Class XII Chemistry

IMPORTANT QUESTIONS and COMMON ERRORS

CHAPTER 1 SOLID STATE

1. Types of packing

i) Square Close Packing

In two dimensions- the co-ordination number of each sphere is 4

In three dimensions- the co-ordination number of each sphere is 6

ii) Cubic Close Packing (ccp / fcc)

In two dimensions- the co-ordination number of each sphere is 6

In three dimensions- the co-ordination number of each sphere is 12

iii) Hexagonal Close packing

In two dimensions- the co-ordination number of each sphere is 6

In three dimensions- the co-ordination number of each sphere is 12

iv) Body centerd cubic unit cell

In three dimensions- the co-ordination number of each sphere is 8

Unit Cell AND Packing efficiency	**No. of atoms per unit cell**	**Distance between nearest neighbours (d)**	**C.N.**	**Radius (r)**
Simple Cubic = 52.4%	**8**	**a**	**6**	**a/2**
Face Centred = 74%	**4**	**$a/\sqrt{2}$**	**12**	**$a/2\sqrt{2}$**
Body Centred = 68%	**2**	**$\sqrt{3}/2$**	**8**	**$\sqrt{3}/4$ a**

Defects in solids :

Any departure from the orderly arrangement of constituent particles in crystal is called imperfections or defect.

Types of defects in solids:

i) Point defects
ii) Line defects

Point defects: When the irregularity in the arrangement of constituent particles exist around a point or an atom in crystalline solid the defect is called a point defect.

NOTE: Only Point defects are there in the syllabus

POINT DEFECTS are of the following types:

i) STOICHIOMETRIC defects
ii) Non-stoichiometric defects
iii) Impurity defects

Stoichiometric defects: The constituent particles are present in the same ratio as predicted by their chemical formula and it does not disturb the overall stoichiometry of the compound.

These are of the following types:

i) vacancy defect **(co-valent compounds)**
ii) Interstitial defect**(co-valent compounds)**
iii) Schottky defect**(ionic solid)-** The ions are missing. Decreases the density of the ionic soild.

Found in compounds having high co-ordination number and small difference in the size of a cation and anion.

iv) Frenkel defect(ionic solid)- The ions occupy the interstitial sites. No change in the density. Found in compounds having low co-ordination number and large difference in the size of a cation and anion.

Non-stoichiometric defects: They are of the following type

i) Metal excess

a) By anionic vacancy-

F-centres: They are the electrons trapped in anionic vacancies.
When Sodium chloride is heated in an atmosphere of sodium vapours then some Na atoms are deposited on the surface of NaCl and some Cl- ions migrate to the surface to form ionic bond with the Sodium ions . Hence sodium atoms deposited on the surface lose one electron each to form Na^+ ions . These electrons lost go and occupy the anionic vacancies created due to the migration of Cl- ions to the surface. These trapped electrons absorb a portion of white light and reflect the remaining portion and this makes NaCl appear yellow.

By the presence of extra cation at the interstitial sites

$$ZnO \text{ ---------}\rightarrow Zn^{2+} + \frac{1}{2} O_2 + 2e-$$

ii) Metal deficiency defect due to missing of a cation of a lower valency and another lattice site is occupied by a cation of higher valency.

Impurity Defect:

Formation interstitial solutions

Doping: The process of adding impurities to a crystalline substance so as to change its properties is called doping.

a) Doping in ionic solids : When NaCl is doped with $SrCl_2$, there are cationic vacancies created.
b) Doping in co-valent solids:
   The impurities added may be electron rich or electron deficient. Accordingly the co-valent solids are called n-type or p-type semi-conductor. These type of defects are called Electronic defects.

When NaCl is doped with $MgCl_2$ one Mg^{2+} replaces two Na^+ ions and this leads to cationic vacancies or metal deficiency defect and it leads to increased electrical conductivity. It is an impurity defect.

ELECTRICAL PROPERTIES OF SOLIDS

SEMICONDUCTORS

Those solids which have intermediate conductivities ranging from 10^{-6} to 10^{4} ohm^{-1} m^{-1} .

The two main types of semiconductors are :

i) Intrinsic semiconductor
ii) Extrinsic semi-conductor

Extrinsic semiconductors are further of two types:

a) n-Type semiconductor
b) p- Type semiconductor

i) Intrinsic Semiconductor-

They are insulators which are capable of conducting at higher temperature . This happens because certain co-valent bonds are broken due to energy supplied. The electrons released conduct electricity. E.g Pure Silicon

ii) Extrinsic Semiconductor-

These semiconductors are formed when some impurity in the form of an element is added to an insulator. This is called as doping. Doping makes available electrons or holes for conductivity. On this bases extrinsic semiconductors are of two types.

a) n-Type semiconductor-

When the impurity atoms contain more number of valence electrons than the parent insulator , they are called electron rich impurities. Negatively charged electrons are responsible for the conduction of electric current hence the name ‘n-Type semiconductor’.

E .g .When traces of group 15 element phosphorus is added to pure silicon . Si has 4 e-s in its valence shell while P has 5 e-s in its valence shell. So Si share 4 e-s with P while the fifth electron of P is not involved in the bond formation and hence is left free for the conductivity.

b) p- Type semiconductor

When the impurity atoms contain lesser number of valence electrons than the parent insulator , they are called electron deficient impurities. Holes i.e. the sight where is deficiency of e- or positively charged holes are responsible for the conduction of electric current hence the name ‘p-Type semiconductor’.

E .g .When traces of group 13 element Boron is added to pure silicon . Si has 4 e-s in its valence shell while B has only 3 e-s in its valence shell. So Si share 3 e-s with B while the fourth electron of Si is not involved in the bond formation and hence is left free for the conductivity.

Magnetic Properties of Solids

- **Paramagnetic substances** are weakly attracted by a magnetic field. Example O2,Cu2+,Fe3+,Cr3+ due to presence of **unpaired electron**. They lose their magnetic in the absence of magnetic field.
- **Diamagnetic substances** are weakly repelled by a magnetic field. Example H_2O, NaCl, C_6H_6 due to the absence of unpaired electron .
- **Ferromagnetic substances** are very strongly attracted by a magnetic field and can be **permanently magnetized**. Example: iron, Cobalt, Nickel and CrO_2. The alignments of magnetic moments of the domains are in the direction the magnetic field.
- **Anti ferromagnetic substances:** The magnetic moments and domains are oppositely oriented and cancel out each other‘ s magnetic moment**.** Example MnO
- **Ferrimagnetic substances:** The magnetic moments of the domains are aligned in parallel and anti parallel directions in unequal numbers. So they are weekly attracted by magnetic field. Example Fe_3O_4 and $ZnFe_2O_4$

Recently asked questions in CBSE 2008 Onwards

Level 1 (Short Answer type questions) :

1. Define 'forbidden zone' of an insulator. (2010)
Ans The large energy gap between valence band and conduction band in an insulator is called forbidden zone.

2. Which point defect in crystal units alters the density of a solid? (2009, 2010)
Ans Interstitial defect (density increases)
Vacancy defect (density decreases) e.g. Scottky defect

3. Crystalline solids are anisotropic in nature. Explain.
4. Frenkel defects are not found in alkali metal halides. Why?
5. How many lattice points are there in one unit cell of a) **fcc b) bcc c) simple cubic**
Ans a) 14 b) 9 c) 8
6. What are the co-ordination numbers of octahedral voids and tetrahedral voids?
Ans 6 and 4 respectively

Level 2
2 MARKS QUESTIONS

1. Explain how electrical neutrality is maintained in compounds showing Frenkel and Schottky defect. In compound showing Frenkel defect, ions just get displaced within the lattice. While in compounds showing Schottky defect, equal number of anions and cations are removed from the lattice. Thus, electrical neutrality is maintained in both cases.
2. Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.
Ans 8 corner atoms × 1/8 atom per unit cell = 1 atom There are four body diagonals in a cubic unit cell and each has two body centre atoms. So **4×2=8 atoms** therefore total number of atoms per unit cell = 1+8=9 atoms

3.The electrical conductivity of a metal decreases with rise in temperature while that of a semi-conductor increases.Explain.
Ans In metals with increase of temperature, the kernels start vibrating and thus offer resistance to the flow of electrons.Hence conductivity decreases. In case of semiconductors, with increase of temperature, more electrons can shift from valence band to conduction band. Hence conductivity increases.

4. What type of substances would make better permanent magnets, ferromagnetic or ferromagnetic,Why?
AnsFerromagnetic substances make better permanent magnets. This is because the metal ions of a ferromagnetic substance are grouped into small regions called domains. Each domain acts as tiny magnet and get oriented in the direction of magnetic field in which it is placed. This persists even in the absence of magnetic field.

5.In a crystalline solid, the atoms A and B are arranged as follows: a. atoms A are arranged in ccp array b. atoms B occupy all the octahedral voids and half of the tetrahedral voids. What is the formula of the compound?
Ans: Let no. of atoms of A be N, No. of octahedral voids = N,
No. of tetrahedral voids = 2N
i)There will be one atom of B in the octahedral void
ii)There will be one atom of B in tetrahedral void (1/2 X 2N)
Therefore, total 2 atoms of B for each atom of A Therefore formula of the compound = AB_2

LEVEL 3

3 Marks questions

7. An element E crystallizes in body centered cubic structure. If the edge length of the cell is 1.49×10^{-10} m and the density is $19.3 gcm^{-3}$, calculate the atomic mass of this element. Also calculate the radius of an atom of the element.

Ans

$$\rho = \mathbf{Z \times M / a^3 \times No}$$

Common Mistake – Interconversión of units of edge length

$1\ \text{pm} = 10^{-12}\text{m} = 10^{-10}\ \text{cm}$

$1\ \text{Å} = 10^{-10}\text{m} = 10^{-8}\ \text{cm}$

$$19.3\text{gcm}^{-3} = \frac{2 \times M}{(1.469 \times 10^{-8}\ \text{cm})^3 \times (6.022 \times 10^{23})}$$

$M = 18.42\text{gmol}^{-1}$

For a bcc structure , the radius of an atom is $= \frac{\sqrt{3}}{4} . a$

$$= \frac{1.732 \times 1.489 \times 10^{-10}\text{m}}{4}$$

$= 6.36 \times 10^{-11}$ m

8. Analysis shows that a metal oxide has the empirical formula $M_{0.96}O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in this crystal.

OR

i) What type of substances show antiferromagnetism?

ii) Assign reason for the fact that silicon doped with phosphorus is a semiconductor.

Ans Suppose M^{2+} = X

M^{3+}= 96-X

Total charge on M^{2+} and M^{3+} is

2X + 3(96-X) = 2

X= 88

% of M^{2+} = 88/96 = 91.7%

% of M^{3+} = 100-91.7 = 8.3%

OR

i) Substances which are expected to possess paramagnetism or ferromagnetism on the basis of magnetic moments of the domains but actually possess zero net magnetic moment. e.g. MnO. It is due to the presence of equal number of domains in the opposite directions.

Si doped with P is an n-type semi-conductor because Si is tetravalent and P is pentavalent and one electron is left free and is not involved in bonding.

9. Calculate the density of silver which crystallizes in face centred cubic form. The distance between nearest metal atoms is 287pm.(molar mass of Ag=107.87gmol-1, No=6.022 x 1023)

Ans: d = Z×M/ a^3 × NA

distance between nearest neighbor, 2r = 287pm therefore ,

a= $\sqrt{2}$x2r = 405.87pm, Z= 4 M=107.87gmol-1 No=6.022 x 10^{23}

d=4x107.87gmol-1 / (405.87x10-10cm)3x6.022 x 10^{23}mol-1

Density = 10.72g /cm^{-3}

Chapter-2 –Solution

- **Relationship between Normality and Molarity :**

$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Mol. wt.}}{\text{Eq. wt.}} = n$$

or $$\text{Molarity} = \frac{\text{Normality}}{n}$$

Normality Equation : $N_1V_1 = N_2V_2$

Molarity Equation : $n_2M_1V_1 = n_1M_2V_2$

where n_1 and n_2 are the number of moles of reactants 1 and 2 as shown by the balanced equation.

If two non-reacting solutions are mixed, the normality of the resulting solution is given by

$$N_1V_1 + N_2V_2 = N_3V_3$$

- **Relationship between Molality (m) and Mole Fraction (x_2) of the Solute :**

$$x_2 = \frac{mM_1}{1 + mM_1}$$

where M_1 represents molecular mass of the solvent.

- **Relation between Molality (m), Molarity (M), Density (d) of the Solution and Molar Mass (M_2) of the Solute :** If the density of the solution is d kg/litre and the molar mass is M_2 kg/mole. Then,

$$\text{Molality } (m) = \frac{M}{d - MM_2}$$

If density is in g/cc and M_2 is molar mass in g mol^{-1}, then

$$\text{Molality } (m) = \frac{M}{1000d - MM_2} \times 1000$$

- **Relation between Molarity (M) of the Solution and Mole Fraction (x_2) of the Solute :**

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{M}{(d - MM_2)/M_1 + M}$$

$$= \frac{MM_1}{M(M_1 - M_2) + d}$$

If both the components are in gas phase.

$$\text{Mole fraction} = \frac{\text{Partial pressure of that component}}{\text{Total vapour pressure}}$$

- **Parts Per Million (ppm) :** ppm is the number of grams of a solute per million grams of solution or the number of cm^3 of solute per million cm^3 of the solution.

$$\text{ppm} = \frac{\text{mass of the component}}{\text{mass of solution}} \times 10^6$$

Solubility of a gas in liquid:

a) Increases with increase of pressure.

b) Decreases with increase of temperature.

As dissolution of gas in liquid is an exothermic process, the solubility should decrease with increase in temperature.

Henry’s law: At constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of gas over the solution.

Or

The partial pressure of the gas in vapour phase (P) is directly proportional to the mole fraction of the gas(x) of the solution.

$P = k_H.x$

k_H = Henryʹ s law constant.

It depends on the nature of gas. Greater the kH value, the lower will be the solubility and vice versa. k_H increases with increase in temperature so solubility of a gas in a liquid decreases with increase of temperature.

Raoult’s law: Raoultʹ s law in its general form can be stated as, ―

For any solution, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction in the solution.‖

According to Raoultʹ s law for a solution of two volatile liquids,

$$P_{soln} = P_1^o \chi_1 + P_2^o \chi_2$$

. According to Raoultʹ s law for a solution containing volatile solvent and non- volatile solute.

When a non- volatile solute is dissolved in a pure solvent, the vapour pressure of the pure solvent decreases. P solution < P^osolvent Because the non-volatile solute particles are present on surface of the solution so the rate of evaporation of molecules of the volatile solvent from the surface of solution decreases.

Liquid- liquid volatile solutions are classified into two types on the basis of Raoult's law as follows:

Ideal solution: The solution which obey Raoult' s law at all concentration and at all temperature i.e

- $P_A = P^o_A.x_A$and $P_B = P^o_B.x_B$
- If the intermolecular attractive forces between the solute – solvent(A – B interaction) are nearly equal to those between the solvent – solvent (A – A) and solute – solute (B – B) it forms ideal solutions.
- Enthalpy of mixing, Δmixing H = 0. Volume change on mixing, Δ_{mixing} V = 0.
- Examples: n - hexane and n-heptane. Bromoethane and chloroethane o Benzene and toluene.

