Chemistry Notes for class 12 Chapter 1 The Solid State

Solids

Solids are the chemical substances which are characterised by define shape and volume, rigidity, high density, low compressibility. The constituent particles (atoms, molecules or ions) are closely packed and held together by strong interparticle forces

Types of Solids

The solids are of two types : Crystalline solids and amorphous solids.

Distinction Between Crystalline and Amorphous Solids

S.No	Crystalline solid	Amorphous solids	
1	These have definite and regular arrangement of the constituent particles in space.	These doesn't have any regular arrangement of the constituent particles in space.	
2	These are true solids.	Theseare super cooled liquids or pseudo soilds.	
3	These have long order arrangement of the particles.	These have short order arrangement of particle.	
4	These are anisotropic in nature, i.e., their physical properties are different in different directions.	These are isotropic in nature i.e., their physical properties are same in all the directions.	
5	They have sharp melting points.	They melt over a certain range of temperature.	
6	They undergo a clean cleavage when cut.	They undergo irregular cleavage when cut.	

Character	lonic solids	Covalent solids	Molecular solids	Metallic solids
Constituent particles	Positive and negative ions	Atoms	Molecules	Positive metals ions (kernels) and free electrons
Bonding forces	Electrostatic attraction	Cova le nt	van der Waals' Dipole-dipole	Electrostatic attraction between positive ions and negative species
Melting point	High melting point	Very high melting	Low melting point	Moderate to high melting point
Hard/soft	Hard and brittle	Very hard	Very soft	Hard and soft
Conductance	Conductor in aqueous solution or in molten state	Non-conductor	Insulator conductor	Good conductor
Examples	NaCl CaF	Diamond, Silica	H ₂ O, CO ₂	Cu, Fe

Types of Crystalline Solids

Structure Determination by X-ray Diffraction (Bragg's Equation)

When a beam of X-rays falls on a crystal plane composed of regularly arranged atoms or ions, the X-rays are diffracted. If the waves are in phase after reflection, the difference in distance travelled by the two rays ti.e., path difference) must be equal to an integral number of Wavelength, $n\lambda$ for constructive.



Thus, path difference = WY + YZ

 $= XY \sin \theta + xy \sin \theta$

= 2 XY sin θ = 2d sin θ

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

This equation is called Bragg's equation.

Where, n = 1.2, 3... (diffraction order)

 λ = wavelength of X rays incident on crystal

d = distance between atomic planes

 θ = angle at which interference occurs.

Unit Cell

The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.

Types of Unit Cell

(i) Simple or primitive Unit cell In which the particles are present at the corners only.



(ii) **Face centred unit cell** In which the particles are present at the corners as well as at the centre of each of six faces



(iii) **Body centred unit cell** In which the particles are present at the corners as well as at the centre of the unit cell.



(iv) **End centred unit cell** In which the particles are present at the corners and at the centre of two opposite faces.



Number of Particles Per Unit Cell

	No. of particles and their contribution			
Unit cell	Corner	- Face	Centre	lotal
Simple cubic	$8 \times \frac{1}{8}$	-	3 <u>—</u> 3	1
Face centred	$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$	27	4
Body centred	$8 \times \frac{1}{8}$	-	1	2
End centred	$8 \times \frac{1}{8}$	$2 \times \frac{1}{2}$		2

Seven Crystal Systems

There are about 230 crystal forms, which have been grouped into 14 types of space lattices, called Bravais Lattices, on the basis of their symmetry and seven different crystal systems on the basis of interfacial angles and axes.

Seven Crystal Systems

		Parameters of unit cell		
	Crystal system	intercepts/axes	Angles	
1.	Cubic	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$	
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	
З.	Rhombohedral	a = b = c	$\alpha = \beta = \gamma \neq 90^{\circ}$	
4.	Orthorhombic	a≠b≠c	$\alpha = \beta = \gamma = 90^{\circ}$	
5.	Monoclinic	a≠b≠c	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	
6.	Triclinic	a≠b≠c	a ≠ β ≠ γ ≠ 90°	
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	

Packing Fraction

It is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the volume of the unit cell.

(i) **Primitive cubic unit cell** Atoms touch each other along edges.

Hence, d = a or r = a / 2

(r = radius of atom and a = edge length)

Therefore, $PF = 4 / 3 \pi r^3 / (2r)^3 = 0.524$ or 52.4%

(ii) Face centred cubic unit cell Atoms touch each other along the face diagonal.

Hence, $d = a / \sqrt{2}$

or $r = \sqrt{2a} / 4$

Therefore; $PF = 4 * 4 / 3 \pi r^3 / (4r / \sqrt{2})r^3 = 0.74 \text{ or } 74\%$

(iii) Body centred cubic unit cell Atoms touch each other along the body diagonal.

Hence, $\sqrt{3a}/2$

or $r = \sqrt{3a} / 4$

Therefore; PF = 2 * 4 / 3 πr^3 / (4r / $\sqrt{3}$) r^3 = 0.68 or 68%

Coordination Number

It is defined as the number of particles immediately adjacent to each particle in the crystal lattice.

[In simple cubic lattice, CN is 6, in body centred lattice, CN is 8 and in face centred cubic lattice, CN is 12].

High pressure increases CN and high temperature decreases the CN.

Close Packing in Crystals

Two Dimensional Packing of Constituent Particles

(i) Square close packing Space occupied by spheres is 52.4%.



(ii) Hexagonal close packing Space occupied by spheres is 60.4%. Hence. It is more efficient.



Three Dimensional Packing of Constituent Particles

(i) ABAB arrangement gives hexagonal close packing (hcp).

(ii) ABCABC arrangement gives cubic close packing or face centred CUbIC packing (ccp or fcc).

- In both these arrangements 740/0 space is occupied
- Coordination number in hop and ccp arrangement is 12 while in bcc arrangement, it is 8.
- Close packing of atoms in cubic structure = fcc > bcc > sc.
- All noble gases have ccp structure except He (hcp structure).

Void or Space or Holes

- Empty or vacant space present bet veen spheres of a unit cell, is called void or space or hole or interstitial void. When particles are closed packed resulting in either cpp or hcp structure, two types of voids are generated:
- **Tetrahedral voids** are holes or voids surrounded by four spheres Present at the corner of a tetrahedron. Coordination number of a tetrahedral void is 4.





 $r_{\rm void} = 0.225 \times r_{\rm sphere}$

(for tetrahedral voids)

• Octahedral voids are holes surrounded by six spheres located on a regular tetrahedron. Coordination number of octahedral void is 6.



[The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral voids present in a lattice is twice to the number of close packed particles.]

Density of Unit Cell (d)

Density of unit cel1 = mass of unit cell / volume of unit cell

$$\mathbf{d} = \mathbf{Z} * \mathbf{M} / \mathbf{a}^3 = \mathbf{Z}\mathbf{M} / \mathbf{a}^3 * \mathbf{N}_{\mathbf{A}}$$

(The density of the unit cell is same as the density of the substance.)

where, d = density of unit cell

M = molecular weight

Z = no. of atoms per unit cell

 $N_A = Avogadro number$

a = edge length of unit cell.

The Structure of Ionic Crystals

The ionic radius ratios of cation and anion, play a very important role in giving a clue to the nature of the crystal structure of ionic substances.

Radius Ratio and Crystal Structure

S. No.	Radius tatio	Coordination number	Shape	Crystal structure	Example
1.	< 0.225	2 or 3	Linear or triangular	Linear or triangular	B ₂ O ₃
2.	0.225-0.414	4	Tetrahedral	ZnS type	CuCl, CuBr, HgS, BaS
3.	0.414-0.732	. 6	Octahedral	NaCl type	MgO, NaBr, CaS, KBr, CaO
4.	0.732 or more	8	Cube	CsCl type	Csl, CsBr, NH ₄ Br

Ionic crystals may be of two types

(i)AB type and

(ii) A_2B or AB_2

Structure of Ionic Crystals

Ionic crystal type	Cation occupy	Anion form	Coordination
NaCl (Rock salt structure) type	All octahedral voids	foc unit cell	6 : 6
CsCI type	Body centre	simple cubic unit cell	8:8
Żn\$ (Sphalerite structure) type	Alternate tetrahedral voids	foc unit cell	4:4
Gaf ₂ (Fluorite structure) type	Alternate body centre	simple cubic unit cell	8:4
Na20 (Antifluorite structure) type	All tetrahedral sites	fcc unit cell	4 : 8

On applying pressure NaC} structure (6 : 6 coordination) changes into CsCI structure (8 : 8 coordination) and reverse of this occur at high temperature (760 K).

Imperfections in Solids

- In a crystalline solid, the atoms, ions and molecules are arranged in a Definite repeating pattern, but some defects may occur in the pattern. derivations from perfect arrangement may occur due to rapid cooling or presence of additional particles.
- The defects are of two types, namely point defects and line defects.

Point Defects

Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance Point defects can be classified into three types : (1) psychometric defects (2) impurity defects (3) non-stoichiometric defects

1. Stoichiometric Defect

These are point defects that do not disturb' the -stoichiometric of the solid. They are also called intrinsic or thermodynamic defects. In ionic solids, basically these are of two types, Frankel defect and Schottky defect

10	Schottky defect	Frenkel defect
1.	It is due to equal number of cations and anions missing from the lattice sites.	It is due to the missing of ions (usually cations) from the lattice sites and they occupy the interstitial sites.
2.	This results in the decrease in density of crystal.	It has no effect on the density of crystal.
3.	This type of defect is found in highly ionic compounds with high coordination number, e.g., NaCl, CsCl, etc.	This types of defect is found in crystal, where the difference in the size of cations and anions is very large, e.g., AgCI, ZnS, etc.

AgBr has both Schottky and Frenkel defects. Frenkel defects are not found in pure alkali metal halides because cations are of large size.

2. Impurity Defect

- It arises when foreign atoms or ions aloe present in the lattice. In case of ionic compounds, the impurity 1S also ionic in nature. When the impurity has the same charge as the host ion. it just substitutes some of the host ions.
- Impurity defects can also be introduced by adding impurity ions having different charge than host ions. e.g. molten NaCl containing a little amount of SrCI₂ is crystallised. In such cases,
- Cationic vacancies produced = [number of cations of higher valence * Difference in valence of the host cation and cation of higher valence

3. Non-Stoichiometric Defect

Non-stoichiometric crystals are those which do not obey the law of constant proportions. The numbers of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. However, the crystal as a whole in neutral.

Types of n-stoichiometric defects are as follows:

(i) **Met excess defect** Metal excess defect due to anionic vacancies: Alkyl halides like NaC1 and KCl show this type of defect. centres ale the sites from where anions are missing and the vacant sites are occupied by electrons. F-centres contribute colour and paramagnetic nature of the crystal [F stands for

German wo\d Farbe meaning colour).

Metal excess defect due to presence of extra cations at interstitial sites, e.g., zinc oxide is white in colour at room temperature. On beating, it loses oxygen and turns yellow.

$ZnO \xrightarrow{Heating} Zn^{2+} + \frac{1}{2}O_2 + 2e^{-1}$

(ii) Metal deficiency defect due to cation vacancy It is due to the absence of a metal ion from its lattice site and charge is balanced by ion having higher positive charge. Transition metals exhibit this defect, e.g., FeO, which is found in the composition range from $Fe_{0.93}$ O to $Fe_{0.96}$ O.

In crystal of FeO, some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

Type of solid	Conductivity	Reason of conductivity	Examples
Conductors	$10^4 - 10^7$ (Very high)	Motion of electrons	Metals like Ag, Al
Insulators	10 ²⁰ to10 ⁻¹⁰ (Very low	Do not permit electricity to pass	Wood, rubber, bakelite
Semiconductors	10 ⁻⁶ – 10 ⁴ (Moderate)	Motion of interstitia electrons or holes of both	Il Si, Ge, etc. r
Partially filled band	Overlapping bands	Conduction band Forbidden zone Valence band	Conduction band Small energy gap Valence band
- chauctor	s (Metals) In	sulator Se	miconductor

Classification of Solids on the Basis of Electrical Conductivity

[The electricity produced on heating a polar crystal is called 'pyroelectricity'.]

When mechanical stress is applied on polar crystals, electricity produced due to displacement of ions is called 'piezoelectricity'

Semiconductors

Electronic conductors having electrical conductivity in the range of $10^4 - 10^7 \Omega^{-1} \text{ cm}^{-1}$ are known as semiconductors. Examples Si, Ge Sn (grey), Cu₂O, SiC and GaAs.

Intrinsic Semiconductors

Pure substances that are semiconductors are known as Intrinsic Semiconductors e.g., Si, Ge

Extrinsic Semiconductors

Their conductivity is due to the presence of impurities. They are formed by doping. It is defined as addition of impurities to a semiconductor to increase the conductivity. Doping of Si or Ge is carried out with P, As, Sb, B, Al or Ga.

