itself between two solutions in a definite manner.

Ex : Succinic acid is added as an impurity to the phenol-water system, then the consolute temperature of it is lowered because succinic acid is soluble in phenol and water.

5. The mutual solubility temperature varies almost linearly with the amount of soluble impurity.

1) IMMISCIBLE LIQUIDS - STEAM DISTILLATION

Immiscible liquids:

The two liquids which do not dissolve at all in each other are called immiscible liquids.

Ex: Benzene and water

Kerosene and water

Steam distillation:

Steam distillation is the process of distillation which is carried out in a current of steam.

- 1) It is applied for the purification of substances which are insoluble in water, volatile in steam and having non volatile impurities.
- 2) In this method non volatile impurities are removed from organic liquids.
- 3) An advantage of steam distillation is decomposition of organic compound is prevented.
- 4) *It is very useful method for temperature sensitive natural organic compounds* having high boiling point at temperatures below 100°C (boiling point of water).

Principle:

A mixture of water and an organic liquid having high boiling point, boils at a lower temp than the boiling point of organic liquid. We know that any liquid boils at a temp at which its vapor pressure equals to the atmospheric pressure.

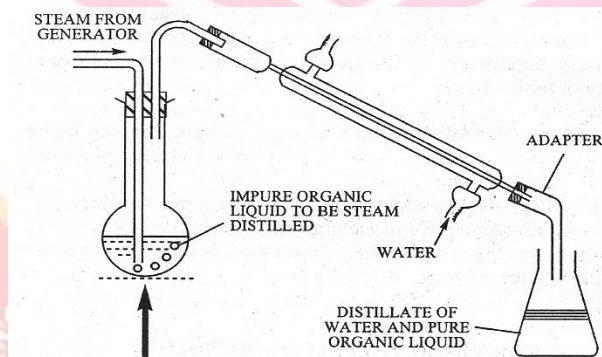
We know, that the vapor pressure of a mixture is equal to the sum of the vapor pressures of the liquids.

$$P = P_L + P_w$$

Where 'P' is the total pressure; 'P_L' is the vapor pressure of organic liquid; 'P_w' is the vapor pressure of water.

$$P_L = P - P_w$$

Since the vapor pressure of liquid is lower than the atmospheric pressure. It means vaporize at low boiling point than the original boiling point. The apparatus is as follows



Steam is bubbled through impure liquid then the boiling of liquid takes place and the vapors of organic substance along with steam comes out and are condensed when passed through a water condenser. The condensate is a mixture of organic layer and water, the condensed vapours will contain a high proportion of the liquid, these two are immiscible. Hence they are separated by separating funnel.

COLLIGATIVE PROPERTIES

The properties of solutions which depend upon the number of particles of the solute in the solution are called Colligative properties. Colligative properties are exhibited by only dilute solutions of non volatile solutes. These properties are independent of the nature of the solute. A few colligative properties are:

- (i) Lowering of vapour pressure of the solvent
- (ii) Osmotic pressure of the solution
- (iii) Elevation in the boiling point of the solvent
- (iv) Depression in the freezing point of the solvent.

OSMOTIC PRESSURE

Osmosis:

Osmosis is defined as the phenomenon in which the solvent molecules pass through a semi permeable membrane from a solution of low concentration to a solution of high concentration.

Osmotic pressure (π):

Osmotic pressure is the pressure developed in a solution when the solution and the solvent are separated by a semipermeable membrane. (or)

The excess pressure which must be applied upon the solution so as to prevent the inflow of the solvent into it when the two are separated by a semi-permeable membrane.

Isotonic solutions

Solutions having the same osmotic pressure are known as isotonic solutions. If two solutions are isotonic there will be no net passage of the solvent in either direction. Isotonic solutions have same molar concentration of solutes.

Ex: A solution containing 342 gm (1 mole) of sucrose in 1 litre of solution is isotonic with a solution containing 180 gm (1 mole) of glucose per litre.

Determination of molecular weight of non-volatile solute from osmotic pressure.