Types of Non-Ideal solutions:

1. Non-ideal solution showing positive deviations □

- In this case, intermolecular attractive forces between the solute and solvent(A – B) are weaker than those between the solvent(A – A) and the solute (B – B) i.e
- $P_A > P^o_A x_A$
- $P_B > P^o_B x_B$ □
- Δ_{mixing} H = +ve □
- Δ_{mixing} V = +ve □
- Dissolution is endothermic so, heating increases solubility.
- Ethanol and acetone, Ethanol and water, CS_2 and acetone.

2. Non-ideal solution showing negative deviations

- In this case, intermolecular attractive forces between the solute and solvent(A – B) are stronger than those between the solvent(A – A) and the solute (B – B) i.e
- $P_A < P^o_A x_A$ $P_B < P^o_B x_B$
- Δmixing H = -ve
- Δmixing V = -ve □
- Dissolution is exothermic so, heating decreases solubility.

- Examples: Chloroform and acetone, Nitric acid and water, Phenol and aniline.

Azeotropes are binary solutions (liquid mixtures) having the same composition in liquid and vapour phase and it is not possible to separate the components of an azeotrope by fractional distillation.

Types of azeotropes:

1. Minimum boiling azeotrope □

- The non- ideal solutions showing positive deviation form minimum boiling azeotrope at a specific composition.
- Example; 95% ethanol and 5% water (by volume)
- Ethanol = 351.3K , Water = 373 K, Azeotrope = 351.1K

2. Maximum boiling azeotrope

- The non- ideal solutions showing negative deviation form maximum boiling azeotrope at a specific composition.
- Example : 68% Nitric acid and 32% water (by mass)
- Nitric acid = 359K , Water = 373 K, Azeotrope = 393.5K

d) $p_A < p^O_A \chi_A$ **and** $p_B < p^O_B \chi_B$

Colligative properties:

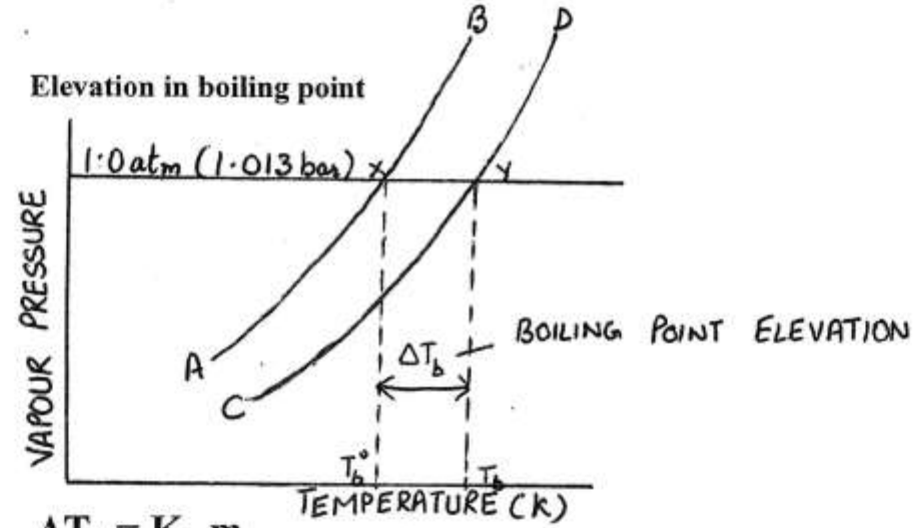
The properties of dilute solutions containing non-volatile solute which depend only upon the number of particles of the non - volatile solute.

The main colligative properties are:

i) Relative Lowering Of Vapour Pressure =

$$\frac{p^O - p_S}{p^O} = \frac{n_2}{n_{2+}n_1}$$

ii) Elevation in boiling point



$$\Delta T_b = K_b\, m$$

K_b = Molal elevation constant(K Kg mol^{-1})

K_b can be calculated from thermodynamic relationship:

$$K_b = \frac{MRT_b^2}{(1000\,.\,\Delta H_{vap})}$$

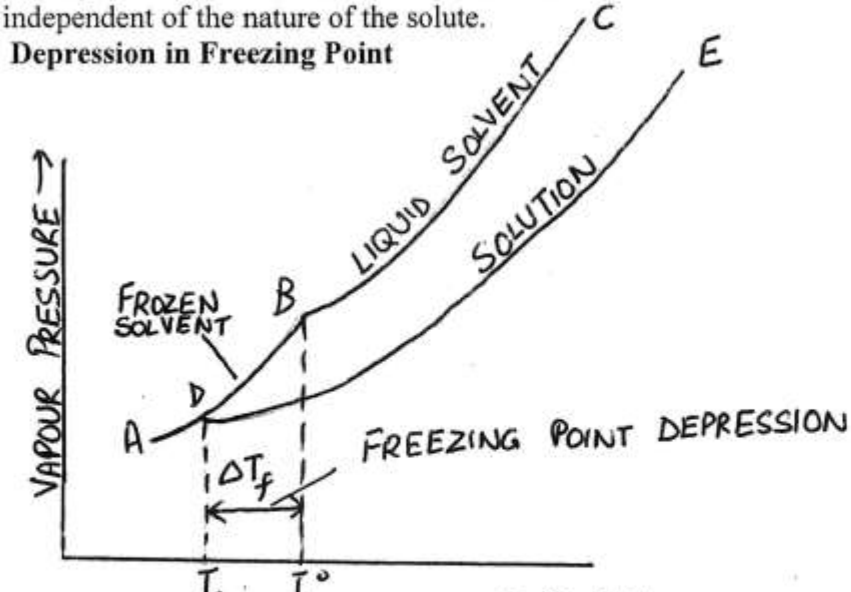
M= Molar mass of the solven tin g mol^{-1}

T_b^o = Boiling Point of the solvent

ΔH_{vap} = Molar enthalpy of vaporization of the solvent in Kg mol^{-1}

K_b depends only on the nature of the solvent but is independent of the nature of the solute.

iii) Depression in Freezing Point



$$\Delta T_f = K_f\, m$$

K_f = Molal depression constant(K Kg mol^{-1}) or Cryoscopic constant

K_f can be calculated from thermodynamic relationship:

$$K_f = \frac{MRT_f^2}{(1000\ .\ \Delta H_{fus})}$$

M= Molar mass of the solven tin g mol^{-1}

T_f^o = Freezing Point of the solvent

ΔH_{fus} = Molar enthalpy of fusion of the solvent in Kg mol^{-1}

K_f depends only on the nature of the solvent but is independent of the nature of the solute.

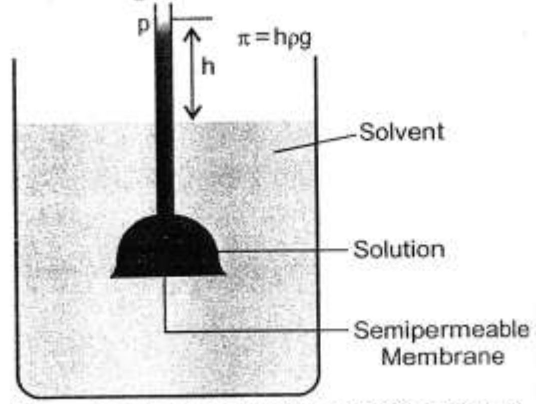
iv) **Osmotic Pressure: It may be defined as extra pressure that must be applied to the solution compartment to prevent the flow of solvent into the solution when the two are separated by SPM(Semi permeable membrane)**

$\Pi = CRT$

C = Molarity

R= Gas constant 0.082 litre atm K^{-1} mol^{-1}

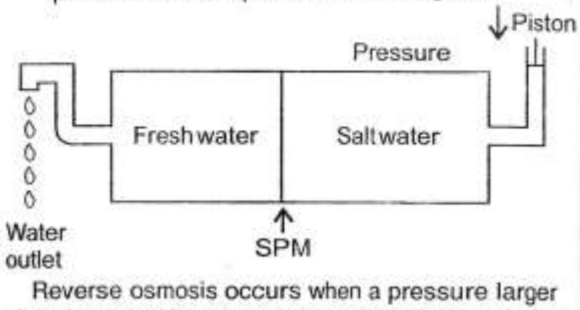
$$M_B = \frac{W_B\ .\ R\ .\ T}{\Pi.\ V}$$



The principle of measuring osmotic pressure. The pressure in excess of atmospheric pressure that must be applied to the solution to prevent it from rising in the tube is the osmotic pressure. This will also be equal to hydrostatic pressure of the liquid column of height, *h*.

Reverse Osmosis: If a pressure larger than the osmotic pressure is applied to the solution side, the pure solvent (or water) flows out of the solution through the semi-permeable membrane. In this way the direction of osmosis is reversed and so the process is called reverse osmosis.

Thus, we can say that reverse osmosis is just opposite to the osmosis when an extra pressure is applied. Reverse osmosis is used in desalination to get pure water from sea water.



Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

Isotonic solutions: Two solutions are said to be isotonic when they exert the same osmotic pressure because they have the same molar concentration. All intravenous injections must be isotonic with body fluids.

Isosmotic solutions: When two isotonic solutions are separated by a semi-permeable membrane, no osmosis occurs. The solutions are called **isosmotic solutions.**

Hypotonic solutions: A solution having lower osmotic pressure than the other solution is said to be hypotonic with respect to other solution.

Hypertonic solutions: A solution having higher osmotic pressure than the other solution is

Abnormal Molecular Masses : When the molecular mass of a substance obtained by using colligative properties does not tally with the theoretical value, this molecular mass is known as **abnormal molecular mass**. This happens when the substance in the solution undergoes association or dissociation. Higher the colligative property of a substance lesser will be the molecular mass (m) of that substance because :

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

Van't Hoff Factor (i) : Van't Hoff factor is the ratio of experimental value of the colligative property to the calculated value of the colligative property.

$$i = \frac{\text{observed value of colligative property}}{\text{calculated value of colligative property}}$$

or

$$i = \frac{\text{calculated value of molecular mass}}{\text{observed value of molecular mass}}$$

Modified Formula : For substances undergoing dissociation or association in the solution :

$$\Delta T_b = iK_b m$$

$$\Delta T_f = iK_f m$$

$$P = i\frac{n}{V}RT$$

Degree of Dissociation : If one mole of a substance A dissociates to form n molecules or ions and α is the degree of dissociation, then

$$\underset{(1 \text{ mole})}{A} \longrightarrow np$$

At equilibrium, $1 - \alpha$ $\quad n\alpha$

After dissociation number of moles $= 1 - \alpha + n\alpha = 1 + (n - 1)\alpha$

so

$$i = \frac{1+(n-1)\alpha}{1}$$

or

$$\alpha = \frac{i-1}{n-1}$$

Degree of Association : If n molecules, 'A' associates to form one molecule and α is the degree of association, then

$$nA \longrightarrow A_n$$

At equilibrium, $1 - \alpha$ $\quad \frac{\alpha}{n}$

After association total number of moles $= 1 - \alpha + \frac{\alpha}{n}$

$$i = \frac{1-\alpha+\frac{\alpha}{n}}{1}$$

or

$$\alpha = (1-i)\frac{n}{n-1}.$$

1. **R = 8.314 JK^{-1} mol^{-1} ,V = m^3 , P = Pascal or N/m^2**
2. **R = 0.082 LatmK^{-1} mol^{-1} ,V = cm^3 or ml , P = atm**
3. **R = 0.083 L bar K^{-1} mol^{-1} V= litre P = bar**

And 1 litre = 1000ml = 1000cm^3 , 1m^3 = 1000litres

Interconversion units of Pressure:
1atm= 101325 Pascals = 1.01325 x 10^5 Pa = 760 torr = 760 mm of Hg = 1.01325bar
1 bar = 10^5 pascals = 0.987atm

Commonly Asked Questions in CBSE
LEVEL 1

SOLVED QUESTIONS 1 MARK QUESTIONS

1.What type of liquids form ideal solutions?
Ans Liquids having similar structures and polarities.

2.Why does chemist prefer to refer concentration of solution in terms of molality?

(Or)

Which of the two molality and molarity is better to express concentration of solution? Why?
Ans Molality does not change with temperature where as molarity changes with temperature because volume changes with temperature. Therefore molality is better.

3. What is van'tHoff factor for KCl in aqueous solution?
i = 2 .

4. What happens when blood cells are placed in pure water?
AnsDue to osmosis water enters the blood cells through the cell wall, as a result it swells and may even burst.

5. Two liquids say X and Y boil at 380 K and 400 K respectively. Which of them is more volatile? Why?
Ans Liquid – X because lower the boiling point more will be volatile (evaporation).

6.What is the effect of rise in temperature on solubility of gases?
Ans. Dissolution of gas is exothermic process. Hence according to Le-Chatelier‘s principle, the solubility of gas should decrease with rise in temperature

7. Mention a large scale use of the phenomenon called ‘reverse osmosis’.
Ans. Desalination of Sea water.

8 .Why it is advised to add ethylene glycol to water in a car radiator while driving in a hill station?
Ans As an antifreeze to lower the freezing point of water.
9. What is the expected Van’t Hoff’s factor ‘i’ value for $K_3[Fe(CN)_6]$?
Ans Therefore, i = 4
10. The molar mass of bio molecules is determined by osmotic pressure and not by other colligative properties. Why?
Ans Osmotic pressure is measured around room temperature whereas biomolecules are generally unstable at higher temperatures.
Q11 State the following:
i) Raoult’s Law in its general form in reference to solutions .
ii) Vant Hoff factor (CBSE Delhi and All India 2010,2013 , 2009)
Ans

i) For a solution of volatile solute the partial vapour pressure of each component in the solution is directly proportional to its mole fraction. For a solution of a non- volatile solute the vapour pressure of the solution is directly proportional to the mole fraction of the solvent.
ii) Vant Hoff factor is defined as the ratio of theoretical molecular mass to the observed molecular mass of the solute on solution.

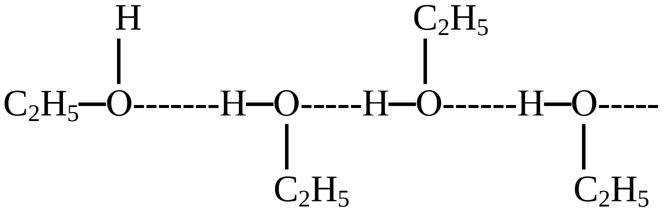
Q12 Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain.
Ans Osmosis : It is the process of movement of solvent from the solvent to the solution.

LEVEL 2

Q1 Give an example of a miscible liquid pair showing positive deviation from the Raoult’s Law. Give reason.

Ans

An example of a miscible liquid pair showing positive deviation from the Raoult's Law is a mixture of Ethyl alcohol and cyclohexane



$$C_2H_5{-}\overset{\overset{H}{|}}{O}\text{-------}H{-}\underset{\underset{C_2H_5}{|}}{O}\text{-----}H{-}\overset{\overset{C_2H_5}{|}}{O}\text{------}H{-}\underset{\underset{C_2H_5}{|}}{O}\text{-----}$$

When cyclohexane is added to ethyl alcohol, the molecules of cyclohexane try to occupy the spaces in between ethyl alcohol molecules. Consequently some hydrogen bonds in alcohol molecules break and attractive forces between the molecules are weakened . The escaping tendency of the molecules of ethanol and cyclohexane from the solution increases due to which the vapour pressure of the solution also increases.