(i) **n**•**type semiconductors** Silicon doped with 15 group elements like phosphorus is called n-type semiconductor. The conductivity is due to the presence of negative charge (electrons),

(ii) **p**•**type semiconductors** Silicon doped with 13 group element like gallium is called p-type semiconductor. The conductivity is due to the presence of positive holes.

- Some typical 13-15 compounds are InSb, AlP and GaAs and SOme typical 12-16 compounds are ZnS, CdS. CdSe and HgTe.
- These exhibit electrical and optical properties of great use in electronic industry.

Magnetic Properties of Solids

Solids can be divided into different classes depending on their response to magnetic field.

1. Diamagnetic Substances

These are weakly repelled by the magnetic field and do not have any unpaired electron, e.g., TiO_2 , V_2O5 , C_6H_6 , NaCI, etc.

2. Paramagnetic Substances

These are attracted by the magnetic field and have unpaired electrons These lose magnetism in the absence of magnetic field, e.g., O_2 , Cu^{2+} , Fe^{3+} , etc.

3. Ferromagnetic Substances

These are attracted by the magnetic field and show permanent magnetism even ill the absence of magnetic field e.g., Fe, Co and Ni.

4. Anti-ferromagnetic Substances

These substances have net magnetic moment zero due to compensatory alignment of magnetic . moments, e.g., MnO, MnO_2 , FeO, etc.

5. Ferrimagnetic Substances

These substances have a net dipole moment due to unequal parallel and anti-parallel alignment of magnetic moments, e.g., Fe_3O_4 , ferrites, etc.

Chapter 2 Solutions

Solution is a homogeneous mixture of two or more substances in same or different physical phases. The substances forming the solution are called components of the solution. On the basis of number of components a solution of two components is called binary solution.

Solute and Solvent

In a binary solution, solvent is the component which is present in large quantity while the other component is known as solute.

Classification of Solutions

(A) Following types of solutions are seen on the basis of physical state of solute and solvent.

S.No.	Solute	Solvent	Examples
Solid solutions	0	10	
1	Solid	Solid	Alloys
2.	Laud	Solid	Hydrated salts, Amalgam of Hg with N
3.	Gas	Solid	Dissolved gases in mineral
Liquid solutions	8	10 10	
4	Solic	ciquid	Salt/sugar solution in water
5	Liquid	Liquid	Alcohol in water
6	Gas	Liguid	Aerated drinks, Op in water
Gaseous solutions		-	•
7.	Solid	Gas	lodine vapour in air
8	Liquid	Gas	Water vapour in air
9.	Gas	Gas	Air $(O_2 + N_2)$

[if water is used as a solvent, the solution is called aqueous solution and if not, the solution is called non-aqueous solution.]

(B) Depending upon the amount of solute dissolved in a solvent we have the following types of solutions:

(i) Unsaturated solution A

solution in which more solute can be dissolved without raising temperature is called an unsaturated solution.

(ii) Saturated solution A

solution in which no solute can be dissolved further at a given temperature is called a saturated solution.

(iii) Supersaturated solution A

solution which contains more solute than that would be necessary to saturate it at a given temperature is called a supersaturated solution.

Solubility

The maximum amount of a solute that can be dissolved in a given amount of solvent (generally 100 g) at a given temperature is termed as its solubility at that temperature.

The solubility of a solute in a liquid depends upon the following factors:

(i) Nature of the solute

(ii) Nature of the solvent

(iii) Temperature of the solution

(iv) Pressure (in case of gases)

Henry's Law

The most commonly used form of Henry"s law states "the partial pressure (P) of the gas in vapour phase is proportional to the mole fraction (x) of the gas in the solution" and is expressed as $p = K_H \cdot x$

Greater the value of K_{H} , higher the solubility of the gas. The value of K_{H} decreases with increase in the temperature. Thus, aquatic species are more comfortable in cold water [more dissolved O_2] rather than Warm water.

Applications

1. In manufacture of soft drinks and soda water, CQ is passed at high pressure to increase its solubility.

2. To minimise the painful effects (bends) accompanying the decompression of deep sea divers. O_2 diluted with less soluble. He gas is used as breathing gas.

3. At high altitudes, the partial pressure of O_2 is less then that at the ground level. This leads to low concentrations of O_2 in the blood of climbers which causes "anoxia".

Concentration of Solutions

The concentration of a solution is defined as the relative amount of solute present in a solution. On the basis of concentration of solution there are two types of solutions.

(i) Dilute solution

(ii) Concentrated solution

Methods of Expressing Concentration of Solutions

Various expression for the concentrations of solutions can be summarised as

(i) Percentage by weight

(w / w %) It is defined as the amount of solute present in 100 g of solution.

w / w % = weight of solute / weight of solution * 100

(ii) Percentage by volume

(w / V%) It is defined as the weight 01 solute present in 100 mL of solution.

w / V % = weight of solute / weight of solution * 100

or the volume of solute present in 100 mL of solution.

u / V % = volume of solute / volume of solution * 100

(iii) Mole fraction

(x) It is defined as the ratio of the number of moles of a component to the total number of moles of all the components. For a binary solution, if the number of moles of A and B are n_A and n_B

respectively, the mole fraction of A will be

Similarly,

$$\chi_A = \frac{n_A}{n_A + n_B}$$
$$\chi_B = \frac{n_B}{n_A + n_B} \quad \because \quad \chi_A + \chi_B = 1$$

(iv) Parts per million

(ppm) It is defined as the parts of a component per million parts (10^6) of the solution. It is widely used when a solute is present in trace quantities.

ppm = number of parts of the component / total number of parts of all the components * 10⁶ (v) Molarity (M) It is the number of moles of solute present in 1L(dm3) of the solution.

M = number of moles of solute / volume of solution (L)

M = mass of solute (in gram) * 1000 / mol. wt. of solute x volume of solution (in mL)

Molarity varies with temperature due to change in volume of solution.

[When molarity of a solution is 1 M, it is called a molar solution. 0.1 M solution is called a

decimolar solution while 0.5 M solution is known as semi molar solution]

Molarity = Percent by mass * density * 10 / molecular weight

Dilution law, $M_1 V_1 = M_2 V_2$ (for dilution from volume V_1 to V_2)

For reaction between two reactants, $M_1 V_1 / n1 = M_2 V_2 / n_2$ where, n_1 and n_2 arc stoichiometric coefficient in balanced equation.

(vi) Molality (m) It is the number of moles of solute per kilogram of the solvent.

Molality = mass of solute in gram * 1000 / mol. wt. of solute * mass of solvent (in g) Molality is independent of temperature.

[When solvent used is water, a molar (1 M) solution is more concentrated than a molal (1 M) solution.]

(vii) Normality (N) The number of gram equivalents of solute present in 1 L of solution.

Normality = number of grams – equivalent of solute / volume of solution in L

Number of gram-equivalents of solute = mass of solute in gram / equivalent weight

[Relationship between normality and molarity N x Eq. weight = M x mol. weight]

If two solutions of the same solute having volumes and molarities V1, M1 and V2, M2 are mixed,

$$\label{eq:v1} \begin{split} & \mathcal{N} \\ \text{Similarly, Normality} (\mathcal{N}) = \frac{V_1 + V_2}{V_1 + N_2 V_2} \\ & \frac{V_1 + V_2}{V_1 + V_2} \end{split}$$

To dilute V_1 mL of a solution having molarity M_1 to molarity M_2 up to the final volume V_2 mL, the volume of water added is

$$V_{2} - V_{1} = \left(\frac{M_{1} - M_{2}}{M_{2}}\right)V_{1}.$$

Similarly, $V_{2} - V_{1} = \left(\frac{N_{1} - N_{2}}{N_{2}}\right)V_{1}$

(viii) Formality (F) It is the number of formula weights of solute present per litre of the solution. Formality = moles of substance added to solution / volume of solution (in L))

(ix) Mass fraction Mass fraction of any component in the solution is the mass of that component divided by the total mass of the solution.

Molality, mole fraction and mass fraction are preferred over molarity, normality, etc., because former involve weights which do not change with temperature.

(x) Demal (D) It represents one mole of solute present in 1L of solution at O°C.

Raoult's Law

The Raoult"s law states "For a solution of two volatile liquids, the vapour pressure of each liquid in the solution is less than the respective vapour pressure of the pure liquids and the equilibrium partial vapour pressure of the liquid is directly proportional to its mole fraction.

For a solution containing two liquids A and B, the partial vapour pressure of liquid A is

where,
$$\chi_A = \frac{n_A}{(n_A + n_B)}$$
 = mole fraction of liquid A

- has

The proportionality constant is obtained by considering the pure liquid when_{χA} = 1 then k = P°_A, the vapour pressure of pure liquid, hence

 $p_A = p_A^* \chi_A$ Similarly, $p_B = p_B^* \chi_B$ The total vapour pressure of the solution, $p_T = p_A + p_B = p_A^* \chi_A + p_B^* \chi_B$ $= p_A^* + (p_B^* - p_A^*) \chi_B$

Konowaloff Rule

At any fixed temperature, the vapour phase is always richer in the more volatile component as compared to the solution phase. In other words, mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.

The composition of vapour phase in equilibrium with the solution is determined by the partial pressure of components. If Y_1 and Y_2 are the

component 1 and 2 respectively in the vapour phase then. using Dalton"s law of partial pressure, p1 = y1 * Ptotal

p2 = y2 * Ptotal

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Ideal Solutions

Those solutions in which solute-solute (B-B) and solvent-solvent (A-A) interactions are almost similar to solvent solute (A-B) interactions are called ideal solutions. These solutions satisfy the following conditions :



(i) Solution must obey Raoult"s law, i.e.,

$$p_A = p_A^\circ \chi_A, p_B = p_B^\circ \chi_B$$

(ii) $\Delta Hmix = 0$ (No energy evolved or absorbed)

(iii) $\Delta V mix = 0$ (No expansion or contraction on mixing)

Some solutions behave like nearly ideal solutions, e.g., benzene + toluene. n-hexane + nheptane, ethyl iodide + ethyl bromide, chlorobenzene + bromobenzene.

Non-ideal Solutions

Those solutions which shows deviation from Raoult"s law is called non-ideal solution.

For such solutions,

 $\Delta Hmix \neq 0$ $\Delta Vmix \neq 0$

(a) Non-ideal solutions showing positive deviation

In such a case, the A – B interactions are weaker than A – A or B – B interactions and the observed vapour pressure of each component and the total vapour pressure are greater than that predicted by Raoult"s law.

$$p_A > p_A^{\circ} \chi_A, \ p_B > p_B^{\circ} \chi_B$$
$$p_{\text{total}} > p_A^{\circ} \chi_A + p_B^{\circ} \chi_B$$

For such solutions



Examples : Ethanol + water. CS_2 + acctone. $CCl_4 + C_0H_0$, $CCl_4 + C_0H_5CH_2$, othanol + cyclohexane. $CCl_4 + CHCl_2$.

(b) Non-ideal solution showing negative deviation

In such a case, the A – B interactions are stronger than A – A or B – B interactions and the observed vapour pressure of each component and the total vapour pressure are lesser than that predicted by Raoult's law.

$$p_A < p_A^\circ \chi_A, \, p_B < p_B^\circ \chi_B$$

$$p_{\text{total}} < p_A^{\circ} \chi_A + p_B^{\circ} \chi_B$$

For such solutions,



Non-ideal solution showing negative deviation

Examples :
$$CHCl_3 + CH_3COCH_3$$
, $CHCl_8 + C_6H_6$, $H_2O + HCl$,

H₂O + HNO₃, methanol + acetic acid. Azeotropic Mixture

A mixture of two liquids which boils at a particular temperature like a pure liquid and distils over in the same composition is known as constant boiling mixtures. These are formed by nonideal solutions.

(i) Minimum boiling azeotropes

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are formed by those liquid pairs which show positive deviation from ideal behaviour. Such azeotropes have boiling points lower than either of the components, e.g., C2H5OH (95.57%) +

H2O (4.43%)(by mass).

(ii) Maximum boiling azeotropes

are formed by those liquid pain; which show negative deviation from ideal behaviour. Such azeotropes have boiling points higher than either of the components. e.g., H2O(20.22O%)+ HCI (79.78%] by mass.

Colligative Properties

[Colligatil1e : from Latin. = Co mean "together'; ligare means "to bind".] Colligative properties are those properties which depends only upon the number of solute particles in a solution irrespective of their nature.

Relative Lowering of Vapour Pressure

It is the ratio of lowering in vapour pressure to vapour pressure of pure solvent. The relative lowering in vapour pressure of solution containing a nonvolatile solute is equal to the mole fraction

of solute in the solution.