From the laws of osmotic pressure,

$$\pi V = nRT$$

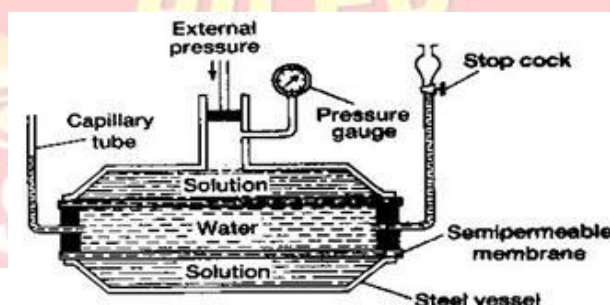
$$\pi V = \frac{w}{m} \times \frac{RT}{V} \quad [n = \frac{w}{m}]$$

$$m = \frac{wRT}{\pi V}$$

From the experimental value of osmotic pressure (π), the molecular weight of the solute (m) can be calculated.

Determination of Osmotic pressure by Berkeley and Hartley's method:

A number of methods are proposed for determination of osmotic pressure, but the accurate and quick method is devised by Berkeley and Hartley. In this method the pressure necessary to prevent the entry of the solvent into a solution separated by a semipermeable membrane is measured. The apparatus consists of a **porous tube** containing within its walls a semipermeable membrane of copper ferrocyanide. One end of the tube is connected to a capillary while the other is connected to dropping funnel provided with a stop clock. The **porous tube** is surrounded by **metal jacket** which is provided with a piston for applying definite pressures. The porous tube is filled with water and the jacket with solution whose osmotic pressure is to be measured. Due to osmosis water tends to pass into solution. External pressure is applied with the help of piston to just prevent entry of water into solution. This is indicated by the constancy of water level in the capillary tube. The external pressure applied is known as the osmotic pressure (π) of the solution.



From the experimental value of osmotic pressure (π), the molecular weight of the solute (m) can be calculated by using the equation:

$$m = \frac{wRT}{\pi V}$$

ELEVATION IN BOILING POINT.**Boiling point of a solution**

The boiling point of a liquid is defined as the constant temperature at which its vapour pressure equal to the atmospheric pressure”.

- 1) The boiling point of a solution is always higher than that of pure solvent.
- 2) The vapour pressure of a solution is always less than that of the pure solvent.

Elevation in boiling point

The difference between the boiling point of a solvent and its solution is known as the elevation in boiling point.

If T_0 is the boiling point of the solvent and T is the boiling point of the solution, T is always greater than T_0 . The elevation in boiling point (ΔT_b) is given by:

$$\Delta T_b = T - T_0$$

Let T_0 , T_1 and T_2 are the boiling points of the pure solvent, solution 1 and solution 2 respectively. The elevation in boiling point is proportional to the lowering of vapour pressure.

Relationship between elevation in boiling point and molecular weight of solute:

$$\Delta T_b = K_b \times \text{molality of solution}$$

$$\text{molality} = \frac{w}{m} \times \frac{1000}{W}$$

$$\Delta T_b = K_b \times \frac{w \times 1000}{m \times W}$$

$$\text{Molecular weight of the solute, } m = K_b \times \frac{w \times 1000}{W \times \Delta T_b}$$

From the experimental value of ΔT_b , the molecular weight of the solute (m) can be calculated.

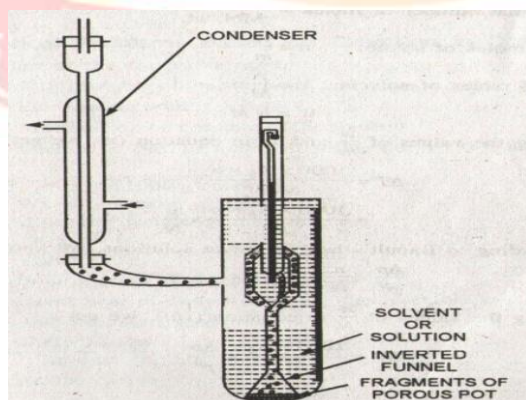
Determination of elevation in boiling point :**Cottrell's method:****Apparatus:**

The Cottrell's apparatus consists of a graduated boiling tube fitted with Beckmann's thermometer. A condenser is fitted to the side arm of the graduated boiling tube so that the vapours of the solvent from the boiling tube condenses in the condenser and returns to the boiling tube. A small inverted funnel with a narrow stem which branches into two or three jets at the top which in turn surround the lower portion of the thermometer.