Q2 Henry's law constant for CO_2 dissolving in water is 1.67×10^8 Pa at 298 K . Calculate the quantity of CO_2 in 1L of soda water when packed under 2.5 atm CO_2 pressure at 298K.

Ans

$K_H = 1.67 \text{ X } 10^8$ Pa

$P = 2.5 \text{ atm} = 2.5 \text{ X } 1.01325 \text{ X } 10^5$ Pa

$\mathbf{P = K_H \chi_2}$

$$\chi_2 = \frac{p}{K_H}$$

$$= \frac{2.533 \text{ X } 10^5 \text{ Pa}}{1.67 \text{ X } 10^8} = 1.517 \text{ X } 10^{-3}$$

Moles of water = $\frac{500}{18} = 27.78$

$$\chi_2 = \frac{n_2}{n_1 + n_2}$$

$$= \frac{n_2}{27.78 + n_2} = 1{,}517 \text{ X } 10^{-3}$$

$n_2 = 0.0419 + 0.0015\, n_2$

$0.9985\, n_2 = 0.0419$

$n_2 = 0.0420$

Amount of CO_2 dissolved = 0.0420 X 44 = 1.85g

Q 3 Differentiate between molarity and molality of a solution. What is the effect of change in temperature on its molality and molarity values?

(CBSE 2009, 2011)

Ans . Molality of a solution is the number of moles of solute present per litre of the solution and it is influenced by temperature change since volume increases with rise in temp and vice versa.

Molarity decreases with increase in temperature . On the other hand , molality of a solution is the number of moles of the solute present per Kg of the solvent and it does not change with temperature.

Q4 i) Why is an increase in temperature observed on mixing chloroform and acetone?

ii) Why does sodium chloride solution freeze at a lower temperature than water?

Ans i) When chloroform and acetone are mixed , the new interactions are stronger i.e. ΔH is negative i.e. heat is evolved and hence the escaping tendency of the molecules from the mixture decreases.

ii) Upon adding a non- volatile solute like NaCl to water, the vapour pressure is lowered. The vapour pressure of this solution becomes equal to that of pure solid solvent which is the freezing point of the solution occurs at a lower temperature. Thus freezing point of NaCl solution is lower than that of pure solvent.

Q10 Define azeotropes. (CBSE 2014)

Ans Azeotropes are the mixtures of liquids which boil at constant temperature and distil out without any change in composition.

Q11 What type of inter molecular attractive forces exist in the pair of

methanol and acetone?

Ans Dipole – dipole interactions

LEVEL- 3

Q12 A solution containing 15g of urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass=180gmol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution.

Ans For urea solution :

$W_2 = 15g$, $M_2 = 60g$ $V = 1L$

$\Pi = W_2RT/ M_2V = 15x\ R\ x\ T/60\ x\ 1$

For glucose solution:

$W_2 =?$, $M_2 = 180gmol^{-1}$, $V= 1L$

$\Pi = W_2RT/ M_2V = W_2x\ R\ x\ T/180\ x\ 1$

As Π (glucose) = Π (urea)

$15x\ R\ x\ T/60\ x\ 1 = W_2x\ R\ x\ T/180\ x\ 1$

$W_2 = 45g$

Q13 15g of an unknown molecular substance was dissolved in 450g of water. The resulting solution freezes at -0.34^{o}C. What is the molar mass of the substance? (K_f for water is = 1.86 K Kg mol^{-1})

(CBSE ALL INDIA – 2010, DELHI -2012)

ANS $\Delta T_f = T^o{}_f - T_f = 0^oC –(-0.34^oC) = 0.34K$

Common Error :

Never convert ΔT_f in ^{o}C into Kelvin

$W_1 = 450\ g = 0.45Kg$

$W_2 = 15g$, $K_f = 1.86\ K\ Kg\ mol^{-1}$

$\Delta T_f = K_f\ x\ W_2 / M_2\ x\ W_1$ therefore $M_2 = 182.35g/mol$

Electrochemistry: Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.

Resistance (R): It is the property of a substance by which it obstructs the flow of electric current through it. The electrical resistance (R) of any object is directly proportional to its length (l) and inversely proportional to its area of cross section (A).

Thus $R \ \alpha \ \frac{L}{A}$ or $R = \rho \frac{l}{A}$

Where ρ (rho) is a constant of proportionality called specific resistance or resistivity.

$$\rho = R\frac{A}{l}$$

Now, if $l = 1$ cm, $A = 1 \text{ cm}^2$ then $R = \rho$

Thus resistivity may be defined as the resistance offered by a conductor of 1 cm length having 1 cm^2 area of cross-section.

Units: $\rho = R\frac{A}{l} = \text{ohm}\frac{\text{cm}^2}{\text{cm}} = \text{ohm cm}$

Its SI units are ohm meter (Ω m).

Conductance (G): It is the reciprocal of resistance and may be defined as the ease with which the electric current flows through a conductor.

$$G = \frac{1}{R}$$

Its SI unit is Siemen (S).

$1 \ S = 1 \text{ ohm}^{-1}$ (mho)

Conductivity (K): It is the reciprocal of resistivity (ρ).

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} = G \times \frac{l}{A}$$

Now if $l = 1$ cm and $A = 1 \text{ cm}^2$, then $\kappa = G$

Hence conductivity of an electrolytic solution may be defined as the conductance of a solution of 1 cm length with area of cross section equal to 1 cm^2.

Units: $\kappa = \frac{1}{\rho} = \frac{1}{\text{ohm cm}} = \text{ohm}^{-1} \text{ cm}^{-1} \ (\text{S cm}^{-1})$

The SI units of conductivity are S m^{-1}.

S. No.	Physical quantity	Unit (CGS)	Unit (SI)
1.	Conductance	ohm^{-1}	S (siemen)
2.	Conductivity or specific conductance	ohm^{-1} cm^{-1}	S m^{-1}
3.	Cell constant	cm^{-1}	m^{-1}
4.	Equivalent conductance	ohm^{-1} cm^2 equiv^{-1}	S m^{-1} (equiv L^{-1})$^{-1}$ or S m^2 (equiv^{-1})
5.	Molar conductance	ohm^{-1} cm^2 mol^{-1}	S m^2 mol^{-1} or S m^{-1} (mol L^{-1})$^{-1}$

Molar conductivity (Λ_m): It may be defined as the conducting power of all the ions produced by dissolving one gram mole of an electrolyte placed between two large electrodes at one centimeter apart.

Mathematically

$$\Lambda_m = \kappa \times V, \quad \Lambda_m = \frac{\kappa \times 1000}{C} \text{ or } \frac{\kappa \times 1000}{M}$$

where, V is the volume of solution in cm^3 containing 1 gram mole of electrolyte and C is the molar concentration.

Units: $\Lambda_m = \frac{\kappa \times 1000}{C} = \frac{S\ \text{cm}^{-1}}{\text{mol cm}^{-3}}$

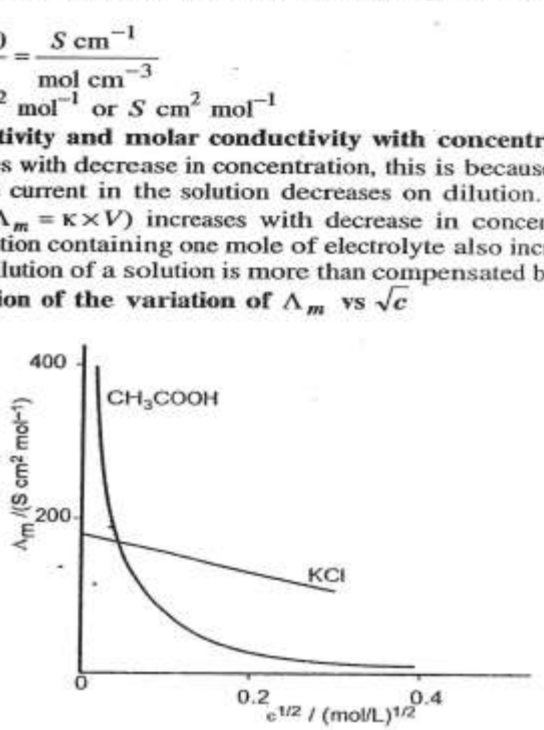
$= \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ or $S\ \text{cm}^2\ \text{mol}^{-1}$

Variation of conductivity and molar conductivity with concentration:

Conductivity decreases with decrease in concentration, this is because the number of ions per unit volume that carry the current in the solution decreases on dilution.

Molar conductivity ($\Lambda_m = \kappa \times V$) increases with decrease in concentration. This is because the total volume V of solution containing one mole of electrolyte also increases. It has been found that the decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Graphic representation of the variation of Λ_m vs $\sqrt{c}$



Limiting Molar conductivity (Λ_m): The value of molar conductivity when the concentration approaches zero is known as limiting molar conductivity or molar conductivity at infinite dilution. It is possible to determine the molar conductivity at infinite dilution (Λ_m^o) in case of strong electrolyte by extra potation of curve of Λ_m vs $\sqrt{c}$. On contrary, the value of molar conductivity of weak electrolyte at infinite dilution cannot be determined by extrapolation of the curve as the curve becomes almost parallel to y-axis when concentration approaches to zero.

- **Kohlrausch's Law:** It States that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

In general, if an electrolyte on dissociation gives ν_+ cations and ν_- anions then its limiting molar conductivity is given by

$$\Lambda_m^o = \nu_+ \lambda_+^o + \nu_- \lambda_-^o$$

Here, λ_+^o and λ_-^o are the limiting molar conductivities of cations and anions respectively.

Applications of Kohlrausch's law:

(*i*) Calculation of molar conductivities of weak electrolyte at infinite dilution. For example molar conductivity of acetic acid at infinite dilution can be obtained from the knowledge of molar conductivities at infinite dilution of strong electrolyte like HCl, CH_3–COO Na and NaCl as illustrated below.

$$\begin{aligned}\Lambda^o_{m(CH_3-COOH)} &= \lambda^o_{CH_3-COO^-} + \lambda^o_{H^+}\\ &= [\lambda^o_{CH_3-COO^-} + \lambda^o_{Na^+}] + [\lambda^o_{H^+} + \lambda_{Cl^-}] - [\lambda^o_{Na^+} + \lambda^o_{Cl^-}]\\ i.e., \Lambda^o_{m(CH_3-COOH)} &= \Lambda^o_{m(CH_3-COONa)} + \Lambda^o_{m(HCl)} - \Lambda^o_{m(NaCl)}\end{aligned}$$

(*ii*) Determination of Degree of Dissociation of weak electrolytes.

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^o}$$

(*iii*) Determination of Dissociation constant (K) of weak electrolytes.

$$K = \frac{c\alpha^2}{1-\alpha}$$

(*iv*) Determination of solubility of sparingly soluble salts.

$$\Lambda_m^o = \frac{K \times 1000}{\text{molarity}} = \frac{K \times 1000}{\text{solubility}}$$

$$\text{or, Solubility} = \frac{K \times 1000}{\Lambda_m^o}$$

Difference between:

	Electrochemical cell or Galvanic cell or Voltaic Cell	**Electrolytic Cell**
1.	A device in which electrical energy is produced from chemical reaction.	A device in which electrical energy is used to bring about a chemical reaction.
2.	E.g. Daniel cell, dry cell, leads storage battery.	E.g. Electrolysis of molten NaCl, Electrolysis of dil. Aq. H_2SO_4 sol. using Pt electrodes.

Electrode potential: the potential difference between electrode (metal) and the electrolyte (metal ion solution).

Cell potential: the potential difference between the two electrodes of a galvanic cell. $E_{cell} = E_{cathode} - E_{anode}$

EMF (electromotive force) of cell: the potential difference between the two electrodes when no current is drawn (flowing) through the cell.

S H E (standard hydrogen electrode):

- It is used as a reference electrode to measure the standard electrode potential of the other electrode by assigning standard electrode potential of SH E is zero. [$E_0 H_+$ = zero].
- It consists of a platinum electrode (foil) coated with finely divided platinum dipped in an acidic solution with 1 M H^+ (aq) ion and pure hydrogen gas (at 1 bar) is bubbled through the solution.
- H (aq) | H_2 (g) | Pt (s)

Nernst equation: It shows the relationship between the electrode potential (electrode) and concentration of metal ions

$$M^{n+} + ne^- \longrightarrow M$$

$$E_{electrode} = E^o_{electrode} - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$E_{cell} = E^o cell - \frac{2.303\ RT}{nF} \log K_c$$

Q1 $Cu^{2+} + 2e^- \text{------------}\rightarrow Cu \quad E^o = 0.34V$

$Ag^+ + 1e^- \text{-----------}\rightarrow Ag \quad E^o = 0.80V$

i) Construct a galvanic cell using the above data.

ii) For what concentration of Ag^+ ions will the emf of the cell be zero at 25^OC , if the conc of Cu^{2+} ions is 0.1 M ? [log 3.919= 0.593].

Ans Since the reduction pot of Cu^{2+}/Cu is less so copper electrode acts as anode and silver electrode acts as cathode. The galvanic cell is

$$\mathbf{Cu/\ Cu^{2+}(C_1)\ //\ Ag^+\ (C_2)\ /\ Ag}$$

EMF = 0.8 – 0.342 = 0.458V

Using Nernst Equation;

$$\mathbf{Ecell = E^Ocell - \frac{0.059}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2}}$$

$$\mathbf{0 = 0.458 - \frac{0.059}{2} \log \frac{[0.1]}{[Ag^+]^2}}$$

$[Ag+] = 5.248 \times 10^{-9}\ molL^{-1}$

Relationship between E $_{cell}$ and Gibbs energy ($\Delta_r G$)

- $\Delta_r G = - nF E_{0\ cell}$
- $\Delta_r G_0 = -nF E_{0cell}$ (at 25$_0$C or 298K 1 atm)

Relationship between $\Delta_r G$ and equilibrium constant K_C

- $\Delta_r G_0 = - 2.303\ RT \log K_C$ **and Maximum work = $\Delta_r G_0$**

Primary Cells: In these the reaction occurs only once and battery then becomes dead after use over a period of time. It cannot be recharged and reused again.

E.g. dry cell, mercury cell

- **Dry cell** (leclanche cell)
- (1.) Anode- Zn container
- (2.) Cathode- graphite rod surrounded by powered MnO_2 and carbon.
- Electrolyte- a moist paste of NH4Cl and $ZnCl_2$.
- Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
- Cathode: $MnO_2 + NH_4^+ + 1e^- \rightarrow MnO(OH) + NH_3$
- Cell potential: nearly **1.5V.**

Mercury cell

  - Anode **–** Zn-Hg amalgam
  - Cathode - A paste of HgO and carbon
  - Electrolyte - a paste of KOH and ZnO
  - Anode: $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e$
  - Cathode**:** $HgO(s) + H_2O + 2e \rightarrow Hg(l) + 2OH^-$
  - Overall cell reaction**:** $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$
  - Cell potential is **1.35V**
  - **Secondary batteries:** After use, they can be recharged by passing current through it in opposite direction and so they can be reused again. E.g. Lead storage battery, nickel-cadmium cell.