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \chi_B$$

where,
$$\frac{p_A^\circ - p_A}{p_A^\circ}$$
 = relative lowering of vapour pressure

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A + n_B}$$

for dilute solutions, $n_B \ll n_A$. Hence,

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A}$$

 $\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{W_B \times M_A}{M_B \times W_A}$

or

$$M_B = \frac{W_B}{W_A} \times M_A \times \frac{p_A}{(p_A^\circ - p_A)}$$

Above expression is used to find the molecular weight of an unknown solute dissolved in a given solvent. Where, W_B and W_A = mass of Solute and solvent respectively. M_B and M_A = molecular

weight of solute and solvent respectively.

Ostwald and Walker method is used to determine the relative lowering of vapour pressure. Elevation in Boiling Point (ΔT_b)

Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. As the vapour pressure of a solution containing a nonvolatile solute is lower than that of the pure solvent, it boiling point will be higher than that of the pure solvent as shown in figure. The increase in boiling point is known as elevation in boiling point, ΔT_b



 $\Delta T_b = T_b - T_b^{\circ} \Delta T_b = K_b m$ (where; m = molality)

 K_{b} is molal elevation constant or ebullioscopic constant. Molecular mass of solute can be calculated as

$$\Delta T_b = \frac{K_b \cdot W_B \times 1000}{M_B \times W_A}$$
$$M_B = K_b \cdot \frac{W_B}{W_A} \times \frac{1000}{\Delta T_b}$$

where, W_B and W_A = mass of solute and solvent respectively.

K_b has units of K / m or K kg mol¹, for water, K_b = 0.52 K kg mol¹
The boiling point elevation of a solution is determined by
(i) Landsberger"s method
(ii) Cottrell"s method

Denression in Freezing Point (ATr)

Depression in Freezing Fonte (AFT)

Freezing point of a liquid is the temperature at which vapour pressure of the solvent in its liquid and solid phase become equal. As we know that vapour pressure of solution containing non-volatile solute is lower than that of pure solvent, solid form gets separated out at a lower temperature as shown in the figure.



This decrease in freezing point of a liquid is known as depression in freezing point. Depression in freezing point (ΔT_f) = T°_f - T_f

$$\Delta T_f = K_f \cdot m = K_f \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

To find molecular mass of solute,

$$M_B = \frac{K_f \cdot W_B \times 1000}{\Delta T_f \cdot W_A}$$

where, K_f is molal depression constant or cryoscopic constant.

 K_f has units of K / m or K kg mot¹.

Ethylene glycol is usually added to water in the radiator to lower its freezing point. It is called antifreeze solution.

[Common salt (NaCl) and anhydrous CaC12 are used to clear snow on the roads because they depress the freezing point of water. The freezing point depression is determined by Beckmann method or Rast method.]

Calculations of molal elevation constant (K_{b}) and molal depression constant (K_{f})

$$K_b = \frac{M_A R(T_b^\circ)^2}{\Delta H_v}, K_f = \frac{M_A \cdot R(T_f^\circ)^2}{\Delta H_f}$$

 T_{b}^{*} = boiling point of solvent

 T_f° = freezing point of solvent

$$\Delta H_f = \text{molar enthalpy of fusion}$$

 $\Delta H_{\mu} = \text{molar enthalpy of vaporisation}$ Osmotic Pressure (π)

Osmosis is the phenomenon of spontaneous flow of the solvent molecules through a semipermeable membrane from pure solvent to solution or from a dilute solution to concentrated solution. It was first observed by Abbe Nollet.

Some natural semipermeable membranes are animal bladder, cell membrane etc.

CU₂[Fe(CN)₆]is an artificial semipermeable membrane which does not work in non-aqueous

solutions as it dissolves in them.

Osmosis may be

(i) Exosmosis

It is outward flow of water or solvent from a cell through semipermeable membrane.

(ii) Endosmosis

It is inward flow of water or solvent from a cell through a semipermeable membrane. The hydrostatic pressure developed on the solution which just prevents the osmosis of pure solvent into the solution through a semipermeable membrane is called **osmotic pressure.**

Osmotic pressure
$$(\pi) = RCT$$
; $\left(C = \frac{n_B}{V} = \frac{W_B}{M_B V}\right)$
 $M_B = \frac{W_B RT}{\pi V}$
 $\pi = \frac{dRT}{M_B}$; $\left(d = \frac{W_B}{V}\right)$

where, d = density, R = solution constant, T = temperature, $M_B = molar mass of solute$

Osmotic pressure can be determined by anyone of the method listed below

(i) Pfeffer"s method

(ii) Berkeley and Hartley"s method (very good method)

(iii) Morse and Frazer"s method

On the basis of osmotic pressure, -the solution can be

(i) Hypertonic solution

A solution is called hypertonic if its osmotic pressure is higher than that of the solution from which it is separated by a semipermeable membrane.

When a plant cell is placed in a hypertonic solution, the fluid from the plant cell comes out and cell shrinks, this phenomenon is called plasmolysis.

(ii) Hypotonic solution

A solution is called hypotonic if its osmotic pressure is lower than that of the solution from which it is separated by a semipermeable membrane.

(iii) Isotonic solution

Two solutions are called isotonic if they exert the same osmotic pressure. These solutions have same molar concentration. 0.91% solution of pure NaCl is isotonic with human RBC"s.

Two solutions are isotonic if they have the same molar concentration, e.g., if x % solution of X is isotonic with y % solution of Y, this means molar concentration of X = Molar concentration of Y

$$\frac{x}{100} \times \frac{1000}{M_X} = \frac{y \times 1000}{100 \times M_Y} \implies \frac{x}{M_X} = \frac{y}{M_Y}$$

Osmotic pressure method is the best method for determining the molecular masses of polymers since observed value of any other colligative property is too small to be measured with reasonable accuracy.

Reverse osmosis

When the external pressure applied on the solution is more than osmotic pressure, the solvent flows from the solution to the pure solvent, I which is called reverse osmosis. Desalination of sea water is done by reverse Osmosis.

Abnormal Molecular Masses

In some cases, observed colligative properties deviate from their normal calculated values due to association or dissociation of molecules. As we know,

Colligative property \propto 1 / M_B

lienee, higher and lower values of molar mass is observed in case of association and dissociation respectively, e.g., in benzene, acetic acid gets associated, so, its observed

molecular mass is 120. Similarly KCl undergoes dissociation in aqueous solution, so its observed molecular mass is 37.25.

These observed values are corrected by multiplying with van"t Hoff factor (i).

van't Hoff Factor (i)

It is the ratio of observed value of colligative property to the calculated value of colligative property.

i = observed value of colligative property / calculated value of colligative property

or i = normal molecular mass / observed molecular mass

or i = number of particles after association or dissociation / number of particles initially

So to correct the observed value of molar mass, van"t Hoff factor (i) must be included in different expressions for colligative properties.

$$\Delta T_b = i K_b \cdot m$$

$$\Delta T_f = i K_f \cdot m$$

$$\pi = i CRT$$

$$\frac{\Delta p}{p_A^o} = i x_B$$

Degree of Dissociation (α) and van't Hoff Factor (i)

(i) If one molecule of a substance gets dissociated into n particles or molecules and α is the degree of dissociation then

	A —	$\rightarrow nP$
Initially	1 mol	0
At eq.	1-α	na.

Total number of moles at equilibrium

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

=

 \Rightarrow

Degree of Association (α) and van't Hoff Factor (i)

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

If n molecules of a substance A associate to form An and $\boldsymbol{\alpha}$ is the degree of association then

	nA —	$\rightarrow A_n$
Initially	1 mol	- 0
v coulibrium	1 - α	α
31 · 4		n

Total number of moles at equilibrium

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

van"t Hoff factor (i) > 1 for solutes undergoing dissociation and it is < 1 for solutes undergoing association.

Chemistry Notes for class 12 Chapter 3 Electrochemistry

Electrochemistry is that branch of chemistry which deals with the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Importance of Electrochemistry

- 1. Production of metals like Na, Mg. Ca and Al.
- 2. Electroplating.
- 3. Purification of metals.
- 4. Batteries and cells used in various instruments.

Conductors

Substances that allow electric current to pass through them are known as conductors.

Metallic Conductors or Electronic Conductors

Substances which allow the electric current to pass through them by the movement of electrons are called metallic conductors, e.g.. metals.

Electrolytic Conductors or Electrolytes

Substances which allow the passage of electricity through their fused state or aqueous solution and undergo chemical decomposition are called electrolytic conductors, e.g., aqueous solution of acids. bases and salts.

Electrolytes are of two types:

- 1. **Strong electrolytes** The electrolytes that completely dissociate or ionise into ions are called strong electrolytes. e.g., HCl, NaOH, K₂SO₄
- 2. Weak electrolytes The electrolytes that dissociate partially (ex < 1) are called weak electrolytes, e.g., CH₃COOH, H₂CO₃, NH₄OHH₂S, etc.

Electrochemical Cell and Electrolytic

	Characteristics	Electrochemical cell (Galvanic cell)	Electrolytic cell
		$M \rightarrow M^{n+} + ne^{-}$ $M^{n+} + ne^{-} \rightarrow M$ Cathode	
1,	Definition	A device used to convert chemical energy into electrical energy.	A device used to carried out non-spontaneous chemical teactions by electrical energy.
2.	Assembly	It is combination of two half-cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
з.	Nature of electrodes	Anode is negative, cathode is positive.	Anode is positive, cathode is negative.
4.	Movement of electrons	From anode to cathode in external circuit.	Electrons enter through cathode and leave by anode.
5.	Spontaneity	Cell reaction is spontaneous	Cell reaction is non-spontaneous.
6.	Salt bridge	Salt bridge is required	Salt bridge is not required.

A cell of almost constant emf is called standard cell. The most common is Weston standard cell.

Galvanic cell is also called voltaic cell.

General Representation of an Electrochemical Cell



Other features of the electrochemical cell are

- 1. There is no evolution of heat.
- 2. The solution remains neutral on both sides.
- 3. The reaction and now of electrons stops after sometime.

Daniell Cell

An electrochemical cell of zinc and copper metals is known as Daniell cell. It is represented as



Cell diagram,

$$\operatorname{Zn}(s)|\operatorname{Zn}^{2+}(aq)||\operatorname{Cu}^{2+}(aq)||\operatorname{Cu}(s)$$

LHS oxidation, $Zn \longrightarrow Zn^{2+} + 2e^{-}$ <u>RHS reduction</u>, $Cu^{2+} + 2e^{-} \longrightarrow Cu$ <u>Overall reaction</u>, $Zn + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu$

By convention cathode is represented on the RHS and anode on the LHS.

Function of salt bridge

- 1. It completes the circuit and allows the flow of current.
- 2. It maintains the electrical neutrality on both sides. Salt-bridge generally contains solution of strong electrolyte such as KNO_3 , KCL etc. KCI is preferred because the transport numbers of K⁺ and Cl⁻ are almost same.

Transport number or Transference number The current flowing through an electrolytic solution is carried by the ions. The fraction of the current carried by an ion is called its transport number or transference number. Thus.

Transport number of cation. $n_c =$ (current carried by cation/total current)

Transport number of cation. $n_a =$ (current carried by anion/total current)

Evidently $n_c + n_a = 1$

Electrode Potential

When an electrode is in contact with the solution of its ions in a half-cell, it has a tendency to lose or gain electrons which is known as electrode potential. It is expressed in volts. It is an intensive property, i.e., independent of the amount of species in the reaction.

Oxidation potential The tendency to lose electrons in the above case is known as oxidation potential. Oxidation potential of a half-cell is inversely proportional to the concentration of ions in the solution.

Reduction potential The tendency to gain electrons in the above case is known as reduction potential. According to IUPAC convention, the reduction potential alone be called as the electrode potential unless it is specifically mentioned.

 $E^{\circ}_{red} = - E^{\circ}_{oxidalion}$

It is not possible to determine the absolute value of electrode potential. For this a reference electrode [NHE or SHE] is required. The electrode potential is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell.

Standard electrode potential The potential difference developed between metal electrode and solution of ions of unit molarity (1M) at 1 atm pressure and 25°C (298 K) is called standard electrode potential.

It is denoted by E°.

Reference Electrode

The electrode of known potential is called reference electrode. It may be primary reference electrode like hydrogen electrode or secondary reference electrode like calomel electrode.

Standard hydrogen electrode (SHE) Standard hydrogen electrode (SHE). also known as normal hydrogen electrode (NHE), consists of platinum wire, carrying platinum foil coated with finely divided platinum black. The wire is sealed into a glass tube. placed in beaker containing 1 M HCl. The hydrogen gas at 1 atm pressure is bubbled through the solution at 298K. Half-cell is pt H_2 (1 atm) H^+ (1 M)



In SHE. at the surface of plantinum, either of (he following reaction can take place

 $2H^+(ag) + 2e^- \rightarrow H_2G$ Reduction

 $H_2(g) \rightarrow 2H^+(ag) + 2e^-$ Oxidation

The electrode potential of SHE has been fixed as zero at all temperatures.

Its main drawbacks are

- 1. It is difficult to maintain 1 atm pressure of H_2 gas.
- 2. It is difficult to maintain H^+ ion concentration 1 M.
- 3. The platinum electrode is easily poisoned by traces of impurities.