Working:

A known weight of the solvent is placed in the boiling tube along with a few porcelain pieces below the mouth of the funnel and the tube is heated on a slow flame. As the solvent boils, the vapours arising from the porcelain pieces pump the boiling liquid through the stem of the funnel. These vapours along with the boiling liquid projects upon the bulb of the thermometer. The constant temperature corresponding to the boiling point of the solvent is noted. A weighed amount of the solute is dissolved in the solvent and the boiling point of the solution is noted in the same way as before. The molecular weight of the solute (m) can be calculated from ΔT_b by using the relation:

$$m = K_b \times \frac{w \times 1000}{W \times \Delta T_b}$$



DEPRESSION IN FREEZING POINT

Freezing point of a liquid

“The freezing point of a liquid is defined as the constant temperature at which the liquid and solid states of a substance have same vapour pressure”.

1) The freezing point of a solution is always lower than that of pure solvent.

Depression in freezing point

The difference between the freezing point of a solvent and its solution is known as the depression in freezing point (ΔT_f).

If T_0 is the freezing point of the solvent and T is the freezing point of the solution, T_0 is always greater than T . The depression in freezing point (ΔT_f) is given by:

$$\Delta T_f = T_0 - T$$

Let T_0 , T_1 and T_2 are the freezing points of the pure solvent, solution 1 and solution 2 respectively.

The depression in freezing point is proportional to the lowering of vapour pressure.

Relationship between depression in freezing point and molecular weight of solute:

Molality of the solution is defined as the number of moles of solute in 1000 gm of solvent.

$$\Delta T_f = K_f \times \text{molality of solution}$$

$$\text{molality} = \frac{w}{m} \times \frac{1000}{W}$$

$$\Delta T_f = K_f \times \frac{w \times 1000}{m \times W}$$

$$\text{Molecular weight of the solute, } m = K_f \times \frac{w \times 1000}{m \times \Delta T_f}$$

From the experimental value of ΔT_f , the molecular weight of the solute (m) can be calculated.

Determination of depression in freezing point:

1. Beckmann's method:

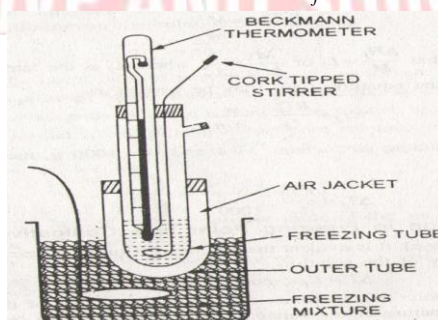
Apparatus:

Beckmann apparatus consists of an inner freezing tube with a side arm through which a known amount of a solute can be introduced. A stopper carrying a Beckmann thermometer and a stirrer is fitted in to the freezing tube. To prevent rapid cooling and ensure uniform cooling of the contents of the inner freezing tube, a glass tube surrounds the inner tube so that there is an air space between the two tubes. This assembly, as a whole, is placed in a wide glass jar which contains a stirrer and freezing mixture (sodium chloride and ice) maintaining a low temperature around 5°C below the freezing point of the pure solvent.

Working:

A known weight of the solvent is taken into the inner freezing tube. The solvent as well as the freezing mixture in the jar are continuously stirred. As a result of super cooling, the temperature of the solvent will fall by about 0.5°C below its freezing point. Vigorous stirring is then set in when solid starts separating and the temperature rises and remains constant, for some time, until all the liquid solvent gets solidified and this steady temperature is noted as freezing point of the solvent. The tube is taken out and the solvent is melted by warming and a known quantity of the solute is added into the freezing tube through the side arm. The contents are stirred till the solid completely dissolves and the freezing point of the solution is determined in the same manner. The difference between the two values of freezing point gives the depression in freezing point (ΔT_f). Thus we can determine the molecular weight of the solute (m) from ΔT_f by using the following equation.

$$m = K_f \times \frac{w \times 1000}{W \times \Delta T_f}$$



ABNORMAL COLLIGATIVE PROPERTIES AND VAN'T HOFF FACTOR

The colligative properties of dilute solutions like lowering of vapour pressure, elevation in B.P, depression in F.P and osmotic pressure depends only on number of solute particles present in the solution but on their nature.

$$m \propto \frac{1}{\text{colligative properties}}$$

If a solute undergoes dissociation in solution, the number of particles increases and consequently values of colligative properties will be high. So molecular weight (m) calculated is higher than the real value of molecular weight.

If a solute undergoes association in solution, the number of particles decreases and consequently values of colligative properties will be low. So molecular weight (m) calculated is lower than the real value of molecular weight.