Lead Storage Battery

Secondary Batteries (Rechargeable) Nickel Cadmium Cell

Lead storage battery:

- **anode** – Pb plate
- **Cathode** – grid of lead packed with PbO_2.
- **Electrolyte** – 38% solution f sulphuric acid (1.3 g / ml)
- **Anode:** $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO4(s) + 2e^-$
- **Cathode:**
- $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow 2PbSO_4(s) + 2H_2O(l)$
- **Overall cell reaction**:
- $Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO4(s) + 2H_2O(l)$

- used in automobiles and inverters. On recharging the battery, the above reaction is reversed.

Nickel- Cadmium cell:

- **Anode:** Cd
- **Cathode:** $Ni(OH)_3$
- Overall cell reaction,
- Cd (s) + 2 Ni $(OH)_3$ (s) → CdO (s) + 2Ni $(OH)_2$ (s) + H_2O (l)
- nickel cadmium cell has longer life than the lead storage cell but more expensive to manufacture.

Fuel Cells:

galvanic cells which convert the energy of combustion of fuels like hydrogen, methane directly into electrical energy.

E.g. **Hydrogen – Oxygen Fuel Cell**

Hydrogen and oxygen are bubbled through porous carbon electrode into concentrated aqueous sodium hydroxide solution. To increase the rate of electrode reaction catalysts like palladium or platinum is used

Anode: 2 H_2 (g) + 4 OH- (aq) → 4 H_2O (l) + 4e

cathode: O_2 (g) + 2H O (l) + 4e → 4 OH-(aq)

Advantages:

1. High efficiency
2. Continuous source of energy
3. Pollution free.

ELECTROCHEMICAL THEORY OF CORROSION

- A PARTICULAR SPOT MADE UP OF IRON ACTS AS ANODE AND OXIDATION TAKES PLACE

2Fe (s) -----→ $2Fe^{2+}$ + 4e- E^o (Fe^{2+}/Fe) = -0.44V

These e-s move through the metal to another spot where oxygen is reduced in the presence of H^+ ions which come from H_2CO_3 formed due to dissolution of CO_2 and water or from other acidic oxides.

- This spot behaves as cathode:

O_2 (g) + $4H^+$ (aq) + 4e- ---------→ $2H_2O$ (l)

$E^O\ H^+ / O_2 / H_2O = 1.23V$

The overall cell reaction is :

$2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O \qquad E^O\ (cell) = 1.67V$

Methods Of Preventing Corrosion:

(1). Galvanization**:** the process of coating Zinc over iron

(2). **Cathodic protection or sacrificial electrode:** In this method more reactive metal like Mg (or) Zn are made as sacrificial anode and are connected to iron pipe or tank.

SOLVED QUESTIONS

1 MARK QUESTIONS

(1). Name two metal which can be used for cathodic protection of iron.

Ans. (Mg, Zn)

(2).What is the relationship between E0 cell and equilibrium constant at 298 K?

Ans. E0 cell = 0.059 log KC

―――――

n

(3). Can a nickel spatula be used to stir a solution of copper sulphate? Support your answer with reason.

Ans. [E^0 Ni^{2+} / Ni = - 0.25V, E^0 Cu^{2+}/Cu = + 0.34V] No, since nickel has lower E0 value than copper it undergoes oxidation.

(4). A Leclanche cell is also called dry cell. Why?

Ans . Leclanche cell consists of zinc anode (container) and carbon cathode. The electrolyte is a moist paste of MnO_2, $ZnCl_2$, NH_4Cl and carbon black. Because there is no free liquid in the cell, it is called dry cell.

(5). What are fuel cells?

Ans. A fuel cell is a galvanic cell for converting the energy of a fuel directly into electrical energy without use of a heat engine.

(6). What is meant by Faraday's constant?

Ans. Faraday's constant is the quantity of electricity carried by one mole of electrons. 1 F = 96500 C/mol

(7). Define the term – Resistivity?

Ans. The resistively of a substance is its resistance when it is one meter long and its area of cross Section is one m^2 .

(8). State the factors that affect the value of electrode potential?

Ans. Factors affecting electrode potential values are –

a) Concentration of electrolyte

b) Temperature.

(9). Define the term – standard electrode potential?

Ans. When the concentration of all the species involved in a half-cell is unity, then the electrode potential is called standard electrode potential.

(10). What does the positive value of standard electrode potential indicate?

Ans. The positive value of standard electrode potential indicates that the element gets reduced more easily than H^+ ions and its reduced form is more stable than Hydrogen gas.

2 MARKS QUESTIONS

(1). Give reasons: (a) Rusting of iron is quicker in saline water than in ordinary water

(b) Aluminium metal cannot be produced by the electrolysis of aqueous solution of aluminium salt.

Ans. (a) Because the conductivity of saline water is more than ordinary water.

(b) Al is highly reactive and cannot be reduced easily as compared to Al^{3+} ions; water is reduced easily since E0 reduction for water is higher.

(2). Predict the products of electrolysis obtained at the electrodes in each case when the electrodes used are platinum.

(a) An aqueous solution of $AgNO_3$.

(b) A dilute aqueous solution of H_2SO_4.

(a) Silver is deposited at cathode and oxygen is anode.

Cathode: $Ag^+ (aq) + 1e^- \rightarrow Ag (s)$,

Anode: $2 H_2O (l) \rightarrow O_2 (g) + 4H^+ + 4e^-$

(b) H_2 gas at cathode and O_2 gas at anode.

Cathode: $H_2O (l) + 1e^- \rightarrow \frac{1}{2} H_2 (g) + OH^-$,

Anode: $2 H_2O (l) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$

. 3.Enlist the factors affecting corrosion? What is SHE? What is its electrode potential?

Ans. Factors affecting corrosion are –

a) Water and air

b) Presence of electrolytes in water.

c) Presence of gases like CO_2 , SO_2. SHE stands for standard Hydrogen electrode.

d) By convention, its electrode potential is taken as 0 (zero).

Specific conductivity of an electrolytic solution may be defined as the conductance of solution of 1cm length with area of cross section equal to $1cm^2$.

$$\Lambda eq = \frac{K \times 1000}{\text{Normality}}$$

$$= \frac{22.4 \times 10^{-2}\ Scm^{-1} \times 1000}{0.12} = 1866.67\ Scm^{2}\ gmeq^{-1}$$

Q2 a) What is time required to deposit 1.5g of siver when 1.5 amperes of current is passed through an aq solution of $AgNO_3$?

b) Write the products of electrolysis of aq $AgNO_3$ solution.

Ans

I = 1.5 Ampere

M= 1.5g

To deposit 108g of Ag charge required is = 96500C

--------------1.5g------------------------------ $= \frac{96500 \times 1.5}{108} = 1340.278C$

Hence the time for which the current was passed is $= Q/I = \frac{1340.278}{1.5}$

= 893.51Seconds

ii) The ions present in the aq soln of $AgNO_3$ are – Ag^+, H^+ , OH^- and NO_3^-.

At cathode ;

Since the discharge potential of Ag+ ion is lesser the H+ ion hence is deposited at the cathode.

$$Ag^+ + e^- \text{------}\rightarrow Ag(s)$$

At Anode:

Since the discharge potential of OH- ion is lesser than NO_3^- the ion hence Oxygen gas is released at the cathode.

H_2O ------→ H^+ + OH^-] x4
$4OH^-$ ------→ $2H_2O + O_2 + 4e-$

$2H_2O$ -----→ $4H^+ + O_2 + 4e-$

---

iii) In case Ag electrodes were used then siver from impure silver anode would be deposited at the pure siver cathode.

At Cathode:

Ag ------→ Ag^+ + e-

At cathode :

Ag^+ + e- ------→ Ag(s)

i) Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery sending out an electric current.

ii) Determine the value of equilibrium constant Kc and ΔG^0 for the following reaction:

Ni(s) + $2Ag^+$ (aq) -------------→ Ni^{2+} (aq) + 2Ag(s)

Given : (1F = 96500C) and E^o = 1.05V

OR

i) Define the term molar conductivity and explain how molar conductivity changes with solution concentration for weak and strong electrolytes.

ii) A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in 1 molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

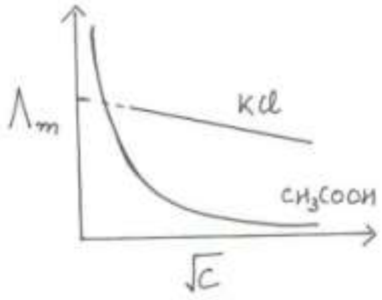
i) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.
ii) Calculate the cell potential E_{cell} at 25°C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and initial concentration of $AgNO_3$ is 1.00 molar.

[$E^o_{Ni^{2+}/Ni} = -0.25V$; $E^{o-}_{Ag+/Ag} = 0.80V$]

Ans.

i)

a) In case of weak electrolytes the dissociation is not complete and with dilution there is an increase in the degree of dissociation of weak electrolyte. At a particular dilution there is a sharp rise in molar conductivity.



b) In case of strong electrolytes there is an increase in the in molar conductivity with dilution because of the decrease in inter-ionic interactions and increase in the mobility of ions.

c) Conductivity of a solution of an electrolyte decreases with decrease in concentration. This is because conductivity depends upon number of ions per unit volume of the solution and with decrease in concentration number of ions per unit volume decreases.

ii) $\Delta G^0 = -n F E^o_{cell}$ ½

$= -2 \times 96500 \times 1.05 = -202650 J/mol$ 1

$Kc = \text{antilog} (n E^o_{cell}) / 0.059$ ½

$= \text{antilog} (2 \times 1.05 / 0.059)$ ½

$Kc = 3.92 \times 10^{35}$ ½

OR

i)

a) Reaction at anode during discharging:

$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4 (s) + 2e^-$ --------------

b) Reaction at cathode during discharging:

PbO_2 (s) + SO_4^{2-}(aq) + $4H^+$ (aq) + 2e- -------→ $PbSO_4$ (s) + 2 $2H_2O$(l)---------

ii)
$Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+} + 2Ag$ ………

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$E^\circ_{cell} = 0.80 + 0.25 = 1.05V$$

$$E_{cell} = 1.05 - \frac{0.059}{2}\log\frac{(0.1)}{(1)^2}$$

$$= 1.05 - \frac{0.059}{2} \times (-1)$$

$$= 1.05 + 0.0295$$

$$E_{cell} = 1.0795V$$

Q4 Write electrode reactions taking place in a dry cell.

Ans
At Anode : Zn --------→ Zn^{2+} + 2e-
At cathode: $2NH^{4+}$ (aq) + $2MnO_2$ (s) + 2e- ----→ 2MnO(OH) + $2NH_3$

Zn + $2NH^{4+}$ (aq) + $2MnO_2$ (s) --------→ Zn^{2+} + 2MnO(OH) + $2NH_3$

Q5 What is change in free energy for electrolytic cell?
Ans ΔG is positive

(i) How much electricity is required in couloumb for the oxidation of 1 mole of H_2O to O_2?
ii) Calculate the emf of the cell :
Cr /Cr^{2+} (0.1M) // Fe^{2+}(0.01M)/Fe
Given that
E^oCr^{3+}/ Cr = -0.75V
E^oFe^{2+}/ Fe = -0.45V

Ans
i) $4H_2O$ --------→4 H^+ + $4OH^-$

$$\mathbf{4OH^- \longrightarrow 2H_2O + O_2 + 4e^-}$$

$$\mathbf{2H_2O \longrightarrow 4\,H^+ + O_2 + 4e^-}$$

Hence 4 X 96500 = 386000 coulombs is required to oxidize 2 moles of water. Therefore 193000 coulombs is required for the oxidation of 1 mole of H_2O to O_2.

ii) $E_{cell} = E^o_{cell} - \frac{0.0591}{2} \log \frac{[Cr^{2+}]}{[Fe^{2+}]}$

$$\mathbf{= 0.30 - 0.0295 \log 0.1/0.01}$$

$\mathbf{E_{cell} = 0.2705V}$

OR

i) How does molar conductivity vary on dilution for strong electrolyte?

ii) The electrical resistance of a column of $0.05 mol l^{-1}$ NaOH solution of diameter 1cm and length 50cm is 5.55×10^3 ohm. Calculate its resistivity and conductivity.

Ans

i) Molar conductivity increases with decreases in concentration. This is because the total volume V of solution containing one mole of electrolyte also increases. It has been found that the decrease in Kappa on dilution of a solution is more than compensated by increase in volume. The graphical representation is shown below:
The limiting value of molar conductivity can be calculated by the extrapolation of the graph.

Q6 Calculate the potential for half cell containing 0.10M $K_2Cr_2O_7$ (aq) , 0.20M Cr^{3+} (aq) and 1.0×10^{-4} M H^+ (aq)
The half cell reaction is :

$Cr_2O_7^{2-}$ (aq) + 14 H^+ (aq) + 6e- ----------$\rightarrow$ 2Cr^{3+} (aq) + 7H_2O
And the standard electrode potential is given as E^o = 1.33V (CBSE All India 2011)
Ans .

$$E_{cell} = E^o cell - \frac{0.0591}{6} \log \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}] \quad [H^+]^{14}} = 0.76V$$

i) Explain how does conductivity and molar conductivity change with solution concentration for weak and strong electrolytes.

ii) Determine the value of equilibrium constant Kc and ΔG^0 for the following reaction:

$$Ni(s) + 2Ag^+ (aq) \text{ -------------}\rightarrow Ni^{2+} (aq) + 2Ag(s)$$

Given : (1F = 96500C) and E^o = 1.05V

OR

i) Write the anode and the cathode reactions occurring in a lead storage battery sending out an electric current.

ii) A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in 1 molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

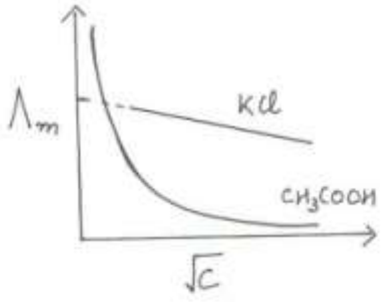
iii) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.

iv) Calculate the cell potential E_{cell} at 25°C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and initial concentration of $AgNO_3$ is 1.00 molar.