Hence, calomel electrodes are conveniently used as reference electrodes, It consists of mercury in contact with $Hg_2 Cl_2$ (calomel) paste in a solution of KCl.

Electromotive Force (emf) of a Cell

It is the difference between the electrode potentials of two half-cells and cause flow of current from electrode at higher potential to electrode at lower potential. It is also the measure of free energy change. Standard emf of a cell,

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{oxi}}^{\circ}$$

No.	Emf - Constant	Cell potential
1.	Potential difference between two electrodes when no current is flowing in the circuit is called emf.	The potential difference of the two half- cells when electric current flows through the cells is called cell potential.
2.	Emf is the maximum voltage which can be obtained from the cell.	It is always less than the maximum voltage obtainable from the cell.
3	Emf is measured by a potentiometer.	It is measured by a voltmeter.

Electrochemical Series

It is the arrangement of electrodes in the increasing order of their standard reduction potentials.

Standard Electrode Potential at 298 K

leaction (Oxidised form) + ne	→	Reduced form	E°/V
$F_2(g) + 2e^-$		2F	2.87
Co ³⁺ + e		Co ²⁺	1.81
$H_2O_2 + 2H^+ + 2e^-$	\rightarrow	2H ₂ 0	1.78
MnO ₄ + 8H ⁺ + 5e ⁻	->	$Mn^{2*} + 4H_2O$	1.51
Au ³⁺ + 3e ⁻	\rightarrow	Au(s)	1.40
Cl ₂ (g) + 2e ⁻	→	2CI-	1.36
Ct207 + 14H + 6e	→	2Cr ³⁺ + 7H ₂ O	1.33
$0_2(g) + 4H^+ + 4e^-$	->	2H ₂ O	1.23
$MnO_2(s) + 4H^+ + 2e^-$	\rightarrow	Mn ²⁺ + 2H ₂ O	1.23
Br ₂ + 2e ⁻	\rightarrow	2Br-	1.09
NO3 + 4H+ + 3e-	->	N0(g) + 2H ₂ O	0.97
2Hg ²⁺ + 2e ⁻	→	Hg ₂ ²⁺	0.92
Ag + + e-	->	Ag(s)	0.80
Fe ³⁺ + e ⁻	→	Fe ²⁺	0.77
$O_2(g) + 2H^+ + 2e^-$	→	H ₂ O ₂	0.68
1 ₂ + 2e ⁻	->	21-	0.54
Cu* + e-	->	Cu(s)	0.52
$Cu^{2+} + 2e^{-}$	\rightarrow	Cu(s)	0.34

Reaction (Oxidised form) + /	i Ra	Reduced form	E F
AgCI(s) + e ⁻	→	Ag(s) + CI	0.22
AgBr(s) + e ⁻	->	Ag(s) + Br-	0.10
2H ⁺ + 2e ⁻	\rightarrow	H ₂ (g)	0.00
Pb ²⁺ + 2e ⁺	→	Pb(s)	- 0.13
Sn ²⁺ + 2e ⁻	\rightarrow	Sn(s)	- 0.14
Ni ²⁺ + 2e ⁻	->	Ni(s)	- 0.25
Fe ²⁺ + 2e ⁻	→	Fe(s)	- 0.44
Cr ³⁺ + 3e ⁻	\rightarrow	Cr(s)	- 0.74
Zn ²⁺ + 2e ⁻	->	Zn(s)	- 0.76
2H ₂ O + 2e ⁻	→	$H_2(g) + 2OH^-(aq)$	- 0.83
Al ³⁺ + 3e ⁻		AI(s)	- 1.66
Mg ²⁺ + 2e ⁻	\rightarrow	Mg(s)	- 2.36
Na* + e-	\rightarrow	Na(s)	- 2.71
Ca ²⁺ + 2e ⁻	→	Ca(s)	- 2.87
K ⁺ + e ⁻	→	K(s)	- 2.93
Li* + e	\rightarrow	Li(s)	- 3.05

Appications of Electrochemical Series (ECS)

1. The lower the value of E° , the greater the tendency to form cation.

 $M \to M^{n+} + ne^{\bar{}}$

Metals placed below hydrogen in ECS replace hydrogen from di1 acids but metals placed above hydrogen cannot replace hydrogen from dil acids.

 $\begin{array}{ccc} \text{Ca} + \text{dil.} \text{H}_2\text{SO}_4 & \longrightarrow & \text{CaSO}_4 + \text{H}_2 \uparrow \\ \text{possible,} & (\text{Ca} + 2\text{H}^* & \longrightarrow & \text{Ca}^{2+} + \text{H}_2) \\ & \text{Cu} + \text{dil.} \text{H}_2\text{SO}_4 & \longrightarrow & \text{CuSO}_4 + \text{H}_2 \uparrow \\ \text{not possible,} & (\text{Cu} + 2\text{H}^* & \longrightarrow & \text{Cu}^{2+} + \text{H}_2) \end{array}$

3. Oxides of metals placed below hydrogen are not reduced by H_2 but oxides of iron and metals placed above iron are reduced by H_2 .

- SnO, PbO, CuO are reduced by H₂
- CaO, K_2O are not reduced by H_2 ·

4. Reducing character increases down the series.

- 5. Reactivity increases down the series.
- 6. Determination of emf; emf is the difference of reduction potentials of two half-cells.
 - $E_{emf} = E_{RHS} E_{LHS}$

If the value of emf is positive. then reaction take place spontaneously, otherwise not.

- 7. Greater the reduction potential of a substance, oxidising power. (e.g., $F_2 > Cl_2 > Br_2 > I_2$)
- 8. A negative value of standard reduction potential shows that it is the site of oxidation.
- 9. Oxides of metals having $E^{\circ}_{red} \ge 0.79$ will be decomposed by heating to form O_2 and metal.

HgO (s) \rightarrow Hg(l)(1/2)O₂(g)

 $({E^{\circ}}_{Hg}^{2+}_{/Hg}=0.79V)$

Nernst Equation

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

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

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{2.303 RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{0.0591}{n} \log \left[\frac{1}{M^{n+}}\right]$$

For a electrochemical cell,

$$aA + bB \longrightarrow cC + dD$$
$$E_{cell} = E_{cell}^* - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Concentration of pure solids and liquids is taken as unity.

Nernst equation and K_c

At equilibrium

: At equilibrium,
$$E_{cell} = 0$$

 $E_{cell}^{\circ} = \frac{0.0591}{n} \log K_c$ at 298K
 $\Delta G^{\circ} = -nFE_{cell}^{\circ}$

Here, ΔG° is the standard Gibbs free energy change.

Type of reaction	ΔG°	E ^o _{cell}	Type of cell
Spontaneous	-ve	+ve	Galvanic
Non-spontaneous	+ve	-ve	Electrolytic
Equilibrium	0	0	Dead battery

Relationship between free energy change and equilibrium constant

 $\Delta G^{\circ} = -2.303 RT \log K_c$

Concentration Cells

(i) Electrode concentration cells Two hydrogen electrodes or different pressures are dipped In the same solution of electrolyte,

e.g..

Pt,
$$H_2(p_1)|H^+|H_2(p_2)Pt, p_1 > p_2$$

 $E_{coll} = \frac{2.303RT}{nF} \log \frac{p_2}{p_1}$

(ii) Electrolyte concentration cells Electrodes are the same but electrolyte solutions have different concentrations, e.g..

$$\begin{aligned} & \operatorname{Zn} |\operatorname{Zn}^{2^{+}}(C_{1})| |\operatorname{Zn}^{2^{+}}(C_{2})| |\operatorname{Zn}, C_{2} > C_{1} \\ & E_{\operatorname{cell}} = \frac{2.303RT}{nF} \log \frac{C_{2}}{C_{1}} = \frac{0.0591}{n} \log \frac{C_{2}}{C_{1}} \end{aligned}$$

Conductance (G)

It is the ease of flow of electric current through the conductor. It is reciprocal of resistance (R).

G = (1/R), units ohm⁻¹ mhos or Ω^{-1}

Specific Conductivity (K)

It is the reciprocal of specific resistance.

$$\kappa - \frac{1}{\rho} = \frac{l}{R.a} = G \times \frac{l}{a} = G \times \text{cell constant} (G^*)$$

$$\left(\frac{l}{a} = \text{cell constant}\right)$$
Units of $\kappa = \Omega^{-1} \text{cm}^{-1}$

$$= S \text{ cm}^{-1} (\Omega^{-1} = S \text{ i.e., Siemens})$$

Unit of cell constant is cm⁻¹ or m⁻¹.

Specific conductivity decreases on dilution. This is because concentration of ions per cc decreases upon dilution.

Molar Conductivity (Λ_m)

The conductivity of all the ions produced when 1 mole of an electrolyte is dissolved in V mL of solution is known as molar conductivity.

It is related to specific conductance as

 $\Lambda_{\rm m} = ({\rm k} \ {\rm x} \ 1000/{\rm M})$

where. M = molarity.

It units are Ω^{-1} cm² mol⁻¹ or S cm² mol⁻¹.

Equivalent conductivity (Λ_m)

The conducting power of all the ions produced when 1 g-equivalent of an electrolyte is dissolved in V mL of solution, is called equivalent conductivity. It is related to specific conductance as

 $\Lambda_{\rm m} = ({\rm k} \ge 1000/{\rm N})$

where. N = normality.

Its units are ohm⁻¹ cm² (equiv⁻¹) or mho cm² (equiv⁻¹) or S cm² (g-equiv⁻¹).

Debye-Huckel Onsagar equation It gives a relation between molar conductivity, Λ_m at a particular concentration and molar conductivity Λ_m at infinite dilution.

 $\Lambda_{m} = \Lambda^{0}{}_{m} - \sqrt{C}$

where, b is a constant. It depends upon the nature of solvent and temperature.

Factors Affecting Conductivity

(i) Nature of electrolyte The strong electrolytes like KNO₃ KCl. NaOH. etc. are completely ionised in aqueous solution and have high values of conductivity (molar as well as equivalent).

The weak electrolytes are ionised to a lesser extent in aqueous solution and have lower values of conductivity (molar as well as equivalent).

ii) Concentration of the solution The concentrated solutions of strong electrolytes have SIgnificant interionic attractions. which reduce the speed of ions and lower the value of Λ_m . and Λ_{eq} .

The dilution decreases such attractions and increase the value of Λ_m and Λ_{eq} .



The limiting value, Λ_{m}^{0} or Λ_{m}^{∞} . (the molar conductivity at zero concentration (or at infinite dilution) can be obtained extrapolating the graph.

In case of weak electrolytes, the degree of ionisation increases dilution which increases the value of Λ_{m} and Λ_{eq} . The limiting value Λ^{0}_{m} cannot be obtained by extrapolating the graph. ~ limiting value, Λ^{0}_{m} , for weak electrolytes is obtained by Kohlrausch law.

(iii) Temperature The increase of temperature decreases inter-ionic attractions and increases kinetic energy of ions and their speed. Thus, Λ_m and Λ_{eq} increase with temperature.

Kohlrausch's Law

At infinite dilution, the molar conductivity of an electrolyte is the sum of the ionic conductivities of the cations and anions, e.g., for $A_x B_y$.

$$\Lambda_m^0 (A_x B_y) = x \Lambda_{A^+}^0 + y \Lambda_{B^-}^0$$
$$\Lambda_{eq}^0 = \Lambda_{A^+}^0 + \Lambda_{B^-}^0$$

Applications

(i) Determination of equivalent/molar conductivities of weak electrolytes at infinite dilution, e.g.,

$$\Lambda_{CH_{3}COOH}^{\infty} = \Lambda_{CH_{3}COONa}^{\infty} + \Lambda_{HCI}^{\infty} - \Lambda_{NaCI}^{\infty}$$
$$\Lambda_{NH_{4}OH}^{\infty} = \Lambda_{NH_{4}CI}^{\infty} + \Lambda_{NaOH}^{\infty} - \Lambda_{NaCI}^{\infty}$$

(ii) Determination of degree of dissociation (α) of an electrolyte at a given dilution.

$$\alpha = \frac{\text{molar conductance at concentration 'C'}}{\text{molar conductance at infinite dilution}} = \frac{\Lambda_m^C}{\Lambda_m^C}$$

The dissociation constant (K) of the weak electrolyte at concentration C of the solution can be calculated by using the formula

$$k_c = (C\alpha^2/1 - \alpha)$$

where, α is the degree of dissociation of the electrolyte.

(iii) Salts like BaSO₄ ..., PbSO₄' AgCl, AgBr and AgI which do not dissolve to a large extent in water are called sparingly soluble salts.