In order to account for these abnormalities, Van't Hoff introduced a correction factor, known as Van't Hoff's factor (*i*).

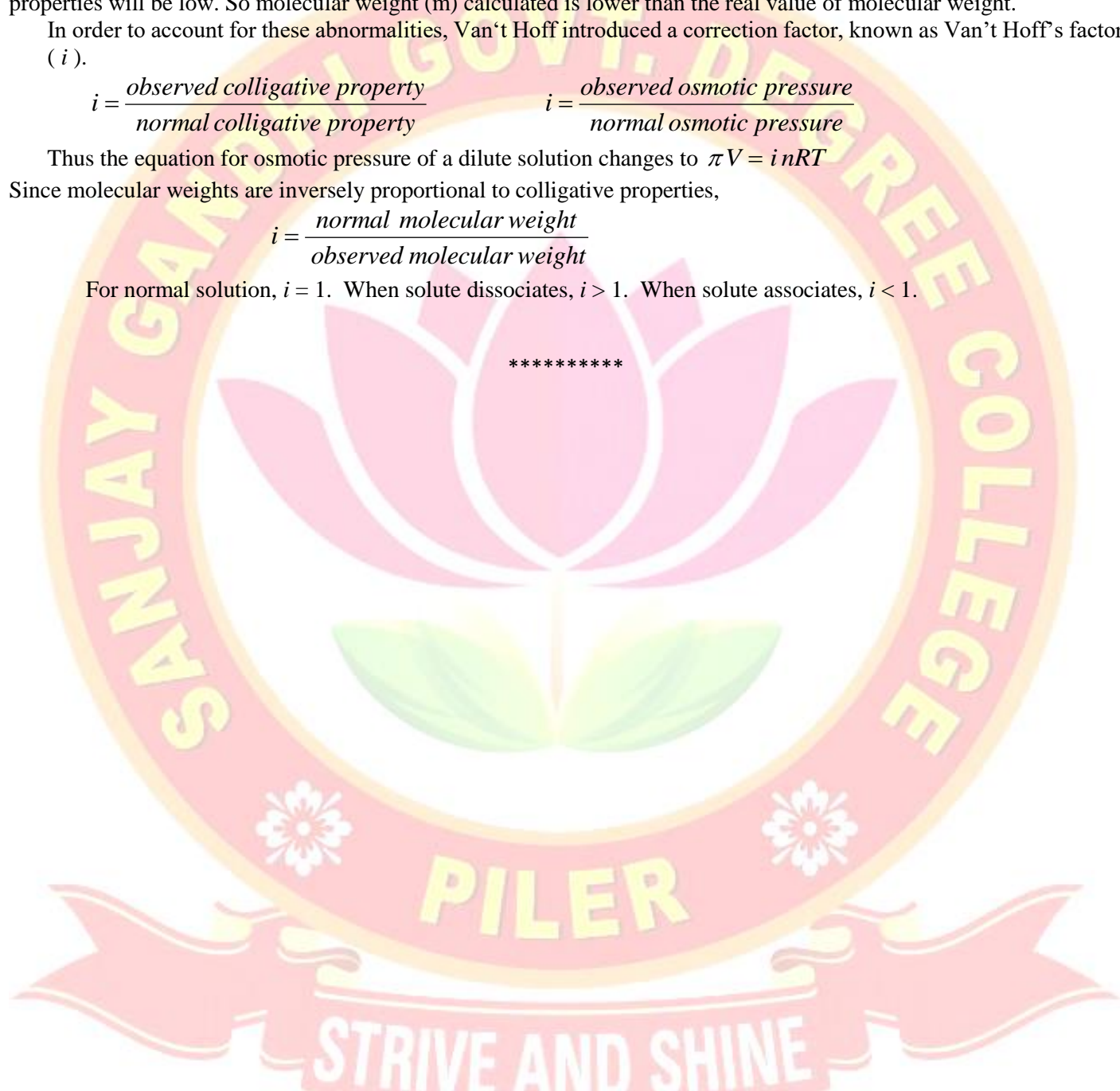
$$i = \frac{\text{observed colligative property}}{\text{normal colligative property}} \qquad i = \frac{\text{observed osmotic pressure}}{\text{normal osmotic pressure}}$$

Thus the equation for osmotic pressure of a dilute solution changes to $\pi V = i nRT$

Since molecular weights are inversely proportional to colligative properties,

$$i = \frac{\text{normal molecular weight}}{\text{observed molecular weight}}$$

For normal solution, $i = 1$. When solute dissociates, $i > 1$. When solute associates, $i < 1$.