[$E^o_{Ni^{2+}/Ni}$ = -0.25V; $E^{o-}_{Ag+/Ag}$ = 0.80V]

ii) Ans.

d) In case of weak electrolytes the dissociation is not complete and with dilution there is an increase in the degree of dissociation of weak electrolye. At a particular dilution there is a sharp rise in molar conductivity.



e) In case of strong electrolytes there is an increase in the in molar conductivity with dilution because of the decrease in inter-ionic interactions and increase in the mobility of ions.

f) Conductivity of a solution of an electrolyte decreases with decrease in concentration. This is because conductivity depends upon number of ions per unit volume of the solution and with decrease in concentration number of ions per unit volume decreases.

ii) $\Delta G^0 = -n F E^o_{cell}$ ½

$= -2 \times 96500 \times 1.05 = -202650 J/mol$ 1

$Kc = \text{antilog} (n E^o_{cell}) / 0.059$ ½

$= \text{antilog} (2 \times 1.05 / 0.059)$ ½

$Kc = 3.92 \times 10^{35}$ ½

OR

i)

a) Reaction at anode during discharging:

$Pb(s) + SO_4^{2-}(aq) \text{-------------}\rightarrow PbSO_4 (s) + 2e^-$ --------------

b) Reaction at cathode during discharging:

PbO_2 (s) + SO_4^{2-}(aq) + 4H^+ (aq) + 2e- -------→ $PbSO_4$ (s) + 2 2H_2O(l)---------

ii)
Ni(s) + 2Ag^+(aq) → Ni^{2+} + 2Ag ………

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$E^{\circ}_{cell} = 0.80 + 0.25 = 1.05V$$

$$E_{cell} = 1.05 - \frac{0.059}{2}\log\frac{(0.1)}{(1)^2}$$

$$= 1.05 - \frac{0.059}{2}\times(-1)$$

$$= 1.05 + 0.0295$$

$$E_{cell} = 1.0795V$$

E^o_{cell} = (0.059/n) log Kc at equilibrium when E_{cell} = 0

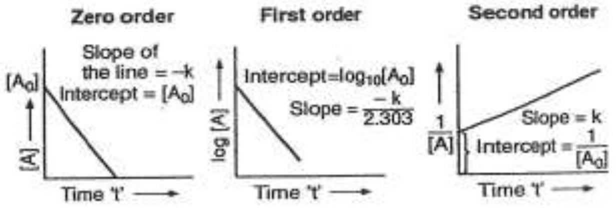
Chemical Kinetics -4

Integrated equations for reactions of different order

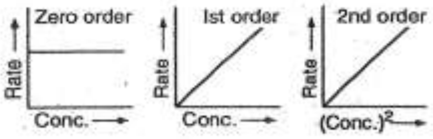
Reaction	Order	Rate law	Integrated equation
$A \rightarrow$ Product	0	Rate = $k[A]^0$	$x = kt$; $[A] = [A_0] - kt$
$A \rightarrow$ Product	1	Rate = $k[A]$	$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$
$2A \rightarrow$ Product	2	Rate = $k[A]^2$	$kt = \frac{1}{[A]} - \frac{1}{[A_0]}$
$A + B \rightarrow$ Product	2	Rate = $k[A][B]$	$kt = \frac{2.303}{[A_0] - [B_0]} \log \frac{[B_0][A]}{[A_0][B]}$
$3A \rightarrow$ Product	3	Rate = $k[A]^3$	$kt = \frac{1}{2}\left[\frac{1}{[A]^2} - \frac{1}{[A_0]^2}\right]$

Order of reaction	Rate law expression	Units of rate constant
1. Zero	Rate = $k[\text{conc.}]^0$	mol litre^{-1} sec^{-1} or atm sec^{-1}
2. First	Rate = $k[\text{conc.}]^1$	sec^{-1}, min^{-1}, etc.
3. Second	Rate = $k[\text{conc.}]^2$	litre mol^{-1} sec^{-1} or atm^{-1} sec^{-1}
4. Third	Rate = $k[\text{conc.}]^3$	litre^2 mol^{-2} sec^{-1} or atm^{-2} sec^{-1}
5. 1.5 or 3/2	Rate = $k[\text{conc.}]^{3/2}$	$\text{litre}^{1/2}$ $\text{mol}^{-1/2}$ sec^{-1} or $\text{atm}^{-1/2}$ sec^{-1}
6. 2.5 or 5/2	Rate = $k[\text{conc.}]^{5/2}$	$\text{litre}^{3/2}$ $\text{mol}^{-3/2}$ sec^{-1} or $\text{atm}^{-3/2}$ sec^{-1}

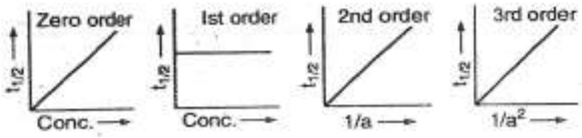
Some typical linear plots for reactions of different orders are given below:



(b) Plots from integrated rate equations:



Plots of half-lives *vs* concentration ($t_{1/2} \propto a^{1-n}$):



Arrhenium Equation: This is an equation which relates rate constant with temperature in the following way :

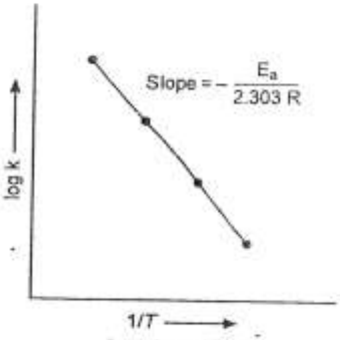
$$k = Ae^{-E_a/RT}$$

where A is constant called frequency factor, E_a is the energy of activation

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\log k = \log A - \frac{E_a}{2 \cdot 303\ RT}$$

A plot of log k vs. $1/T$ is a straight line whose slope is $-\frac{E_a}{2 \cdot 303\ R}$ and interception is log A.



Log k vs 1/T -

If k_1 and k_2 are the rate constants at two temperatures T_1 and T_2, we have

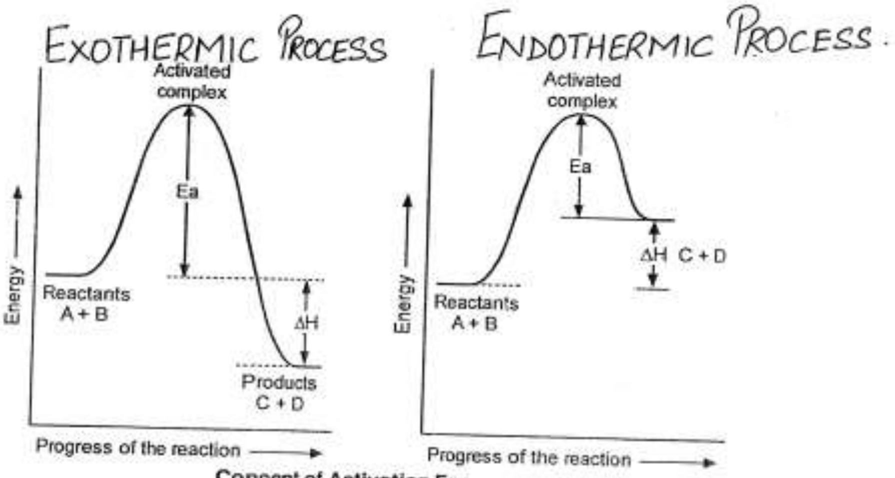
$$\log k_1 = \log A - \frac{E_a}{2 \cdot 303\ RT_1}$$

$$\log k_2 = \log A - \frac{E_a}{2 \cdot 303\ RT_2}$$

Subtracting (*i*) from (*ii*), we get,

$$\log k_2 - \log k_1 = \frac{E_a}{2 \cdot 303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2 \cdot 303\ R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$



Concept of Activation Energy

Qn:- Write the average and instantaneous rate expressions of the following reaction

$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

Ans

r_{av} = -Δ[Br-]/ Δt × 1/5 = -Δ[BrO_3-]/Δt = - Δ[H+]/Δt ×1/6 =
+ Δ[Br_2]/Δt×1/3 = + Δ[H_2O]/Δt×1/3

r_{inst} = - d [Br-]/dt ×1/5 = -d [BrO_3-]/dt = +d[Br_2]/dt ×1/3
= +d[H2O]/dt ×1/3

Qn:-In a reaction 2A→Products , the concentration of A decreases from 0.5 mol L-1 to 0.4 molL-1 in 10 minutes . Calculate the rate during this interval.

Rate = -Δ[A]/Δt×1/2
= ½ (0.4-0.5) mol L-1/10 min = 0.005 mol L-1 min-1

Qn:- A chemical reaction

2A→ 4B + C

in gas phase occurs in a closed vessel. The concentration of B is found to increase by 5×10^{-3} mol L-1 in 10 seconds, Calculate (a) the rate of appearance of B (b) the rate of disappearance of A.

Sol:- rate = -1/2 x Δ[A]/Δt
= +1/4 x Δ[B]/Δt = +Δ[C]/Δt Rate of appearance of B = 5×10^{-3} mol L-1/10 s
= 5×10-4 mol L-1 s-1
Rate of disappearance of A,
ie Δ[A]/Δt = 2/4×Δ[B]/Δt
= $1/2\times5\times10^{-4}$ mol $L^{-1}S^{-1}$ =2.5×10^{-4} mol $L^{-1}s^{-1}$

***Rate law** :- The expression in which reaction rate is given in terms of molar concentrations of reactants with each term raised to some power , which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

For a general reaction

aA + bB→ cc + dD The rate law expression is

Rate =k $[A]^x[B]^y$

Rate constant is independent of concentration of the reaction

Order of a reaction :- The sum of exponents of the concentration of the reactants in the rate law expression

In the rate law expression ; rate = $[A]^x [B]^y$
_x‘--- order of the reaction w.r.t reactantA ,‘y‘ order of the reaction w.r.t reactant B
x+y is the overall order of the reaction *****for **nth** order reaction the unit of rate constant **‘k’** is **(mol L-1)$^{1-n}$ s^{-1}**
Qn:- The rate constant of a reaction is 2.3x 10-5mol-1Ls-1 . What is the order of the reaction ?
Ans :- Here 1-n = -1 ,so n=2 ie, the reaction is of second order.

- Complex reactions involving more than three molecules in the stoichiometric equation, must(is assumed to be) take(ing) place in more than one step (elementary reaction) *****
- The overall order of the reaction is controlled by the slowest step ,called rate determining step
- ***** The rate can be written from the slowest step *****
- For a single step reactions, the order and molecularity will be the same

Pseudo first order reaction :- reaction which appears to be a second order ,but actually first order are called pseudo first order reaction
Eg:- hydrolysis of esters

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H+} CH_3COOH + C_2H_5OH$$

Rate law for this reaction is ; rate = $k[CH_3COOC_2H_5][H_2O]$
But the concentration of water does not change during the course of the reaction
So ; $[H_2O]$ is constant Therefore rate = $k1[CH_3COOC_2H_5]$. The reaction behaves as a first order reaction
***Arrhenius equation for temperature dependence of rate constant:-**
k= Ae-Ea/RT Or
log k = logA – Ea/2.303RT log k_2/k_1 = Ea/2.303[T_2-T_1/T_1T_2] A = pre exponential factor ; Ea — Activation energy
slope = -Ea/2.303R

***Activation energy** :- The energy required to form the reaction intermediate

***Effect of catalyst on reaction rate** :- A catalyst alters the rate of a reaction as it provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier

***A catalyst**

(a) does not alter the Gibb's energy ΔG of a reaction

(b) catalyses only spontaneous reactions

(c) does not change the equilibrium constant of a reaction (d) is highly specific **.**

Collision theory of chemical reactions

(a) collision frequency :- The number of collisions per second per unit volume of the reaction mixture

(b) According to collision theory ; **rate = p ZAB e –Ea/RT**

P --- probability factor ; Z----collision frequency of reactants A&B e-Ea/RT represents the fraction of molecules with energies equal to or greater than Ea

Important Questions:

i) Graphically represent the variation in the concentration Vs time for a zero order reaction.

ii) A first order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$ of the reaction.

OR

i) Draw the distribution curve showing temperature dependence on a rate of a reaction.

ii) The activation energy of first order reaction at 300K is 60 kJ/mol . In the presence of a catalyst, the activation energy gets lowered to 50 kJ/mol at 300K. How many times the reaction rate changes in presence of a catalyst at the same temperature?

Ans

i) Graph to represent the variation in the concentration Vs time for a zero order reaction :

ii) $$K = \frac{2.303}{40 \times 60} \frac{\log 10}{6}$$

$$= 2.12 \times 10^{-4}\ s^{-1}$$

$$t_{1/2} = \frac{0.693}{2.12 \times 10^{-4}} = 0.327 \times 10^{4} \text{ seconds}$$

OR

i) The distribution curve showing temperature dependence on a rate of a reaction

Qn Discuss the Maxwell,s distribution of Molecular energies.

Ans For most of the reactions , the rate of reaction becomes nearly double or even more for $10^{o}C$ rise in temperature.

At a particular temperature T all the reacting molecules do not have the same Kinetic Energy. The Maxwell's distribution of fraction of molecules and kinetic energies is shown in the graph above.the peak of the graph shows K.E. possessed by maximum fraction of molecules and is called the most kinetic energy

At higher temperature the curve shifts to the right indicating that the fraction of molecules having energy more than the threshold energy have become double with every $10^{o}C$ rise in temp.

This rise in the rate of reaction with rise in temp is due to increase in the number of effective collisions.

.

Ans

$$\log K' = \log A - \frac{50}{2.303\ R\ T}$$

$$\log K = \log A - \frac{60}{2.303\ R\ T}$$

$$\log \frac{K'}{K} = \frac{10}{2.303 \times 8.314 \times 300}$$

$$\frac{K'}{K} = \text{Antilog } 1.7409 = 5.507 \text{ X } 10 = 55\text{times}$$

Q2 Consider the reaction:

$$2A + B \text{ ---------------}\rightarrow C + D$$

Following result were obtained in experiments designed to study the rate of reaction:

Experiment No.	Initial conc of [A] $MolL^{-1}$	Initial conc of [B] $MolL^{-1}$	Initial rate of formation of [D] (Mol/min)
1	0.10	0.10	$1.5 \text{ X } 10^{-3}$
2	0.20	0.20	$3.0 \text{ x } 10^{-3}$
3	0.20	0.40	$6.0 \text{ x } 10^{-3}$

Solution:

The initial rate is $= k[A]_o^{\ p} [B]_o^{\ q}$

Comparing Exp I and IV and substituting the values we get

$(\text{Rate})_1 = k(0.1)^p (0.1)^q$ --------- (i)

$= 1.5 \text{ X } 10^{-3}$

$(\text{Rate})_2 = k(0.20)^p (0.20)^q = 3.0 \text{ x } 10^{-3}$ --------------- (ii)

$(\text{Rate})_3 = k(0.20)^p (0.40)^q = 6.0 \text{ x } 10^{-3-}$--------------------------(iii)

Dividing eq (ii) by (iii) we get:

$$\frac{(0.4)^q}{(0.2)^p} = \frac{6.0 \text{ X } 10^{-3}}{3.0 \text{ x } 10^{-3}} = 2$$

$$2^q = 2^1$$

$$q = 1$$

Similarly compare experiments I and II

$$\frac{(0.2)^p}{(0.1)^p} \text{x } 2\_ = \frac{3.0\text{X } 10^{-3}}{1.5 \text{ X } 10^{-3}}$$

$$2^q = 2$$

$$2^p = 1$$

$$p = 0$$

Qn The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume . CBSE DELHI 2014

$$SO_2Cl_2\ (g) \longrightarrow SO_2\ (g) + Cl_2\ (g)$$

Experiment No.	Time/Sec	Total Pressure/ atm
1.	0	0.5
2.	100	0.6

Calculate the rate of the reaction when total pressure is 0.65atm.