The solubility of a sparingly soluble salt can be calculated as

$$\Lambda_m^{\circ} = \frac{\kappa \times 1000}{\text{solubility (in mol L-1)}}$$

Solubility (in mol L⁻¹) = $\frac{\kappa \times 1000}{\Lambda_m^{\circ}}$

Electrolysis

It is the process of decomposition of an electrolyte when electric current is passed through either its aqueous solution or molten state,

1. In electrolytic cell both oxidation and reduction takes place in the same cell.

- 2. Anode is positively charged and cathode is negatively charged, In electrolytic cell.
- 3. During electrolysis of molten electrolyte, cations are liberated at cathode. while anions at the anode.
- 4. When two or more ions compete at the electrodes. the ion with higher reduction potential gets liberated at the cathode while the ion with lower reduction potential at the anode.

For metals to be deposited on the cathode during electrolysis, the voltage required is almost the same as the standard

electrode potential. However for liberation of gases, some extra voltage is required than the theoretical value of the standard electrode potential. The extra voltage thus required is called over voltage or bubble voltage.

How to Predict the Products of Electrolysis?

When an aqueous solution of an electrolyte is electrolysed, if the cation has higher reduction potential than water (-0.83 V), cation is liberated at the cathode (e.g.. in the electrolysis of copper and silver salts) otherwise H₂ gas is liberated due to reduction of water (e.g., in the electrolysis of K, Na, Ca salts, etc.) Similarly if anion has higher oxidation potential than water (-1.23 V), anion is liberated (e.g., Br⁻), otherwise O² gas is liberated due to oxidation of water (e.g., in caseof F⁻, aqueous solution of Na₂SO₄ as oxidation potential of SO²⁻₄ is -0.2 V).

Discharge potential is defined as the minimum potential that must be applied across the electrodes to bring about the electrolysis and subsequent discharge of the ion on the electrode.

Faraday's Laws of Electrolysis

1. First law

The amount of the substance deposited or liberated at cathode directly proportional to the quantity of electricity passed through electrolyte.

 $W \propto I \ge t = I \ge t \ge Z = Q \ge Z$

- I current in amp, t = time in sec,
- Q = quantity of charge (coulomb)
- Z is a constant known as electrochemical equivalent.

When I = 1 amp, t = 1 sec then Q = 1 coulomb, then w = Z.

Thus, electrochemical equivalent I" the amount of the substance deposited or liberated by passing 1A current for 1 sec (i.e., 1 coulomb, I x t = Q)

2. Second law

When the same quantity of electricity is passed through different electrolytes. the amounts of the substance deposited or liberated at the electrodes arc directly proportional to their equivalent weights, Thus,

$$\frac{\text{Mass of } A}{\text{Mass of } B} = \frac{\text{eq. wt. of } A}{\text{eq. wt. of } B}$$
$$\frac{\omega_1}{\omega_2} = \frac{E_1}{E_2} \Longrightarrow \frac{Z_1 Q}{Z_2 Q} = \frac{E_1}{E_2}$$

Hence, electrochemical equivalent \propto equivalent weight.

Batteries

These are source of electrical energy which may have one or more cells connected in series. For a good quality battery it should be reasonably light. compact and its voltage should not vary appreciably during its use.

Primary Batteries

In the primary batteries. the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again.

(i) Dry cell or Leclanehe cell

Anode-Zinc container

Cathode-Graphite rod surrounded by MnO₂ powder

Electrolyte-Paste of $NH_4Cl + ZnCl_2$

Cathode reaction,

 $2MnO_2(s) + 2 NH_4^+(aq) + 2e^- \rightarrow Mn_2O^3(s) + 2NH_3(g) + H_2O(l)$

Anode reaction,

 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

Cell potential 1.25 V to 1.5 V

(ii) Mercury cell

Anode-Zn-Hg amalgam

Cathode-Paste of (HgO + C)

Electrolyte-Moist paste of KOH-ZnO

Cathode reaction,

 $HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$

Anode reaction,

 $\operatorname{Zn}(\operatorname{Hg}) + 2\operatorname{OH}^{-}aq \longrightarrow \operatorname{ZnO}(s) + \operatorname{H}_2O(l) + 2e^{-}$

Net reaction,

 $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

Cell potential 1.35 V

Secondary Batteries

These cells can be recharged and can be used again and again, e.g.,

(i) Lead Storage battery

Anode-Spongy lead

Cathode-Grid of lead packed with PbO₂

Electrolyte-38% H₂SO₄ by mass

Anode reaction,

 $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^{-1}$

Cathode reaction,

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

Net reaction,

 $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

When recharged the cell reactions are reversed.

(ii) Nickel-cadmium storage cell

Anode-Cadmium

Cathode-Metal grid containing NiO₂

Electrolyte-KOH solution

Anode reaction,

 $Cd(s) + 2OH^{-}(aq) \rightarrow Cd(OH)_{2}(s) + 2e^{-}$
Cathode reaction, $NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$ Net reaction,

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Cell potential = 1.4 V

Fuel Cells

Galvanic cells which use energy of combustion of fuels like H_2 , CH_4 , CH_3OH , etc., as the source to produce electrical energy are called fuel cells. The fuel cells are pollution free and have high efficiency.

Hydrogen-Oxygen Fuel Cell

Electrodes-Made of porous graphite impregnated with catalyst (Pt, Ag or a metal oxide).

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Electrolyte-Aqueous solution of KOH or NaOH
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Oxygen and hydrogen are continuously fed into the cell.

Oxidation Half-cell reaction.

 $2H_2(g) + 4OH (aq) \longrightarrow 4H_2O(l) + 4e$ (at anode)

Reduction half-cell reaction,

 $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$ (at cathode)

Net reaction.

 $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

EMF of the cell 1 V.

Thermodynamic efficiency of a fuel cell,

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H}$$

Corrosion

Slow formation of undesirable compounds such as oxides, sulphides or carbonates at the surface of metals by reaction with moisture and other atmospheric gases is known as corrosion.

Factors Affecting Corrosion

- 1. Reactivity of metals
- 2. Presence of moisture and atmospheric gases like CO₂, SO₂, etc.
- 3. Presence of impurities
- 4. Strains in the metal

5. Presence of electrolyte

Rusting of Iron-Electrochemical Theory

An electrochemical cell, also known as corrosion cell, is developed at the surface of iron.

Anode- Pure iron

Cathode-Impure surface

Electrolyte,

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^2$$

Anode reaction,

$$2 \text{Fe(s)} \longrightarrow 2 \text{Fe}^{2+}(aq) + 4e^{-}$$

Cathode reaction,

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

Net reaction,

$$2\mathrm{Fe}(s) + 4\mathrm{H}^{+}(aq) + \mathrm{O}_{2}(g) \longrightarrow 2\mathrm{Fe}^{2+}(aq) + 2\mathrm{H}_{2}\mathrm{O}(l)$$

At surface,

$$4\operatorname{Fe}^{2+}(aq) + \operatorname{O}_{2}(g) + 4\operatorname{H}_{2}\operatorname{O}(l) \longrightarrow 2\operatorname{Fe}_{2}\operatorname{O}_{3}(s) + 8\operatorname{H}^{+}(aq)$$
$$\operatorname{Fe}_{2}\operatorname{O}_{3}(s) + x\operatorname{H}_{2}\operatorname{O}(l) \longrightarrow \operatorname{Fe}_{2}\operatorname{O}_{3} \cdot x\operatorname{H}_{2}\operatorname{O}(\operatorname{Rust})$$

Rusting of iron can be prevented by the following methods :

- 1. Barrier protection through coating of paints or electroplating.
- 2. Through galvanisation or coating of surface with tin metal.
- 3. By the use of antirust solutions (bis phenol).
- 4. By cathodic protection in which a metal is protected from corrosion by connecting it to another metal that is more easily oxidised.

Chemistry Notes for class 12 Chapter 4 Chemical Kinetics

The branch of chemistry, which deals with the rate of chemical reactions. the factors affecting the rate of reactions and the mechanism of the reaction. is called **chemical kinetics**.

Chemical Reactions on the Basis of Rate of Reaction

- 1. **Fast/instantaneous reactions** Chemical reaction which completes in less than Ips (10⁻¹² s) time, IS known as fast reaction. It IS practically impossible to measure the speed of such reactions, e.g., ionic reactions. organic substitution reactions.
- 2. Slow reactions Chemical re actions which completes in a long time from some minutes to some years are called slow reactions. e.g., rusting of iron. transformation of diamond etc.
- 3. **Moderately** slow reactions Chemical reactions which are intermediate between slow and fast reactions are called moderately slow reactions.

Rate of Reaction

Rate of a chemical reaction IS the change in the concentration of any one of the reactants or products per unit time. It is expressed in mol $L^{-1} s^{-1}$ or Ms^{-1} or atm time⁻¹ units.

Rate of reaction

= (decrease/increase in the concentration of reactant/product/time taken)

This rate of reaction is known as average rate of reaction $(r_{av}).(r_{av} \text{ can be calculated by dividing the concentration difference by the time interval}).$

For a chemical reaction,

For a chemical reaction,

 $aA + bB \longrightarrow cC + dD$ Average rate of reaction $(r_{av}) = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t}$ $= \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$ Rate of disappearance of $A = -\frac{\Delta[A]}{\Delta t}$ Rate of disappearance of $B = -\frac{\Delta[B]}{\Delta t}$ Rate of appearance of $C = \frac{\Delta[C]}{\Delta t}$ Rate of appearance of $D = \frac{\Delta[D]}{\Delta t}$

Instantaneous Rate of Reaction

Rate of a chemical reaction at a particular moment of time, is known as instantaneous rate of reaction.

For reaction,

For reaction,
$$R \longrightarrow P$$

 $r_{ins} = -\frac{\Delta[R]}{\Delta t} \text{ or } \frac{\Delta[P]}{\Delta t} \text{ as } \Delta \rightarrow d$
 $\Rightarrow \quad r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$

Methods for measuring reaction rate (i) pH measurement, (ii) change in optical activity, (iii) change in pressure, (iv) change in conductance.

Slowest step of a reaction was called rate determining step by van't Hoff.

Factors Affecting Rate of Reaction

- 1. Nature and concentration of reactant
- 2. Temperature

- 3. Surface area of reactant
- 4. Radiations and catalyst
- 5. Pressure of gas

Rate Law Expressions

According to the law of mass action,

For a chemical reaction,

 $aA + bB \rightarrow Products$

Rate $\alpha [A]^{a} [B]^{b} = k[A]^{a} [B]^{b}$

But experimentally, it is observed that the rate of reaction is found to depend upon ' α ' concentration terms of A and ' β ' concentration terms of B Then,

Rate $\alpha [A]^{\alpha} [B]^{\beta} = k[A]^{\alpha} [B]^{\beta}$

where, [A] and [B] molar concentrations of A and B respectively and k is the velocity constant or rate constant. The above expression is known as rate law.

Rate Constant

In the above expression, k is called rate constant or velocity constant.

Rate constant may be defined as the specific rate of reaction when the molar concentrations of the reactants is taken to be unity, i.e.,

Rate = k, if [A] = [B] = 1

Units of rate constant or specific reaction rate for a nth order reaction is given as

 $K = (1/Time) \times (1/[Conc.]^{n-1})$

Characteristics of rate constant

- 1. Greater the value of rate constant, faster is the reaction.
- 2. Each reaction has a particular value of rate constant at a particular temperature.
- 3. The value of rate constant for the same reaction changes with temperature.
- 4. The value of rate constant for a reaction does't depend upon the concentration of the reactants.