**SOLUBILITY PRODUCT**

It is defined as the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature.

1. It is denoted by the symbol K_{sp} .

2. The solubility product is a kind of equilibrium constant and its value depends on temperature. K_{sp} usually increases with an increase in temperature due to increased solubility.

Ex :

Suppose Bariumsulphate along with its saturated aqueous solution is taken. The following equation represents the equilibrium set up between the undissolved solids and ions



The equilibrium constant in the above case is:

$$K = \frac{[\text{Ba}^{2+}][\text{SO}_4^{-2}]}{[\text{BaSO}_4]}$$

In case of pure solid substances the concentration remains constant, and so we can say

$$\begin{aligned} K_{sp} &= K[\text{BaSO}_4] \\ &= [\text{Ba}^{2+}][\text{SO}_4^{-2}] \end{aligned}$$

Here K_{sp} is known as the solubility product constant.

Criteria of precipitation of an electrolyte

Case 1 : When $K_{ip} < K_{sp}$ then solution is unsaturated in which more solute can be dissolved.

Case 2 : When $K_{ip} = K_{sp}$ then solution is saturated in which no more solute can be dissolved.

Case 3 : When $K_{ip} > K_{sp}$ then solution is supersaturated and precipitation takes place.

No precipitation of the electrolyte occurs if the ionic product is less than the solubility product.

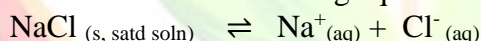
Precipitation of the electrolyte occurs if the ionic product is greater than the solubility product.

Application of Solubility product principle

Ex:

1. Purification of common salt.

The principle of solubility product is also applicable in the precipitation of soluble salts in pure state from their saturated solution. This phenomenon, known as salting out, is used in the purification of sodium chloride. This is done by preparing a saturated solution of commercial NaCl in water when the following equilibrium exist

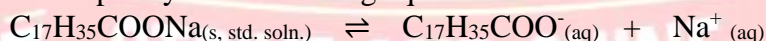


$$K_{sp} = [\text{Na}^{+}] [\text{Cl}^{-}]$$

HCl gas is passed through this solution. The $[\text{Cl}^{-}]$ therefore increases considerably. Hence ionic product exceeds the concentration solubility product of NaCl and therefore, it precipitates out from the solution in pure state. The soluble impurities remain in solution.

2. Salting out of soap.

The same principle is made use of in the salting out of soap which may be considered as Sodium salt of stearic acid for simplicity. The following equilibrium exists



$$K_{sp} = [\text{C}_{17}\text{H}_{35}\text{COO}^{-}] [\text{Na}^{+}]$$

Some sodium chloride is now added. The $[\text{Na}^{+}]$ therefore increases. Hence, the ionic product exceeds the concentration solubility product of Sodium stearate. The soap, therefore, separates out from solution.

COMMON ION EFFECT

The common ion effect is an effect that suppresses the ionization of an electrolyte when another electrolyte is added which contains an ion which is also present in the first electrolyte, i.e. a common ion will lead to an increase in the degree of association of ions.

1. It is considered to be a consequence of Le-Chatlier's principle .

AB is the weak electrolyte. Considering its dissociation



and applying Law of mass action

$$K = \frac{[A^+][B^-]}{[AB]}$$

The equilibrium constant K, has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution , it will increase the concentration of either A^+ ions (or) B^- ions and in order that 'K' may remain constant, the concentration of AB must increase, i.e., the equilibrium will shift to the left hand side.

2. This effect cannot be observed in the compounds of transition metals. This is because the d-block elements have a tendency to form complex ions.
3. This can be observed in the compound Cuprous chloride, which is insoluble in water. This compound can be dissolved in water by the addition of chloride ions leading to the formation of the $CuCl_2$ complex ion, which is soluble in water.

Ex:

The addition of NH_4Cl to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion of NH_4^+ .

Application of Common ion effect.

1. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.
2. The common ion effect can be used to obtain drinking water from aquifers (underground layer of water mixed with permeable rocks or other unconsolidated materials) containing chalk or limestone. Sodium carbonate (chemical formula Na_2CO_3) is added to the water in order to decrease the hardness of the water.