Ans $K = \frac{2.303}{t} \log \frac{P_i}{p_f} = \frac{2.303}{t} \log \frac{P_i}{(2P_i - P_t)} = \frac{2.303}{360} \log \frac{35}{(2x\ 35 - 54)}$

$= 2.175x\ 10^{-3}\ s^{-1}$

Surface Chemistry Ch- 5

POINTS TO REMEMBER

Adsorption:The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid

Adsorbate:The molecular species or substance, which concentrate at the surface.

Adsorbent:The material on the surface of which the adsorption takes place. Adsorption is essentially a surface phenomenon.

Desorption:The process of removing an adsorbed substance from a surface on which it is adsorbed.

Factors featuring adsorption The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Easily liquefiable gases(i.e., with higher critical temperatures) are readily asodrbed .

Adsorption is accompanied by decrease in enthalpy as well as decrease in entropy of the system.

Types of Adsorption

S,No.	Physisorption	Chemisorption
1.	.It arises because of van der Waals' forces.	It is caused by chemical bond formation.
2.	It is not specific in nature.	It is highly specific in nature.
3.	It is reversible in nature.	It is irreversible.
4.	Enthalpy of adsorption is low (20-40 kJ mol–1)in this case	Enthalpy of adsorption is high (80-240 kJ mol–1) in this case.
5.	No appreciable activation energy req	High activation energy is required.
6.	It results into multimolecular layers on adsorbent surface under high pressure	It results into unimolecular layer

Homogeneous catalysis When the reactants and the catalyst are in the same phase (i.e.,liquid or gas.)

Eg:- Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.
$2SO_2(g) + O_2(g)$ $NO(g)$ $2SO_3(g)$

Heterogeneous catalysis The catalytic process in which the reactants and the catalyst are in different phases. is known as heterogeneous catalysis.
Eg:- Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt. $2SO_2(g) \rightarrow 2SO_3(g)$
The mechanism of heterogeneous catalysis involves five steps:
(i) Diffusion of reactants to the surface of the catalyst.
(ii) Adsorption of reactant molecules on the surface of the catalyst.
(iii) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate (iv) Desorption of reaction products from the catalyst surface.
(v) Diffusion of reaction products away from the catalyst's surface.
Important features of solid catalysts
(a) Activity The activity of a catalyst depends upon the strength of chemisorptions to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst (but not so strongly) to become active. Eg:- $2H_2\,(g) + O_2\,(g)$ Pt$\rightarrow$ $2\,H_2O(l)$
(b) Selectivity The selectivity of a catalyst is its ability to direct a reaction to yield a particular product.
Eg:- **Shape-selective catalysis:** The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant. Zeolites are good shape-selective catalysts. Eg:- ZSM-5 converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons. Enzymes :The enzymes are **biochemical catalyst**
Eg:- Inversion of cane sugar: The invertase enzyme converts cane sugar into glucose and fructose.

	Lyophilic colloids	**Lyophobic colloids**
	1.Solvent liking	1. Solvent hating
	2.Reversible sols	2.Irreversible sols
	3.Quite stable	3.Unstable.Need stabilising agents to preserve
	4.Cannot be easily Coagulated	4.Can be coagulated easily by adding small amount of electrolyte

(iii)Based on the type of the particles of the dispersed phase

Multimolecular colloids	**Macromolecular colloids**	**Associated colloids (Micelles)**	
Atoms or molecules aggregate together to form colloidal range species . Eg:- gold sol,sulphur sol	Solutions in which the size of the macro molecules may be in the colloidal range. Eg:- starch sol	At low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. **Eg:- soaps & detergents**	

Kraft temperature (**Tk**)- Temperature above which the formation of micelles takes place.

C**ritical micelle concentration (CMC)** – Concentration above which the formation of micelles takes place.

Peptization_ Process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte.

Dialysis: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.

Electro-dialysis: Dialysis can be made faster by applying an electric field .

Properties of colloidal solutions

(i)Tyndall effect :- The scattering of light rays by colloidal particles due to which the path of light is illuminated.

Tyndalleffect is observed only when

(a) The diameter of the dispesed particles is not much smaller than the wave length of the light used

(b) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude

(ii)Brownian movement :- The zig-zag movement of colloidal particles due to the unbalanced bombardment of the dispersed particles with the molecules of the dispersion medium.

(iii) Electrophoresis :- The movement of colloidal particles under an applied electric potential .

Charge on colloidal particles :- The colloidal particles develop charge due to the following reasons

(a) Electron capture by sol particles during electrodispersion of metals

(b) Due to preferential adsorption of ions from solutions

(c) Due to formulation of electrical double layer.

Coagulation or precipitation of colloidal particles :- the process of settling of colloidal particles.

Caused due to

(a) addition of electrolytes

(b) electrophoresis

(c) boiling

(d)mixing two oppositely charged sols

Hardy – Schulze rule :- Greater the valence of the coagulating ion added to a sol, the greater is its power to cause precipitation . The coagulation power of some of the cations is in the order

$Al^{3+} > Ba^{2+} > Na^{+}$. The coagulating power of some of the anions is in the order $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$ Coagulating value of an electrolyte: The minimum concentration of an electrolyte in millimols per litre required to cause precipitation of a sol in two hours

Emulsion :- colloidal system where a liquid is dispersed in another liquid.

Types of emulsions :

(a) oil in water type (o/w) eg: milk, vanishing cream

(b) water in oil type (w/o) eg: butter , cold cream Emulsions are stabilized by emulsifying agents . eg : soaps

CHAPTER -6

General principles and processes of isolation of elements

1\. **Some important terms**

Pyrometallurgy → The process of extracting the metal by heating the metal oxide with suitable reducing agent.
The process of reducing the metal oxide with coke charcoal or carbon monoxide is called Smelting.
Hydrometallurgy→ The isolation of a metal present in the soluble complex by a more reactive metal.
Van Arkel process→ This consists of heating titanium or zirconium vapours to for ZrI_4 which when heated over tungsten filament at 2075K decomposes to give pure zirconium or titanium.

$$\underset{\text{Impure Zirconium}}{Zr} + 2I_2\,(g) \xrightarrow{870K} ZrI_4\,(g) \xrightarrow[\text{Tungsten filament}]{2075K} Zr(s) + 2I_2(g)$$

$$\underset{\text{Impure Zirconium}}{Ti} + 2I_2\,(g) \xrightarrow{523K} TiI_4\,(g) \xrightarrow[\text{Tungsten filament}]{1700K} Ti(s) + 2I_2(g)$$

MOND PROCESS
It is used for refining of Nickel. When impure Ni is heated in a current of CO at 330-350K, it forms volatile Nickel tetracarbonyl complex and leave the impurities behind. Upon further heating at 450-470K Nickel tetracarbonyl complex decomposes to give pure Nickel.

$$\mathbf{Ni + 4CO \xrightarrow{330K-\ 350K} Ni(CO)_4 \xrightarrow{450\text{-}470K} Ni + 4\ CO}$$

Silver ores and native gold have to be leached with cyanides. Give a reason for that.
Ans Silver and gold form water soluble salt with alkali metal cyanides (KCN, NaCN) and from these soluble salts pure metal can be precipitated by adding a more electropositive metals such as Zn. Due to this reason silver and gold are extracted by leaching with alkali metal cyanides.

2\. **Smelting**- FeS is oxidised to FeO which combines with SiO_2 to from slag.

$$FeO + SiO_2 \xrightarrow{heat} FeSiO_3$$

Bessemerisation.

$$Cu_2S + 2Cu_2O \xrightarrow{heat} 6Cu + SO_2$$

3\. **DEFINITION OF FLUX**
Flux is a substance which combines with Gangue (impurities) present in roasted ore to form easily fusible material called slag
Gangue + Flux -------→Slag

	Thus flux helps to remove impurities from the roasted or calcinated ore .	
4.	The limestone is added in the extraction of iron from the Haematite ore because of the following reason: $CaCO_3$ is used as a flux. It forms a slag of calcium silicate. $CaCO_3 \xrightarrow{heat} CaO + CO_2$ $CaO + SiO_2 \longrightarrow CaSiO_3$ (flux) (gangue) (slag) This slag is in the molten state and it floats on the surface of molten iron and it prevents the oxidation of Fe into Fe_2O_3 and helps to remove sand i.e. SiO_2 which would otherwise clog the furnace.	
5.	SiO_2 (silica) is an acidic flux and it is used when the gangue is basic in nature eg; copper ore usually contains basic gangue FeO, so silica is used as a flux in such cases $FeO + SiO_2 \longrightarrow FeSiO_3$.	
6.	The **sulphide ores are roasted before reduction using carbon** because: Carbon is generally used for the reduction of ores and if we try to reduce a sulphide ore directly with carbon,CS_2 is formed which is difficult to remove. So sulphide ore is first roasted to convert it into a metal oxide, so that it can be easily reduced to metal using carbon.	
7.	**LEACHING:** It is a process of used for the concentration of ORES. The impure ore is treated with a suitable reagent such as an acid or a base, when ore particles dissolve due to chemical reaction is called **LEACHING**, while the gangue particles or impurities do not react. This process of concentration has been successfully used for the aluminum ORE bauxite _($AL_2O_3.2H_2O$), argentite Ag_2S and also for gold ores. **Example** **I Leaching of alumina from bauxite** 1) The bauxite ore usually contains SiO_2, iron oxide and titanium oxide TiO_2 as impurities 2) Bauxite ore is treated with concentrated solution of NaOH at 473-523k and 35-36 bar pressure as shown in the equation below- $\mathbf{Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq)}$ Alumina (Al_2O_3)is removed from the impure ore as sodium aluminate. $\mathbf{SiO_2 + 2NaOH\ (aq) \xrightarrow{473-523K} Na_2SiO_3\ (aq) + H_2O(l)}$ 3) To recover Al_2O_3 from the aluminate solution $\mathbf{2Na[Al(OH)_4]\ (aq) + CO_2(g) \longrightarrow Al_2O_3.XH_2O(s) + 2NaHCO_3(aq)}$ 4) The hydrated alumina is filtered, dried and heated to give pure Al_2O_3 $\mathbf{Al_2O_3.xH_2O(s) \xrightarrow{1470K} Al_2O_3(s) + xH_2O(g)}$ **II LEACHING in case of Ag or Au** Here the impure metal is leached with a dil solution of NaCN or KCN in the	

	presence of air **$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \text{-----}\rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)$** **(M = Ag ,Au)** **$4Au + 8KCN + 2H_2O + O_2 \text{------}\rightarrow 4K[Au(CN)_2] + 4KOH$** **Pot dicyanoaurate** **(soluble complex)** **Note : Absolutely same equation is for Ag** **Metal is obtained by displacement with a more reactive metal.)** **$2[M(CN)_2]^-(aq) + Zn(s) \text{---}\rightarrow [Zn(CN)_4]^{2-} + 2M(s)$.** **III LEACHING of low grade ores and scarps to obtain copper** **$Cu^{2+}(aq) + H_2(g) \text{-}\rightarrow Cu(s) + 2H^+(aq)$** Copper is extracted by leaching the low grade ore using acid or bacterias. The solution containing Cu^{2+} is treated with H_2 or scrap iron.	
8.	The use of Zinc in the recovery of silver; **$Zn + 2[Ag(CN)_2]^- \text{-------}\rightarrow [Zn(CN)_4]^{2-} + 2Ag(ppt)$** Zinc is highly electropositive .	
9.	**Froth stabilizers** are **Cresols and Aniline** During the concentration of sulphide ores by froth floatation process : The mineral particles become wet by oils and the gangue particles by water. The froth of oil is made by rotating a paddle in the oil. The froth being lighter rises upwards and carries the mineral particles. **Separation of a mixture of two sulphide ores:** **By adjusting the proportion of oil to water with the help of depressants . In an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come to the froth.** **$4NaCN + ZnS \text{---------}\rightarrow Na_2[Zn(CN)_4] + Na_2S$**	
10.	The role of silica in the metallurgy of copper During the roasting , the copper pyrites are converted in to mixture of FeO and Cu_2O through following reactions: $2CuFeS_2 + O_2 \text{------}\rightarrow Cu_2S + 2FeS + SO_2$ Copper pyrites $2Cu_2S + 3O_2 \text{-----}\rightarrow 2Cu_2O + 2SO_2$ $2FeS + 3O_2 \text{----}\rightarrow 2FeO + 2SO_2$ $2FeS + 3O_2 \text{----}\rightarrow 2FeO + 2SO_2$ Silica is used as an acidic flux to remove basic FeO in the form of $FeSiO_3$.	

Qn Copper can be extracted by hydro metallurgy but not zinc . Explain
Ans Copper dissolves in aqueous solution , as it can easily form complexes . From the solution , copper can be precipitated by adding a strong electropositive metal like zinc. On the other hand zinc being a strong reducing agent, can't be extracted by this method . Zinc has less tendency to form soluble complexes .

Qn Name the common elements present in anode mud in the electrolytic refining of copper. Why are they so present ?
Ans The anode mud contains Ag, Au, Se, Te. These elements are less reactive than copper and do not undergo oxidation at anode & hence settle down as such.

How is leaching carried out in case of low grade copper ores ? It is leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2.
$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+} (aq)$
$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+ (aq)$

Ammonia

In large scale it is manufactured by **Haber's process**
N_2 (g) +$3H_2$ = 2NH3 (g) ΔH^0= -46.1 kJ/mol
According to **Lechatelier's** principle the favourable conditions for the manufacture of NH_3 are
Optimum temperature : 700 K
High pressure : 200 atm
Catalyst : iron oxide Promoter : K_2O & Al_2O_3

PROPERTIES

- Ammonia is a colourless gas with pungent odour.
- Highly soluble in water.
- In solid & liquid states it exists as an associated molecule due to hydrogen bonding which accounts for high melting & boiling points of NH_3

- . Trigonal pyramidal shape NH_3 molecule.

- Aqueous solution of ammonia is weakly basic due to the formation of OH- ions. It precipitates the hydroxides of many metals from their salt solution

- Eg: $ZnSO_4 + 2NH_4OH \rightarrow Zn(OH)_2 + (NH4)_2SO_4$

- Ammonia can form coordinate bonds by donating its lone pair on nitrogen, ammonia forms complexes.

- $CuSO4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$

- $AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$

Nitric acid HNO_3

Preparation by **Ostwald's Process**

1. $4NH_3\ (g) + 5O_2 \xrightarrow{\text{Pt/Rh gauze catalyst}} 4NO\ (g) + 8H_2O$
2. $2NO\ (g) + O_2\ (g)$ ===== $2NO_2(g)$
3. $3NO_2\ (g) + H_2O\ (l) \longrightarrow 2HNO_3\ (aq) + NO(g)$

Conc HNO_3 IS A STRONG OXIDISING AGENT

$HNO_3 \longrightarrow NO_2$
$I_2 \longrightarrow IO_3^{-1}$
$C \longrightarrow CO_2$
$S_8 \longrightarrow SO_4^{2-}$
$P_4 \longrightarrow PO_4^{3-}$

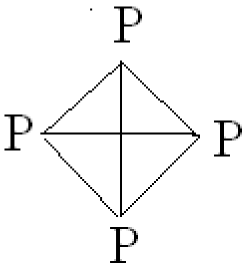
Brown Ring Test:

It depends upon the ability of Fe^{2+} to reduce nitrates into NO nitric oxide which combine with Fe^{2+} ion to form a brown coloured complex $[Fe(H_2O)_5(NO)]^{2+}$

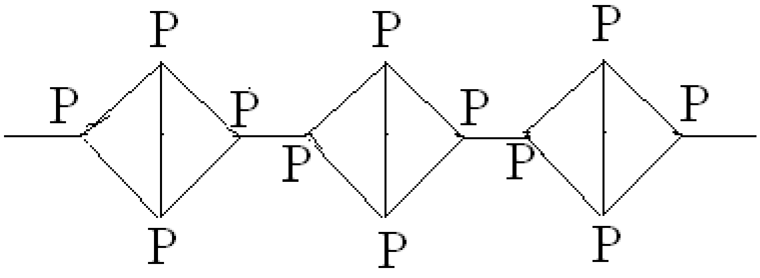
MOST important topic PHOSPHORUS:

Allotropic forms: White, red, α- black & β-black.