19	Order of reaction	Molecularity of reaction		
1.	Order of reaction is the sum of the concentration terms on which rate of reaction actually depends. Or It is also defined as sum of the exponents of the molar concentrations in the rate law equation.	Molecularity of a reaction is the number of atoms, ions or molecules that must collide with one another to form products in a chemical reaction.		
2.	It can be fractional as well as zero.	It cannot be zero or fractional.		
3.	It is an experimentally determined term.	It is theoretically determined term.		
4.	Order of reaction is applicable to elementary as well as complex reactions,	Molecularity is applicable only to elementary reactions.		
5.	Negative order reaction is also possible, e.g., $2O_3 \longrightarrow 3O_2$ Rate = $k[O_3]^2[O_2]^{-1}$ Order w.r.t to O_2 is -1.	Molecularity can never be negative.		
6.	Types of reactions depending upon orders	Types of reactions depending upon molecularity		
	(i) Zero order reaction (i) $H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl$ (ii) $2NH_3 \xrightarrow{Pt} N_2 + 3H_2$	(i) Unimolecular reaction, $N_2O_4(g) \longrightarrow 2NO_2(g)$		
<u>II 22</u>	(ii) First order reaction (1) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ (II) Radioactive disintegration (III) Inversion of cane sugar.	(ii) Bimolecular reactions, $2HI(g) \longrightarrow H_2(g) + I_2(g)$ (iii) Termolecular reactions, $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$		
	 (iii) Second order reaction (i) 2HI → H₂ + I₂ (II) Alkaline hydrolysis of ester (saponification) 	*		
	(iv) Third order reaction $2NO + O_2 \longrightarrow 2NO_2$			

Integrated Rate Equation for Zero Order Reactions

$$k_0 = \frac{1}{t} \{ [A]_0 - [A] \}$$

[where, $[A]_0$ is initial concentration and [A] is final concentration]

$$t = t_{y_2}$$
 when $[A] = \frac{[A]_0}{2}$

Half-life period, $t_{1/2} = \frac{[A]_0}{2k_0}$

Units of rate constant, $k_0 = \text{mol } \mathbf{L}^{-1} \mathbf{s}^{-1} = \text{units of rate}$

For zero order gaseous reactions,

$$k_0 = \frac{1}{t} [p_0 - p]$$
 and $t_{1/2} = \frac{p_0}{2k_0}$

Integrated Rate Equation for First Order Reactions

$$k_{1} = \frac{2.303}{t} \log \frac{[A]_{0}}{[A]}$$
$$[A] = [A]_{0} e^{-k_{1}t}$$

 $Half\text{-life period } (t_{1/2): \ It \ is \ concentration \ independent \ term.}$

$$t = t_{1/2}, [A] = \frac{[A]_0}{2}$$

Amount of a substance after *n* half-lives = $\frac{[A]_0}{2^n}$ 0.698

$$t_{1/2} = \frac{0.694}{k_1}$$

For such reactions, $t_{75\%} = 2 \times t_{50\%}$

$$t_{99.9\%} = 10 \times t_{1/2}$$

All radioactive changes follow the first order kinetics. Integrated rate equation for first order gaseous reactions,

Initial pressure $p_0 \operatorname{atm} 0 0$ Pressure at $t \quad [p_0 - p] \operatorname{atm} p \operatorname{atm} p \operatorname{atm} p$ $k_1 = \frac{2.303}{t} \log \frac{p_0}{(2p_0 - p_t)}$

For first order chemical reactions,

$$CH_{3}COOC_{2}H_{5} + H_{2}O \xrightarrow{H^{+}} CH_{3}COOH + C_{2}H_{5}OH$$
$$k_{1} = \frac{2.303}{t} \log\left(\frac{V_{\infty} - V_{0}}{V_{\infty} - V_{t}}\right)$$

(V_o, V_t, and $_{\infty}$ are the volumes of NaOH solution used for the titration of same volume of the reaction mixture after times 0, t and ∞ respectively.)

Pseudo First Order Reaction

Chemical reactions which appear to be of higher order but actually are of the lower order are called pseudo order reactions. In case of pseudo first order reaction, chemical reaction between two sr" stances takes place and one of the reactant is present in execess. e.g., hydrolysis of ester.

 $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$ So, in this reaction,

Rate =
$$k [CH_3COOC_2H_5]$$

For chemical reaction,

$$C_{12}H_{22}O_{11} + H_{2}O \xrightarrow{H^{+}} C_{\theta}H_{12}O_{\theta} + C_{\theta}H_{12}O_{\theta}$$
glucose
fructose
$$k = \frac{2.303}{t} \log\left(\frac{r_{0} - r_{\infty}}{r_{t} - r_{\infty}}\right)$$

 $[r_0 r_t, and r_{\infty}]$. are the polarimetric readings at t = 0, t and ∞ , respectively.]

Methods to Determine Order of Reaction

(i) Graphical method



(ii) Initial rate method In this method, the order of a reaction is determined by varying the concentration of one of the

reactants while others are kept constant.

(iii) Integrated rate law method In this method out different integrated rate equation which gives the most constant value for the rate constant corresponds to a specific order of reaction.

(iv) Half-life period $(t_{1/2})$ method In general half-life period $(t_{1/2})$ of a reaction of nth order is related to initial concentration of the reactant as



This method is employed only when the rate law involved only one concentration term.

(v) Ostwald's isolation method This method is employed in determining the order of complicated reactions by isolating one

of the reactants so far as its influence on the reaction rate is concerned.

Temperature Dependence of Rate of a Reaction

For every 10°C rise in temperature, the rate of reaction becomes double, but only 16% collisions increases. It can be explained by Arrhenius equation.

Temperature coefficient is the ratio of rate constant of a reaction at two temperature differing by 10. Temperature selected are usually 298 K and 308 K

Temperature coefficient = $\Re_t + 10/\Re_t \approx 2$ to 3

Arrhenius Equation

Arrhenius equation is a mathematical expression to give a quantitative relationship between rate constant and temperature, and the expression is



where, A = frequency or Arrhenius factor. It is also called pre-exponential factor

R = gas constant

 $E_a = activation energy$

Activated complex (or transition state)

Activated complex is the highest energy unstable intermediate between the reactants and products and gets decomposed immediately (having very short life), to give the products. In this state, bonds of reactant are not completely broken while the bonds of products are not completely formed.



Threshold energy (E_T) The minimum amount of energy which the reactant must possess in order to convert into products is known as threshold energy.

Activation energy (E_a) The additional amount of energy, required by the reactant so that their energy becomes equal to the threshold value is known as activation energy.

 $\Rightarrow E_a = E_T - E_R$

Lower the activation energy, faster is the reaction.

Different reactions have different rates because their activation energies are different.

Larger the value of Eo, smaller the value of rate constant and greater is the effect of a given temperature rise on K

Important points about Arrhenius equation

(i) If \Re_2 and \Re_1 are rate constant at temperature T_2 and T_1 ; then

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

ii) Fraction of molecules with energy equal to or greater than the activation energy is called Boltzmann factor and is given by

$$x = \frac{n}{N} = e^{-E_{\alpha}/RT}$$
$$\log x = \frac{-E_{\alpha}}{2.303 RT}$$

(iii) E_a is constant for a particular reaction.

(iv) E_a does't depend on temperature, volume, pressure, etc., but gets affected by catalyst.

In the Arrhenius equation, when $T \rightarrow \infty$ then $\Re = Ae^{\circ} = A$ when $E_a = 0, k = A$ and the rate of reaction becomes independent temperature.

Role of Catalyst in a Chemical Reaction

A catalyst is a chemical substance which alters the rate of a reaction WIthout itself undergoing any permanent chemical change.

In the chemical reactions, catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence. lowering the potential energy barrier as shown.



In the presence of catalyst, activation energy decreases and hence.

$$\frac{k_P}{k_a} = e^{(E_a - E_P)RT} = e^{\Delta E/RT}$$

where, P denotes presence of catalyst and a denotes absence of catalyst.

Theory of Reaction Rates

Collision Theory

According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur, when molecules collide with each other.

The number of collisions between the reacting molecules taking place per second per unit volume is known as collision frequency (Z_{AB}) .

But only those collisions in which the colliding species are associated with certain minimum amount of energy and collide in proper orientation result in the product formation, such collisions are called **fruitful collisions or effective collision**.

Here, rate = -(dv/dt) = collision frequency x fraction of effective collision

 $= Z_{AB} \ x \ f = Z_{AB} \ x \ e^{-E_{a}/RT}$

where, Z_{AB} represents the collision frequency of reactants, A and B $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .

So, to account for effective collisions, another factor, P called the probability or steric factor is introduced.

So, rate = $PZ_{AB}e^{-E/RT}_{a}$

The Activated Complex Theory or Transition State Theory

Reactants \Leftrightarrow Activated complex \rightarrow Products

This theory is based on the fact that bond cleavage and bond formation, involved in a chemical reaction, must occur simultaneously. Hence, the reactants are not converted directly into the products. There is an energy barrier or activated complex [intermediate product with partially formed bond] between the reactants and products. The reactants must cross this energy barrier before converting into products. The height of the barrier determines the threshold energy.

Photochemical Reactions

Chemical reactions, that occur on exposure to visible radiation are called photochemical reactions.

- 1. The rate of a photochemical reactions is affected by the the intensity of light.
- 2. Temperature has little effect on photochemical reactions.

Quantum yield or quantum efficiency of a photochemical reaction,

 φ = (number of reactant molecules reacting in a given time / number of photons (quanta) of light absorbed ill the same time)

Chemistry Notes for class 12 Chapter 6 General Principles and Processes of Isolation of Elements

Earth crust is the source of many elements. Out of these elements, 70% are metals. Aluminium is the most abundant metal of earth crust and iron comes second. The percentage of different elements in earth crust are

O-49%, Si-26%, Al-7.5%, Fe-4.2%, Ca-3.2%, Na-2.4%, K-2.3%, Mg-2.3%, H-1%

Metals occur in two forms in nature (i) in native state (ii) in combined state, depending upon their chemical reactivities.

Native State

Elements which have low chemical reactivity or noble metals having least electropositive character are not attacked by oxygen. moisture and CO_2 of the air. These elements, therefore, occur in the free state or in the native state, e.g., Au, Ag, Pt, S, O, N, noble gases, etc.

Combined State

Highly reactive elements such as F, CI, Na, K, etc., occur in nature combined form as their compounds such as oxides, carbonates sulphides. halides, etc.

Hydrogen is the only non-metal which exists in oxidised form only.

Minerals and Ores

The naturally occurring substances in the form of which the metals occur in the earth crust are called minerals.

Every mineral is not suitable for the extraction of the metal. The mineral from which the metal is economically and conveniently extracted is called an ore.

Thus, all ores are minerals but all minerals are not ores.

Combined state	Element	Ore/mineral			
Oxides	Fe	Haematite (Fe ₂ O ₃), Magnetite (Fe ₃ O ₄), Limonite (Fe ₂ O ₃ · 3H ₂ O), Chromite (FeO · Cr ₂ O ₃)			
	AI	Bauxite (Al ₂ O ₃ · 2H ₂ O), Diaspore (Al ₂ O ₃ · H ₂ O), Corundum (Al ₂ O ₃)			
7	Mn	Pyrolusite (MnO ₂)			
	Zn	Zincite (ZnO)			
2 V	Ті	Rutile (TiO ₂)			
	Cu	Cuprite (Cu ₂ O)			
	Sn	Cassiterite or tin stone (SnO2)			
Carbonates	Ca	Calcite (CaCO ₃)			
	Mg	Magnesite (MgCO ₃)			
	Ca, Mg	Dolomite (CaCO ₃ · MgCO ₃)			
	Cu	Malachite [CuCO3 · Cu(OH)2]			
	Zn	Calamine (ZnCO ₃)			
	Fe	Siderite or spathic ore (FeCO ₃)			
	Pb	Cerrusite (PbCO ₃)			
	Au	Azurite [2CuCO3 · Cu(OH)2]			
Sulphides	Fe	Iron pyrite (FeS2)			
	Cu	Copper glance (CuS ₂)			
	Cu,Fe	Copper pyrite or chalcopyrite (CuFeS ₂)			
	Hg	Cinnabar (HgS)			
	Zn	Zinc blende (ZnS)			
	Pb	Galena (PbS)			
	Ag	Argentite or silver glance (Ag ₂ S)			
Halides	Na	Common salt or Rock salt (NaCl)			
	AI .	Cryolite (Na ₃ AIF ₆)			
	K, Mg	Carnallite (KCI · MgCl ₂ · 6H ₂ O)			
	Ag	Horn silver (AgCi)			

Gangue or Matrix

Impurities associated with ores are called gangue or matrix.

Metallurgy

The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

Types of Metallurgical Processes

- 1. Pyrometallurgy Extraction of metals takes place at very high temperature. Cu, Fe, Zn, Sn, etc .. are extracted by this method.
- 2. Bydrometallurgical process In this method, metals are extracted by the use of their aqueous solution. Ag and Au are extracted by this method.
- 3. Electrometallurgical process Na, K, Li, Ca, etc., are extracted from their molten salt solution through electrolytic method.

Steps Involved in Metallurgy

Following steps are involved in the metallurgy :



Crushing of the Ore

The big lumps of ore are crushed into smaller pieces with the help of jaw-crushers. The process of grinding the crushed ore into fine powder with the help of the stamp mills is called pulverisation.

Concentration of Ores

Removel of unwanted materials (e.g., sand. clays, etc.) from the ore is known as ore concentration, ore dressing or ore benefaction. It can be carried out by various ways depending upon the nature of the ore.

Hydraulic Washing/Gravity Separation/Levigation

The process by which lighter earthy impurities are removed from the heavier ore particles by washing WIth water is called levigation. The lighter impurities are washed away. Thus. this method is based on the difference in the densities (specific gravities) of ore and gangue.

This method is commonly used for oxide ores such as haematite, tin stone and native orcs of Au, Ag, etc.

Froth Floatation

This method is used for the concentration of sulphide ores. This method is based on the preferential wetting of ore particles by oil and that of gangue by water .. As a result. the ore particles become light and rise to the top in the form of froth while the gangue particles become heavy and settle down. Thus, adsorption is involved in this method.

The froth can be stabilised by the addition of stabilisers (aniline or cresols).

Activator They activate the floating property of one of the component of the ore I and help in the separation of different minerals present in the same ore $(CuSO_4 is used as activator.)$

Depressants These are used to prevent certain types of particles from forming the froth with air bubbled, e.g., NaCN can be used as a depressant in the separation of ZnS and PbS ores. KCN is an another depressant.

Collectors It increases the non-wettability of ore particles by water, e.g., pine oils, xanthates and fatty acids.

Electromagnetic Separation

This method of concentration is employed when either the ore or the Impurities associated with it are magnetic in nature. e.g., chromite, $FeCr_2O_4$, containing magnetic SiliCIOUS gangue and wolframite FeWO₄, Containing cassiterite, $8nO_4$ (non-magnetic impurities) can be separated by this method.

Electrostatic Separation

This method is used for the separation of lead sulphide (good conductor) which is charged immediately in an electrostatic field and is thrown away from the roller from zinc sulphide (poor conductor) which is not charged and hence, drops vertically from the roller.

Chemical Method-Leaching

Leaching is the process in which the ore is concentrated by chemical reaction with a suitable reagent which dissolves the ore but not the impurities, e.g., bauxite is leached with a hot concentrated solution of NaOH which dissolves aluminium while other oxides (Fe_2O_3 , TiO_2 , SiO_2), remain undissolved and noble metals (Ag and Au) are leached with a dilute aqueous solution of NaCN or KCN in the presence of air.

and

Al_2O_3 · $2H_2O$ + 2NaOH	\longrightarrow	2NaAlO ₂ + 3 H ₂ O
bauxite		sod. meta aluminate
$Ag_2S + 4NaCN$	\longrightarrow	$2 \operatorname{Na}[\operatorname{Ag}(\operatorname{CN})_2] + \operatorname{Na}_2 S$
argentite	sod. argento cyanide	

Extraction of Crude Metals from Concentrated Ore

The concentrated ore is usually converted to oxide before reduction, as oxides are easier to reduce. Thus, isolation of crude metal from concentrated ore involves two major steps:

- 1. Conversion to oxide.
- 2. Reduction of the oxides to metal.

Conversion to Oxides

(i) Calcination It is the process of converting an ore into its oxides by heating it strongly, below its melting point in a limited supply of air or in absence of air.

During calcination, volatile impurities as well as organic matter and moisture are removed.

 $\begin{array}{ccc} \mathrm{Al}_{2}\mathrm{O}_{3} \cdot 2\mathrm{H}_{2}\mathrm{O} & \xrightarrow{\mathrm{Heat}} & \mathrm{Al}_{2}\mathrm{O}_{3} & + 2\mathrm{H}_{2}\mathrm{O} \\ & & & & \\ \mathrm{CaCO}_{3} & \xrightarrow{\mathrm{Heat}} & \mathrm{CaO} + \mathrm{CO}_{2} \\ & & & \\ \mathrm{CaCO}_{3} \cdot \mathrm{MgCO}_{3} & \xrightarrow{\mathrm{Heat}} & \mathrm{CaO} + \mathrm{MgO} + 2\mathrm{CO}_{2} \end{array}$

Calcination is used for metal carbonates and hydroxides and is carried out in reverberatory furnace.

(ii) **Roasting** It is the process of converting an ore into its metallic oxide by heating it strongly. below its melting point m excess of air. This process is commonly used for sulphide ores and is carried out in blast furnace or reverberatory furnace. Roasting helps to remove the non-metallic impurities and moisture.

 $2\text{ZnS} + 2\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2^{\uparrow}$ $2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2^{\uparrow}$

The furnaces used in calcination and roasting employ refractory materials which resist high temperature and do not become soft.

- Acidic refractories : SiO₂ and SiO₂ + Al₂O₃
- Basic refractories : CaO and MgO
- Neutral refractories : Graphite, chromites. etc.

Heavy metals like Cu. Zn, Fe. So, etc., arc obtained by roasting and smelting.

Reduction of the Oxides to Metal

The roasted or the calcined ore is then converted to the free metal by reduction. Reduction method depends upon the activity of metal.

Metals which are low in the activity series (like Cu, Hg, Au) are obtained by heating their compounds ID air: metals which are in the middle of the activity "cries (like Fe. Zn, Ni, Sn) are obtained by heating their oxides with carbon while metals which are very high in the activity series (e.g., Na, K, Ca, Mg, Al) are obtained by electrolytic reduction method.

(i) Smelting (reduction with carbon) The process of extracting the metal by fusion of its oxide ore with carbon (C) or CO is called smelting. It is carried out in a reverberatory furnace.

 $ZnO + C \longrightarrow Zn + CO\uparrow$ e.g., $Fe_{9}O_{3} + CO \xrightarrow{823 \text{ K}} 2FeO + CO_{9}$ $Fe_{2}O_{3} + 3C \longrightarrow 2Fe + 3CO^{\uparrow}$

During smelting a substance. called flux is added which removes the non-fusible impurities as fusible slag. This slag is insoluble in the molten metal and is lighter than the molten metal. So, it floats over the molten metal and is skimmed off.

Acidic flux For basic impurities, acidic flux is added.

e.g., CaO + SiO₂ \rightarrow CaSiO₃

 $FeO + SiO_2 \longrightarrow FeSiO_3$ acidic flux fusible sla fusible slag

Basic flux For acidic impurities, basic flux is added.

e.g.,

 $SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2^{\uparrow}$ $SiO_2 + MgCO_3 \longrightarrow MgSiO_3 + CO_2 \uparrow$ basic flux fusible slag

In the extraction of Cu and Fe, the slag obtained are respectively FeSiO₃ and CaSiO₃.

The obtained slag is used in road making as well as in the manufacturing of cement and fertilizers.

(ii) Reduction by hydrogen It is done for W or Mo oxide.

 $WO_3 + 3H_2 \xrightarrow{Heat} W + 3H_2O$

iii) Reduction by aluminium It is known as alumino thermic reduction or Gold Schmidt thermite process. Aluminium powder is used for this purpose.

e.g., $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$

Mixture of the oxide and Al i.n the ratio of 3:1 is known as thermite and mixture of $BaO_2 + Mg$ powder acts as ignition powder.

(iv) Auto reduction This is used for reduction of sulphide ores of Pb, Hg, Cu, etc. The sulphide ore is heated in a supply of air at 770-970 K when the metal sulphide is partially oxidised to form its oxide or sulphate which then reacts with the remaining sulphide to give the metal.

e.g.,

 $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$ $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

(v) Reduction by Mg

 $TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti$ (Kroll's process)

vi) Electrolytic reduction or electrometallurgy It is the process of extracting highly electropositive (active) metals such as Na, K, Ca, Mg, Al, etc by electrolysis of their oxides, hydroxides or chlorides in fused state, e.g., Mg is prepared by the electrolysis of fused salt of MgCl₂ (Dow's process).

Thermodynamic Principle in Extraction of Metals

The free energy change (ΔG) occurring during the reduction processes help in deciding the suitable method for reduction.

For the spontaneous reduction of an oxide, halide or sulphide by an element, the essential condition is that there is a decrease in the free energy of the system (-ve ΔG).

More the negative value of ΔG , the higher is the reducing power of an element. ΔG can be given as

 $\Delta G = \Delta H - T \Delta S$

- where, $\Delta H =$ enthalpy change;
- $\Delta G = Gibbs$ free energy
- T = temperature;
- $\Delta S = entropy change$

For the reduction of a metal oxide with a reducing agent, the plot of ΔG° against temperature is studied, which is called **Ellingbam diagram.**



Characteristics of Ellingham Diagram

1. All the plots slope upwards since ΔG° becomes more positive when temperature increases, i.e., stability of oxides decreases.

2. A metal will reduce the oxide of other metals which lie above it in Ellingham diagram, i.e., the metals for which the free energy of formation (ΔG°_{f}) of their oxides is more negative can reduce those metal oxides which has less negative ΔG°_{f}

3. The decreasing order of the negative values of ΔG°_{f} of metal oxides is Ca > Mg (below 1773 K) > AI > Ti > Cr > C > Fe > Ni> Hg > Ag

Thus, AI reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773 K.

Mg can reduce A1₂O₃ below 162 K but above 1023 K, Al can reduce MgO.

4. CO is more effective reducing agent below 1073 K and above 1073 K. coke is more effective reducing agent, e.g., CO reduces F_2O_3 below 1073 K but above it, coke reduces Fe_2O_3 .

Coke reduces ZnO above 1270 K.

Refining or Purification of Crude Metals

Physical Methods

(i) Liquation This method is used for refining the metals having low melting points (such as Sn. Pb, Hg, Bi) than the impurities, The impure metal is placed on the sloping hearth and is gently heated. The metal melts and flows down leaving behind the non-fusible impurrties.

(ii) **Distillation** This is useful for low boiling metals such as Zn, Hg. The impure liquid metal is evaporated to obtain the pure metal as distillate.

(iii) Cupellation

This method is used when impure metal contains impurities of other metals which form volatile oxides.

e.g., traces of lead ore removed from silver (as volatile PbO) by this process.

Chemical Methods

(i) **Poling** This method is used when the impure metal contains impurities of Its own oxide, e.g., CU_2O in blister copper and SnO_2 in impure Sn. The molten impure metal is stirred with green wood poles. At this high temperature, wood liberates gases such as CH_4 which reduces any oxides present in the metal.

(ii) Electro-refining

In this method, impure metal forms the anode while the cathode is a rod or sheet of pure metal. The electrolytic solution consists of a soluble salt of the metal.



On passing electricity, the pure metal gets deposited on the cathode while the insoluble impurities settle down below the anode as anode mud or anode sludge. Metals like Cu, Ag, Au, Cr, Zn, Ni, etc are purified by this method.

(iii) **Zone-refining** This method is based upon the principle of fractional crystallisation, i.e., difference in solubilities of impurities in molten and solid state of metal. Semiconductors like silicon, germanium, gallium arsenide and indium antimonide are purified by this method. Elements of very high purity are obtained by this method.

(iv) Vapour phase refining In this method, crude metal is made free from impurities by first converting it Into its volatile compound by heating with a chemical reagent at low temperature. After this, the volatile compound is decomposed by heating to some higher temperature to give pure metal.

(a) van Arkel method This method is used for preparing ultra-pure metal used in space technology (e.g., Ti, Zr, etc.)

 $\begin{array}{ccc} \mathrm{Ti}(s) + 2\mathrm{I}_{2}(s) & \xrightarrow{523 \mathrm{K}} & \mathrm{Ti}\mathrm{I}_{4}(g) & \xrightarrow{1700 \mathrm{K}} & \mathrm{Ti}(s) + 2\mathrm{I}_{2}(g) \\ & & & & \\ \mathrm{impure} & & & \\ \end{array} \\ \begin{array}{c} \mathrm{Zr}(s) + 2\mathrm{I}_{2} & \xrightarrow{870 \mathrm{K}} & \mathrm{Zr}\mathrm{I}_{4}(g) & \xrightarrow{1800 \mathrm{K}} & \mathrm{Zr}(s) + 2\mathrm{I}_{2}(g) \\ & & & & \\ \mathrm{pure} & & \\ \end{array} \end{array}$

(b) Mond's process It is used for refining of nickel.



(v) Chromatographic method Adsorption chromatography is generally used. The impure metal is dissolved in a suitable solvent and the solution is allowed to run slowly into an adsorbent column packed with alumina (Al_2O_3). The metal and the impurities present are adsorbed at different rates. These are then eluted with suitable eluent (solvent). In this method.

weakly adsorbed component is eluted first and the strongly adsorbed component is eluted afterwards.

Occurrence and Extraction of Some Metals

1. Metal Aluminium (AI)

Occurrence

- 1. Bauxite Al₂O₃.XH₂O
- 2. Cryolite Na₃AlF₆

Common method of extraction Electrolysis of Al_2O_3 dissolved in molten Na_3A1F_6 (neutral flux).

Neutral flux is the neutral compound added to the ore to decrease its melting point and to make it conducting, e.g., CaF_2 , cryolite (Na₃AlF₆) etc.

2. Metal Iron (Fe)

Occurrence

- 1. Haematite Fe_2O_3
- 2. Magnetite FE_3O_4

Common method of extraction Reduction of the oxide with CO and coke in blast furnace.

The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn) and is known as **pig iron.**

Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Wrought iron or **malleable iron** is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide.

 $Fe_2O_2 + 3C \rightarrow 2Fe + 3CO$

3. Metal Copper (Cu)

Occurrence

- 1. Copper pyrites CuFeS₂
- 2. Copper glance Cu_2S

Common method of extraction Roasting of sulphide partially and reduction.

 Cu_2S + FeS is called matte. Blister copper contains 96-98% copper with small amounts of Ag and Au as impurity.

4. Metal Zinc (Zn)

Occurrence

- 1. Zinc blen de or sphalerite-ZnS
- 2. Calamine ZnCO₃
- 3. Zincite ZnO

Common method of extraction Roasting followed by reduction with coke.

The metal may be purified by fractional distillation.