- White phosphorous is more reactive than red phosphorous because white P exists as discrete P4 molecules.
- In red P several P4 molecules are linked to formed polymeric chain.



White



Red

PHOSPHINE

Preparation :

It is prepared in laboratory by heating white P with conc. NaOH solution in an inert atmosphere of CO_2

VV Imp **$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$**

Phosphorous halides Phosphorous forms two types of halides PX_3 & PX_5 (X=F, l, Br)

Trihalides have pyramidal shape & penta halides have a trigonal bipyramidal structure.

$P_4 + 8SOCl_2 \text{------------}\rightarrow 4PCl_3 + 4\,SO_2 + 2\,S_2Cl_2$

Qn Why does PCl_5 fume in moist air?

Ans Due to release of HCl gas

$PCl_3 + 3H_2O \text{---------}\rightarrow H_3PO_3 + HCl$

Qn Why is PCl_5 a good Chlorinating agent?

In the solid state PCl_5 exists in the ionic form as $[PCl_4]^+ [PCl_6]^-$

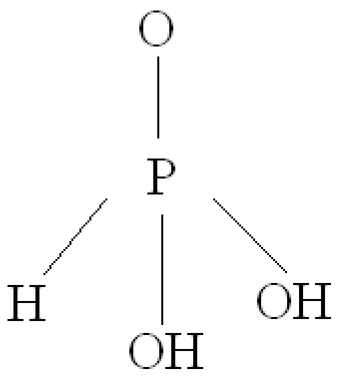
OXOACIDS OF PHOSPHROUS

The acids in +3 oxidation state disproportionate to higher & lower oxidation.

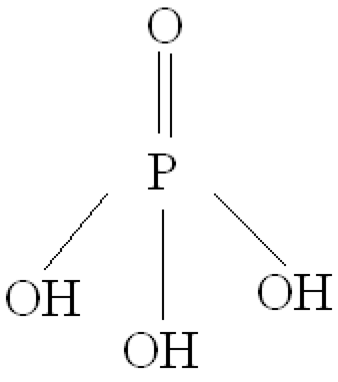
$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

Acids which contains P—H bond have strong reducing properties.
EX:-H_3PO_2
Hydrogen atoms which are attached with oxygen in P—OH form

are ionisable & cause the bascity.



Dibasic



Tribasic

GROUP 16

Elements are : O, S, Se, Te and Po

ATOMIC & PHYSICAL PROPERTIES

- Ionization enthalpy decreases from oxygen to polonium.
- Oxygen atom has less negative electron gain enthalpy than S because of the compact nature of the oxygen atom. However from the S onwards the value again becomes less negative upto polonium.
- Eletronegativity gradually decreases from oxygen to polonium, metallic character increases from oxygen to polonium.
- Oxygen & S are non-metals, selenium & tellurium are metalloids. Po is a radioactive metal.
- Oxygen is diatomic gas while S, Se & Te are octa atomic S_8, Se_8 & Te_8 molecules which has puckered ‗ring‘ structure.

CHEMICAL PROPERTIES

- Common oxidation states : -2, +2, +4 & +6.

- Due to inert effect, the stability of +6 state decreses down the group and stability of +4 state increases.
- Oxygen exhibits +1 state in O_2F_2, + 2 in OF_2.
- **Anamalous behaviour of oxygen** –
- due to its small size,
- high electronegativity and
- absence of d-orbitals.
- **TRENDS IN PROPERTIES**
- Acidic character - $H_2O < H_2S < H_2Se < H_2Te$
- Thermal stability - $H_2O > H_2S > H_2Se > H_2Te$
- Reducing character - $H_2S < H_2Se < H_2Te$
- Boiling point - $H_2S < H_2Se < H_2Te < H_2O$
- Reducing property of dioxides – $SO_2 > SeO_2 > TeO_2$
- Stability of halides - $F^- > Cl^- > Br^- > I^-$
- **HALIDES DI HALIDES:** sp 3 hybridisation but angular structure**.**
- **TETRA HALIDES**: sp^3d hybridization – see-saw geometry
  HEXA HALIDES: $sp^3 d^2$,octahedral SF_6

OZONE

PREPARATION

Prepared by subjecting cold, dry oxygen to silent electric discharge

$$3O_2 \rightarrow 2O_3$$

PROPERTIES Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. For e.g., it oxidizes lead sulphide to lead sulphate and iodide ions to iodine.

$PbS+4O_3 \rightarrow PbSO_4+ 4O_2$

$2KI+H_2O+O_3 \rightarrow 2KOH+I_2+O_2$

IMPORTANT QUESTIONS

QN Why is ozone thermodynamically unstable?

Ans $O_3 \rightarrow O_2 + O$ For this reaction ΔH = -ve, ΔS = +ve, So ΔG = -ve, Which makes decomposition of Oxygen highly spontaneous.

Qn How is Ozone estimated quantitatively?

Ans When ozone is treated with excess of KI soln buffered with borate buffer, I_2 is liberated which is titrated with a standard solution of sodium thiosulphate.

O_3 is a good bleaching agent.

In Ozone both O-O bond lengths are same due to resonance.

Sulpur Di- Oxide
$SO_2 + 2NaOH \text{ --------}\rightarrow Na_2SO_3 + H_2O$
$SO_2 + Cl_2 \text{ ---------}\rightarrow SO_2Cl_2$ SULPHURYL CHLORIDE

SO_2 IS Reducing IN NATURE AND IT DECOLOURISES ACIDIFIED $KMnO_4$ which is a chemical test for SO_2
$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5 SO_4^{2-} + 4H^+ + 2Mn^{2+}$
SO_2 molecule is angular .

OXOACIDS OF SULPHUR
SULPHURIC ACID PREPARATION
It is manufactured by contact process which involves 3 steps
1. Burning of S or sulphide ores in air to generate SO_2.
2. Conversion of SO_2 to SO_3 in presence of V_2O_5 catalyst
3. Absorption of SO_3 in H_2SO_4 to give oleum.

PROPERTIES (i) In aqueous solution it ionizes in 2 steps
$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$
$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$
(ii) It is a strong dehydrating agent
Eg:- charring action of sugar
$C_{12}H_{22}O_{11} \text{ --------}\rightarrow 12C + 11H_2O$
(iii) It is a moderately strong oxidising agent.
Cu + 2 H_2SO4(conc.) $\rightarrow CuSO_4 + SO_2 + 2H_2O$
C + 2 H_2SO_4(conc.) $\rightarrow CO_2 + 2 SO_2 + 2H_2O$
$S \text{ -------}\rightarrow SO_2$

Group 17

ATOMIC & PHYSICAL PROPERTIES

(i) Atomic and ionic radii increase from fluorine to iodine .

(ii) Ionisation enthalpy gradually decreases from fluorine to iodine due to increase in atomic size.

(iii) Electron gain enthalpy of fluorine is less than that of chlorine. It is due to the small size of fluorine & repulsion between newly added electron & electrons already present in its small 2p orbital.

(iv) Electronegativity decreases from fluorine to iodine. Fluorine is the most electronegative element in the periodic table..

(v) The colour of halogens is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level.

(vi)Bond dissociation enthalpy of fluorine is smaller than that of chlorine is due to electron-electron repulsion among the lone pair in fluorine molecules where they are much closer to each other than in case of chlorine. The trend: Cl -Cl Br-Br F-F I-I.

CHEMICAL PROPERTIES

Oxidation states :–1. However, chlorine, bromine and iodine exhibit + 1,+ 3, + 5 and + 7 oxidation states also. Fluorine forms two oxides OF_2 and O_2F_2. These are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen.

Anamalous behaviour of fluorine –

- due to its small size,
- highest electronegativity,
- low F-F bond dissociation enthalpy and
- absence of d-orbitals.

TRENDS IN PROPERTIES

- Oxidising property – $F_2 > Cl_2 > Br_2 > I_2$
- Acidic strength – HF< HCl< HBr< HI
- Stability & bond dissociation enthalpy - HF> HCl> HBr> HI
- Stability of oxides of halogens – I > Cl > Br
- Ionic character of halides – MF > MCl> MBr> MI

CHLORINE PREPARATION

1. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
2. $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$
3. $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

PROPERTIES (i) With cold and dilute alkalies Cl_2 produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

VVimp $2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$
(cold and dilute)
$6NaOH + 3Cl_2 + \quad 5NaCl + NaClO_3 + 3H_2O$
(Hot and concentrated)

(ii) With dry slaked lime it gives bleaching powder.

$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OH)_2 + CaCl_2 + 2H_2O$

(iii) It is a powerful bleaching agent; bleaching action is due to oxidation. $Cl_2 + H_2O \rightarrow 2HCl + (O)$
Coloured substance + (O) → colourless substance
(iv) Action of concentrated
H_2SO_4 on NaCl give HCl gas.
$NaCl + H_2SO_4$ 420K→ $NaHSO_4 + HCl$
3: 1 ratio of concentrated HCl and HNO_3 is known as aquaregia & it is used for dissolving noble metals like Au and Pt.

OXOACIDS OF HALOGENS

HOX Hypohalous acids , HOClO ---Halous acid, $HOClO_2$ --- Halic acid , $HOClO_3$ Perhalic acids
The oxidizing character increases ---------→

INTER HALOGEN COMPOUNDS:

- Inter halogen compounds are prepared by the direct combination of halogens. Ex:ClF,ClF_3,BrF_5,IF_7.
- They are more reactive than halogens because X-X′ is weaker than X-X bonds in halogens (except F-F).

XX'3	Bent T – shaped
XX'5	Square pyramidal
XX'7	Pentagonal bipyramidal

GROUP 18 ELEMENTS

- Group 18 elements: **He, Ne, Ar, Kr, Xe & Rn**
- General electronic configuration: ns^2np^6
- Atomic radii –large as compared to other elements in the period since it corresponds to vander Waal radii.
- Inert - Due to complete octet of outermost shell, very high ionization enthalpy &electron gain enthalpies are almost zero.
- The first noble compound prepared by Neil Bartlett was $XePtF_6$ by mixing PtF_6 & xenon.$O_2^+PtF_6^-$ led to the discovery of $XePtF_6$ since the first ionisation enthalpy of molecular oxygen (1175 kJmol–1) was almost identical with that of xenon (1170 kJ mol–1).

Properties OF Xe PAGE 205 of NCERT is a MUST

$$Xe + F_2 \xrightarrow{\text{1bar 673K}} XeF_2$$

$$Xe(g) + 2F_2(g) \xrightarrow{\text{7bar 873k}} XeF_4(s)$$

$$Xe(g) + 3F_2(g) \xrightarrow{\text{60-70bar 573k}} XeF_6(s)$$

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

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

$$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF\text{(partial hydrolysis)}$$

SOLVED QUESTIONS 1 MARK QUESTIONS

1.Ammonia has higher boiling point than phosphine. Why?
Ammonia forms intermolecular H- bond.

2. Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements ?
It is the least stable hydride of group 15

3. Why does PCl_3 fume in moisture?
In the presence of (H_2O), PCl_3 undergoes hydrolysis giving fumes of HCl.

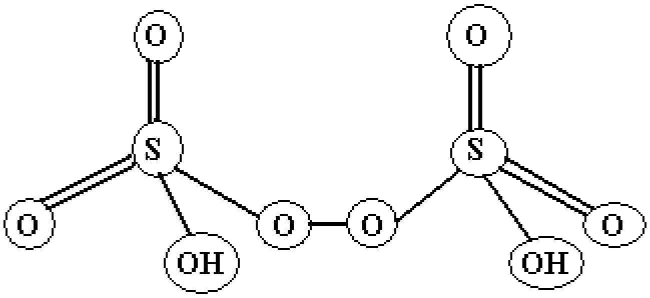
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

4. What happens when H_3PO_3 is heated ?
It disproportionates to give orthophosphoric acid and phosphine.
$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

5. Why H_2S is acidic and H_2O is neutral ?
The S---H bond is weaker than O---H bond because the size of S atom is bigger than that of O atom. Hence H_2S can dissociate to give H+ ions in aqueous solution.

6. Name two poisonous gases which can be prepared from chlorine gas.
phosgene ($COCl_2$), tear gas(CCl_3NO_2

7. Name the halogen which does not exhibit positive oxidation state.
Fluorine being the most electronegative element does not show positive oxidation states.
8. Iodine forms I^{3-} but F_2 does not form F^{3-} ions. Why?
Due to the presence of vacant d-orbitals, I_2 accepts electrons from I- ions to form I^{-3} ions, but because of the absence of d-orbital F^{+2} does not accept electrons from F- ions to form F^{-3} ions.
9. Draw the structure of peroxosulphuric acid.



10.Phosphorus forms PCl5 but nitrogen cannot form NCl5.why?

Due to the availability of vacant d orbitals in P.

2 MARK QUESTIONS

1.Why is HF acid stored in wax coated glass bottles?
This is because HF does not attack wax but reacts with glass. It dissolves SiO2 present in glass forming hydrofluorosilicic acid.
$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O_2$.

2. What is laughing gas? Why is it so called? How is it prepared?
Nitrous oxide (N_2O) is called laughing gas, because when inhaled it produces hysterical laughter. It is prepared by gently heating ammonium nitrate. $NH_4NO_3 \rightarrow N_2O + 2H_2O$

3. Give reasons for the following:
(i) Conc HNO_3 turns yellow on exposure to sunlight.
(ii) PCl_5 behaves as an ionic species in solid state.
Ans (i) Conc HNO_3 decomposes to NO_2 which is brown in colour & NO_2 dissolves in HNO_3 to it yellow.

(ii) It exists as $[PCl_4]^+[PCl_6]^-$ in solid state.

4. What happens when white P is heated with conc. NaOH solution in an atmosphere of CO_2 ? Give equation.
Ans Phosphine gas will be formed.
$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

5. Account for the following.
(i) SF_6 is less reactive than
(ii) Of the noble gases only xenon forms chemical compounds.
Ans (i) In SF_6 there is less repulsion between F atoms than in SF_4
(ii) Xe has low ionisation enthalpy & high polarising power due to larger atomic size.

6. Arrange the following in the increasing order of the property mentioned.

(i) HOCl, $HClO_2$,$HClO_3$, $HClO_4$ (Acidic strength)

(ii) As_2O_3, ClO_2,GeO_2,Ga_2O_3 (Acidity)

(iii) NH_3,PH_3,AsH_3,SbH_3 (H-E-H bond angle)

(iv) HF,HCl,HBr,HI (Acidic strength)

(v) MF, MCl,,MBr, MI (ionic character)

Ans. (i) Acidic strength: HOCl < $HClO_2$< $HClO_3$< $HClO_4$

(ii) Acidity: $Ga_2O_3 < GeO_2 < As_2O_3 < ClO_2$

(iii) Bond angle: $SbH_3 < AsH_3 < PH_3 < NH_3$

(iv) Acidic strength: HF < HCl < HBr < HI

(v) Ionic character: MI < MBr < MCl < MF

Chapter- 8 (d and f-Block elements)

POINTS TO REMEMBER

- The elements of‗d‘ block in the periodic table are called transition elements.
- The elements of ‗f‘ block are called inner transition elements
- The general electronic configuration of d block elements is $(n\text{-}1)\ d^{1\text{-}10}\ ns^{1\text{-}2}$
- Zn, Cd, and Hg (group 12) are not considered as transition metals due to fully filled ‗d‘orbitals
- Transition metals have high melting points due to strong inter atomic bonding which involves large number of unpaired electrons.
- Transition metals have high enthalpy of atomization due to strong inter atomic bonding
- The atomic and ionic radii of 3d series shows progressive decrease as the atomic number Increases
- The atomic / ionic radii of 4d and 5d series are almost same. This is due to lanthanoid Contraction.
- The second ionization enthalpy of Cr and Cu are exceptionally high due to stable d^5 and d^{10} Configuration respectively.
- Among the 3d series Mn shows max. Number of oxidation states i.e., from +2 to +7. But the common oxidation state is +2 for 3d series. The tendency to show highest Oxidation state increase from Sc to Mn and then this tendency decreases.
- Transition metals show variable oxidation states due to the involvement of (n-1) d electrons along with ns electrons in bond formation
- The E0 (Mn+/M) values for 3d series does not follow a regular trend .This is due to irregularity in ionization enthalpy and heat of atomization.
- Transition metals and their ions show Para magnetism due to presence of unpaired electrons

- The magnetic moment μ is given by the formula

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

- Transition metals and their compounds show colour. This is due to presence of unpaired electrons. These unpaired electrons undergo excitation from lower energy d orbital to a higher energy d orbital in the same shell by absorbing certain frequency of light. The colour of the metal /compound will be the complementary colour of the one which is absorbed
- What is Lanthanoid contraction? What are its consequences?
- Ans. It is filling up of 4f orbital before 5d orbital results in a regular decrease in atomic radii is called Lanthanoid contraction.

Transition metals form complex compounds due to (a) comparatively small size of the metal ion (b) high ionic charge (c) availability of vacant d - orbital's

Transition metals form interstitial compounds due to presence of voids in their crystal structure which can accommodate small molecules of Hydrogen, Boron etc.

Transition metals form alloys due to comparable size of their atoms.

Transition metals and their compounds are used as catalyst. This is due to their ability to show variable oxidation states and presence of vacant d - orbitals.

LANTHANOIDS AND ACTINOIDS

- The general electronic configuration of the Lanthanoid is

$[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$

- The regular decrease in size amongst Lanthanoids atomic number increases is known as lanthanoid contraction. This is due to the imperfect shielding of one electron by another in the same 4f sub shell.
- The common oxidation state of Lanthanoid is +3.
- Lanthanoid ions are coloured due to the presence of unpaired electrons in 4f level.
- Lu^{3+} is colourless due to fully filled 4f level.

- Ce shows +4 oxidation states which has a stable configuration of Xenon
- Eu shows +2 oxidation states because of $4f^7$ configuration
- Yb also shows +2 oxidation states due to the stable $4f^{14}$ configuration.
- Eu^{2+} and Yb^{2+} are strong reducing agrnts while Ce 4+ is strong oxidizing agent.
- The general electronic configuration of Actinoids is [Rn] $5f^{1-14}$ $6d^{0-1}$ $7s^2$
- The irregularities is in the electronic configuration of Actinoids are related to the stability of $5f^0$, $5f^7$, $5f^{14}$ configurations.
- The common oxidation states are +3 and +4
- Like Lanthanoids, Actinoids also show regular decrease in atomic and ionic size, which is called Actinoid Contraction.

- Consequences of lanthanoid contraction
  - (i) There is similarity in the properties of second and third transition series.
  - (ii) (ii)Separation of lanthanoids is possible due to lanthanoid contraction.
  - (iii) It is due to lanthanide contraction that there is variation in the basic strength of lanthanide hydroxides.
  - (iv) (Basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$

Qn How is $K_2Cr_2O_7$ prepared?

Ans

$K_2Cr_2O_7$ is prepared from chromite ore ($FeCr_2O_4$).

The following steps are involved

(a) Fusion of chromite with Na_2CO_3 in free access of air.

$8Na_2CO_3 + 4FeCr_2O_4 + 7O_2 \rightarrow 8Na_2CrO_4$(yellow) $+ 2Fe_2O_3 + 8CO_2$

(b) Acidification of Na_2CrO_4

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7$ (orange) $+ Na_2SO_4 + H_2O$

At Low pH

$2CrO_4{}^{2-}$(yellow) $+ 2H^+ +$ $Cr_2O_7{}^{2-}$(orange) $+ H_2O$ High pH

(d) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Qn Explain the oxidizing property of $K_2Cr_2O_7$.

Ans . $K_2Cr_2O_7$ acts as an oxidizing agent.
In acid medium it undergoes reduction toCr^{3+}
$Cr_2O_7^{2-} + 14H^{+} + 6e^- \rightarrow 2Cr^{3+}$(green) + $7H_2O$
Eg: acidified $K_2Cr_2O_7$ will oxidize
(a) Fe2+ to F3+
$Cr_2O_7{}^{2-} + 6Fe^{2+} + 14H^{+} \rightarrow 2Cr^{3+}$ + 6Fe3+ + $7H_2O$
(b) Iodide to iodine $Cr_2O_7^{2-} + 6I^{-} + 14H^{+} \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

7.How is $KMnO_4$ obtained from pyrollusite?
Ans pyrolusite is fused with KOH and air. This produces a green colored mass, i.e, Potassium manganate .
$2KOH + MnO_2 + \frac{1}{2} O_2 \rightarrow K_2MnO_4 + H_2O$
Manganate ion disproportionate in neutral or acidic medium to give pink coloured Permanganate.
8.Explain the oxidizing property of $KMnO_4$
Ans $KMnO_4$ is a strong oxidizing agent in both acidic and basic medium
In acid medium
MnO^{4-} (Pink) + $8 H^{+} + 5e^- \rightarrow Mn^{2+}$ (colourless) + $4H_2O$
Eg : Acidified $KMnO_4$ oxidises

- Fe^{2+} to Fe^{3+}
- S^{2-} to S
- $C_2O_4^{2-}$ to CO_2
- I^{-} to I_2
- SO_3^{2-} to SO_4^{2-}
- NO_2^{-} to NO_3^{-}

In basic medium:

- MnO_4^{-} --------→ MnO_2
- ---------→ IO_3^{-}
- $S_2O_3^{2-}$ ----------→ SO_4^{2-}

Qn The chemistry of the actinoid elements is not so smooth as that of the Lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.
Ans : Lanthanoids primarily show three oxidation states (+2, +3, +4). Among these oxidation states, +3 state is the most common. Lanthanoids display a limited number of oxidation states because the energy difference

between 4f, 5d, and 6s orbitals is quite large. On the other hand, the energy difference between 5f, 6d, and 7s orbitals is very less. Hence, actinoids display a large number of oxidation states. For example, uranium and plutonium display +3, +4, +5, and +6 oxidation states while neptunium displays +3, +4, +5, and +7. The most common oxidation state in case of actinoids is also +3.

Qn Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behaviour.

(ii) The enthalpies of atomisation of the transition metals are high.

(iii) The transition metals generally form coloured compounds.

(iv) Transition metals and their many compounds act as good catalyst.

Ans : (i) Transition metals show paramagnetic nature. Paramagnetism arises due to the presence of unpaired (n-1)d electrons.

(ii) Transition elements have high effective nuclear charge and a large number of valence electrons. Therefore, they form very strong metallic bonds. As a result, the enthalpy of atomization of transition metals is high.

(iii) Most of the complexes of transition metals are coloured. This is because of the absorption of radiation from visible light region to promote an electron from one of the d−orbitals to another (d-d transition).

(iv) The catalytic activity of the transition elements can be explained by two basic facts. (a) Owing to their ability to adopt variable oxidation states (b) Transition metals also provide a suitable surface for the reactions to occur.

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Account for the following:

i) Actinoid elements show wide range of oxidation states.

ii) Which transition metal of 3d series has positive E^o (M^{2+}/ M) value and why?

iii) Out of Cr^{3+} and Mn^{3+} , which is a stronger oxidizing agent and why?

iv) Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

v) Complete the following equation:

MnO^{4-} (Pink) + 8 H^+ + 5e ------------→

Ans

i) This is because of comparable energies of 7s, 6d and 5f orbitals.
ii) Cu, because of high enthalpy of atomization and high enthalpy hydration.
iii) Mn^{3+} is a stronger oxidizing agent because Mn^{2+} is more stable half filled $3d^5$ config.
iv) Eu
v) MnO^{4-} (Pink) + 8 H^+ + 5e- → Mn^{2+} (colourless) + $4H_2O$

Pl do the configuration of Lanthanoids and Actinoids.

Ch-9 Co-ordination Compounds

Ligands may be classified as-

a) **Monodentate/Unidentate**: Ligands bound to the central metal atom/ion through a single donor atom. Ex- Cl- ; H_2O ; NH_3 ; NO_2^-.

b) **Didentate**: Ligates through two donor atoms. Ex- $C_2O_4{}^{2-}$ (ox); $H_2NCH_2CH_2NH_2$(en)

c) **Polydentate**: which ligates through two or more donor atoms present in a single ligand. Ex- $(EDTA)^{4-}$

d) **Chelating ligands**: Di- or polydentate ligands that uses two or more donor atoms to bind to a single metal ion to form ring- like complexes. (Ox); (edta)

e) **Ambidentate ligand**: A ligand that can ligate through two different atoms, one at a time. Ex-NO_2^- ; SCN-

ISOMERISM IN COORDINATION COMPOUNDS

Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism.

Coordination compounds show two main types of isomerism-

A) Structural Isomerism B) Stereoisomerism

STRUCTURAL ISOMERISM:- It arises due to the difference in structures of coordination compounds. It is further subdivided into the following types-

1) **Ionisation isomerism :** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionization isomers $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

2) **Hydrate or solvate isomerism**: This form of isomerism is known as ‗hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

3) **Linkage Isomerism**: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is

provided by complexes containing the thiocyanate ligand, NCS–, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN.

4) **Coordination isomerism:** It arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex .

Example $[Co(NH_3)_6][Cr(CN)_6]$ & $[Cr(NH_3)_6][Co(CN)_6]$

STEREOISOMERISM: Stereo isomers have the same chemical formula and chemical bonds but they have different spatial arrangement.

They are of two kinds A. Geometrical isomerism B. Optical isomerism

GEOMETRICAL ISOMERISM-

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.

Important examples of this behaviour are found with coordination numbers 4 and 6.

In a square planar complex of formula $[MX_2L_2]$

(X and L are unidentate),

the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer [MABXL]-Where A,B,X,L are unidentates

Two cis- and one trans- isomers are possible.

Chapter- 7 p- Block Elements

GROUP 15 ELEMENTS

Group 15 elements: N, P, As, Sb & Bi General electronic configuration: ns_2np_3

PHYSICAL PROPERTIES

- Dinitrogen is a diatomic gas while all others are solids.
- N & P are non-metals. As & Sb metalloids & Bi is a metal .This is due to decrease in ionisation enthalpy & increase in atomic size.
- Electro negativity decreases down the group.

CHEMICAL PROPERTIES

- Common oxidation states : -3, +3 & +5.
- Due to inert effect, the stability of +5 state decreses down the group and stability of +3 state increases.
- In case of nitrogen all oxidation states from +1 to +4 tend to disproportionate in acid solution for eg:- $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

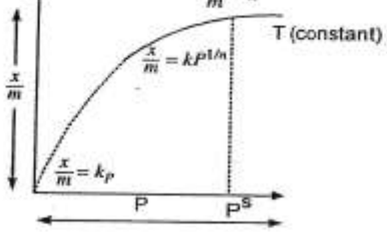
Anamalous behaviour of nitrogen - due to its small size, high electronegativity, high ionization enthalpy and absence of d-orbitals. N_2 has unique ability to form pπ-pπ multiple bonds where as the heavier members of this group do not form pπ-pπ bond because their atomic orbitals are so large & diffuse that they cannot have effective overlapping. Nitrogen exists as diatomic molecule with triple bond between the two atoms where as other elements form single bonds in elemental state. N cannot form dπ-pπ bond due to the non-availablity of d-orbitals where as other elements can. **TRENDS IN PROPERTIES** Stability - $NH_3>PH_3>AsH_3>SbH_3>BiH_3$. Bond dissociation enthalpy - $NH_3>PH_3>AsH_3>SbH_3>BiH_3$ Reducing character - $NH_3<PH_3<AsH_3<SbH_3<BiH_3$ Basic character - $NH_3>PH_3>AsH_3>SbH_3>=BiH_3$. Acidic character - $N_2O_3> P_2O_3> As_2O_3> Sb_2O_3> Bi_2O_3$

Freundlich adsorption isotherm.

A plot between the amount of gas adsorbed per gram of adsorbent $\left(\frac{x}{m}\right)$ and the pressure of the adsorbate at constant temperature is called *adsorption isotherm.*
Freundlich adsorption isotherm

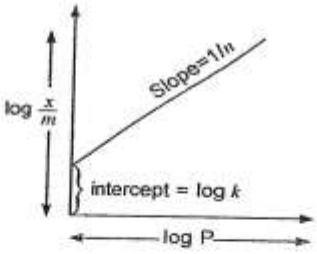
$$\frac{x}{m} = kP^{1/n} \text{ (at moderate pressure)}$$

where x is the amount of gas adsorbed by m gram of the adsorbent at a pressure P, while K and n are constants.



Taking logarithm of equation (*i*), we get

$$\log \frac{x}{m} = \frac{1}{n} \log P + \log k$$



As the plot of $\log \frac{x}{m}$ versus $\log P$ is a straight line the Freundlich adsorption is valid. This isotherm explains the behaviour of adsorption approximately and $\frac{1}{n}$ can have any value between 0 and 1.

(*i*) When $\frac{1}{n}$ (slope) $= 0$, $\frac{x}{m} =$ constant which shows that adsorption is independent of pressure.

(*ii*) When $\frac{1}{n} = 1$, $\frac{x}{m} = kP$ *i.e.*, $\frac{x}{m} \propto P$, the adsorption varies directly as pressure. Both these conditions are experimentally varified, however the experimental isotherm always sum up to approach saturation at high pressure. This cannot be explained by freundlic adsorption isotherm.