97-98% pure zinc is called spelter.

5. Metal Nickel (Ni)

Occurrence

- 1. Penta landite (Ni, Cu, Fe)S
- 2. Kupfernickel NiAs
- 3. Smaltite (Fe, Co. Ni) As

Common method of extraction Roasting followed by Refining is done by Mond's Process.

Water gas is used as a reducing agent for nickel oxide.

$2NiO + CO + H_2 \longrightarrow 2Ni + CO_2 + H_2O$ water gas

p-BLOCK ELEMENTS

p-BLOCK ELEMENTS

GROUP 15 ELEMENTS : THE NITROGEN FAMILY

Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth. As we go down the group, there is a shift from nonmetallic to metallic through metalloidic character. Nitrogen and phosphorus are non-metal, arsenic and antimony metalloid and bismuth is a typical metal.

Electronic Configuration :

The valence shell electronic configuration of these element is $ns^2 np^3$ the s orbital in these element is completely filled and p orbitals are half- filled, making their electronic configuration extra stable.

Atomic and Ionic Radii :

Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and / or f orbitals in heavier members.

Ionisation Enthalpy:

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half- filled p-orbital electronic configuration and smaller size, the ionisation enthalpy of the group 15 element is much greater than of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is

$\Delta_{i}H_{1} < \Delta_{i}H_{2} < \Delta_{i}H_{3}$ Electronegativity :

The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

Physical Properties:

All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphours are non – metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen, all the elements show allotropy.

Element		N	Р	As	Sb	Bi
Atomic Number		7	15	33	51	83
Atomic Mass		14.01	30.97	74.92	121.76	208.98
Electronic configuration		[He] 2s ² 2p ³	[Ne] 3s ² 3p ³	[Ar] $3d^{10} 4s^2 4p^3$	[Kr] 4d ¹⁰ 5s ² 5p ³	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
Covalent Radius / pm		70	110	120	140	150
lonic Radius / pm a = M ^{3−} , b = M ⁺³		171 ^a	212 ^a	222 ^a	76 ^b	103 ^b
lani-ation antheless	Ι	1402	1012	947	834	703
$/ (k_1 \text{ mol}^{-1})$	II	2856	1903	1798	1595	1610
, (Ko mor)	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9

ATOMIC & PHYSICAL PROPERTIES

Chemical Properties :

Oxidation States and trends in a chemical reactivity :

The common oxidation states of these elements are -3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group, bismuth hardly forms any compound in -3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF₅. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. Phosphours also shows +1 and +4 oxidation states in some oxoacids.

In the case of nitrogen , all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example ,

$$3 \text{ HNO}_2 \longrightarrow \text{ HNO}_3 + \text{H}_2\text{O} + 2 \text{ NO}$$

Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid. However +3 oxidation state in case of arsenic, antimony and bismuth become increasingly stable with respect to disproportionation.

Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding. The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PF_6^{-} .

Anomalous properties of nitrogen :

Nitrogen differs from the rest of the members of this group due to its smaller size , high electronegativity , high ionisation enthalpy and non – availability of d orbitals. Nitrogen has unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C ,O). Heavier elements of this group do not form $p\pi - p\pi$ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms. Consequently , its bond enthalpy (941.1 kJ mol⁻¹) is very high. On the contrary , phosphorus , arsenic and antimony form metallic bonds in elemental state. However , the single N – N bond is weaker than the single P – P bond because of high interelectronic repulsion of the non – bonding electrons , owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four , nitrogen cannot form $d\pi - p\pi$ bonds as the heavier elements can e.g., $R_3P = O$ or $R_3P = CH_2$ (R = alkyl group). Phosphours and arsenic can form $d\pi - p\pi$ bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

(i) Reactivity towards hydrogen :

All the elements of Group 15 form hydrides of the type EH_3 where E = N, P, As, Sb or Bi. Some of the properties of these hydrides are shown in Table. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order

 $NH_3 > PH_3 > AsH_3 > SbH_3 \ge BiH_3$.

Properties of Hydrides of Group 15 Elements

Property	NH ₃	PH ₃	AsH ₃	\mathbf{SbH}_{3}	BiH ₃
Melting point / K	195.2	139.5	156.7	185	-
Boiling point / K	238.5	185.5	210.6	254.6	290
(E – H) Distance / pm	101.7	141.9	151.9	170.7	-
HEH angle (⁰)	107.8	93.6	91.8	91.3	-
$\Delta_{\rm f} {\rm H}^-$ / kJ mol ⁻¹	- 46.1	13.4	66.4	145.1	278
$\Delta_{diss}H^{-}(E - H) / kJ mol^{-1}$	389	322	297	255	_

(ii) Reactivity towards oxygen :

All these elements form two types of oxides : E_2O_3 and E_2O_5 . The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphours are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

(iii) Reactivity towards halogens :

These elements react to form two series of halides : EX_3 and EX_5 . Nitrogen does not form pentahalide due to non – availability of the d – orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF₃ is known to be stable. Trihalides except BiF₃ are predominantly covalent in nature.

(iv) Reactivity towards metals :

These elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

p-BLOCK ELEMENTS

NITROGEN (N):

O PREPARATION:

(i) By heating a mixture of NH_4Cl and $NaNO_2$. N₂ is collected by the downward displacement of water.

* $NH_4Cl + NaNO_2 \xrightarrow{\Delta} NH_4NO_2 + NaCl; NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O$ By treating an aqueous solution of ammonium chloride with sodium nitrate. It is laboratory method of preparation.

- $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + H_2O(\ell) + NaCl_{(aq)}$
- (ii) By heating ammonium dichromate:

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 \uparrow + 4H_2O + Cr_2O_3$$

(iii) By oxidation of ammonia

(A) At lower temperature

(a) $8NH_3(\ell) + 3Cl_2(g) \longrightarrow 6NH_4Cl + N_2\uparrow$

If excess of Cl₂ is used in this reaction, nitrogen trichloride is formed as per the following reaction,

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

Nitrogen trichloride is an explosive substance.

(b) By reation of ammonia with calcium hypochlorite or Br_2

$$4NH_3 + 3Ca(OCI)_2 \longrightarrow 3CaCl_2 + N_2 + H_2O$$

(B) At higher temperature

(v)

By passing ammonia over heated cupric oxide or PbO :

 $2NH_3 + 3CuO \longrightarrow N_2\uparrow + 3Cu + 3H_2O$

(iv) By heating urea with a nitrite in presence of dilute H_2SO_4 :

$$NH_2CONH_2 + 2NaNO_2 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2N_2\uparrow + 3H_2O + CO_2\uparrow$$

By heating urea solution with sodium hypobromite:

$$NH_2CONH_2 + 3NaOBr \xrightarrow{\Delta} N_2\uparrow + 3NaBr + 2H_2O + CO_2\uparrow$$

(vi) By passing nitric oxide and NH₃ over red hot copper gauze:

$$4NH_3 + 6NO \longrightarrow 5N_2\uparrow + 6H_2O$$

- (vii) By passing HNO₃ vapours on red hot copper: $5Cu + 2HNO_3 \longrightarrow 5CuO + N_2^{\uparrow} + H_2O$
- (viii) Very pure nitrogen ; $Ba(N_3)_2 \xrightarrow{\Lambda} Ba + 3N_2$

Sodium azide also gives N_2 on heating.

INDUSTRIAL METHODS OF PREPARATION:

- (i) From liquefied air by fractional distillation : The bp of N_2 is -196°C and that of oxygen is -183°C and hence they can be separated.
- (ii) From producer gas from furnaces : Producer gas is a mixture of CO and N_2 . When the mixture of CO and N_2 is passed over heated CuO, the CO gas is oxidized to CO₂ which is absorbed in alkalies & N_2 remains which is collected in gas cylinders.

O PROPERTIES:

- (i) N_2 is a colourless, odourless gas insoluble in water.
- (ii) It is non-polar covalent and neutral molecule.
- (iii) It is neither combustible nor a supporter of combustion.
- (iv) It is absorbed by heated Mg and Al. The nitrides formed thus react with water to form NH_3 .

$$3Mg + N_2 \longrightarrow Mg_3N_2 (+ 6H_2O) \longrightarrow 3Mg(OH)_3 + 2NH_3 \uparrow$$

 $2Al + N_2 \longrightarrow 2AlN (+ 6H_2O) \longrightarrow 2Al(OH)_2 + 2NH_3 \uparrow$

(v) Reaction with H_2 : At 200 atm and 500°C, and in the presence of iron catalyst and molybdenum promoter, N_2 combines with H_2 reversibly to form ammonia. The process is called Haber's Process and is the industrial method of manufacturing ammonia. The reaction is exothermic.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

(vi) Reaction with oxygen: When air free from CO₂ and moisture is passed over an electric arc at about 2000 K, nitric oxide is formed. This reaction is endothermic.

$$N_2 + O_2 \longrightarrow 2NO$$

Reaction with CaC₂ and BaC₂: At 1100°C, these carbides react with N₂ forming CaCN₂ and Ba(CN)₂ respectively. (vii)

 $CaC_2 + N_2 + \xrightarrow{\Delta} CaCN_2 + C$ (nitrolim, a fertilizer); $BaC_2 + N_2 + \xrightarrow{\Delta} Ba(CN)_2$ CaCN₂ reacts with H₂O in the soil to produce NH₃ gas. NH₃ gas is converted by the nitrating bacteria present in soil into nitrates. (The nitrates are readily absorbed by the plants and meet their requirement of the element nitrogen.) USES :

Ο

- for providing an inert atmosphere during many industrial processes where presence of air or O₂ is to be avoided. (i)
- for manufacture of NH₃ by the Haber's process. (ii)
- for manufacture of HNO₃ by the Birkeland-Eyde process. (iii)
- for manufacture of nitrolim. (iv)

COMPOUNDS OF NITROGEN:

\cap **AMMONIA:**

- Ο **PREPARATION:**
- (i) By the action of any base or alkali on any ammonium salt :

$$NH_{4}Cl + NaOH \xrightarrow{\Delta} NH_{3}\uparrow + NaCl + H_{2}O; \qquad (NH_{4})_{2}SO_{4} + 2NaOH \xrightarrow{\Delta} 2NH_{3}\uparrow + Na_{2}SO_{4} + 2H_{2}O$$
$$NH_{4}NO_{3} + NaOH \xrightarrow{\Delta} NH_{3}\uparrow + NaNO_{3} + H_{2}O; \qquad (NH_{4})_{3}PO_{4} + 3NaOH \xrightarrow{\Delta} 3NH_{3}\uparrow + Na_{3}PO_{4} + 3H_{2}O$$

 $(NH_4)_2SO_4 + CaO \xrightarrow{\Delta} 2NH_3^{\uparrow} + CaSO_4 + H_2O$

This is a general method and is used as a test for ammonium salts.

- By the hydrolsis of metal nitrides like AlN or Mg_3N_2 . (ii) $AlN + NaOH + H_2O \longrightarrow NaAlO_2 + NH_3$
- From oxides of nitrogen: When oxides of nitrogen are mixed with H₂ and the mixture is (iii) passed over heated platinum catalyst, NH₃ gas is evolved.

 $2NO + 5H_2 \longrightarrow 2NH_3^{\uparrow} + 2H_2O$; $2NO_2 + 7H_2 \longrightarrow 2NH_3^{\uparrow} + 4H_2O$

From organic amides: When an organic amide is heated with NaOH solution ammonia is (iv) evolved.

 $CH_3CONH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3^{\uparrow}$

From nitrates and nitrites: When a metal nitrate or nitrite is heated with zinc powder and (v) concentrated NaOH solution ammonia is obtained. The reactions are $NaNO_{2} + 7NaOH + 4Zn \longrightarrow 4Na_{2}ZnO_{2} + NH_{2}\uparrow + 2H_{2}O$

$$NaNO_2 + 3Zn + 5NaOH \longrightarrow 3Na_2ZnO_2 + H_2O + NH_2$$

Thus a nitrite or a nitrate can be identified by this reaction but this test cannot make distinction between them. CP

The ammonia evolved is passed through quick lime to dry it and collected by the downward displacement of air. Ammonia cannot be dried using CaCl₂, P₂O₅, or conc. H₂SO₄ because NH₃ reacts with all of these.

$$CaCl_{2} + 8NH_{3} \longrightarrow CaCl_{2} \cdot 8NH_{3} ; P_{2}O_{5} + 6NH_{3} + 3H_{2}O \longrightarrow 2(NH_{4})_{3}PO_{4}$$
$$H_{2}SO_{4} + 2NH_{2} \longrightarrow (NH_{4})_{2}SO_{4}$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

INDUSTRIAL METHODS OF PREPARATION:

Haber's process : $N_2 + 3H_2 \xrightarrow{500^{\circ}\text{C}, 200 \text{ atm.}}_{\text{Ironoxide}+K_2O\&Al_2O_3}$ $\rightarrow 2NH_3$ (i)

(ii) From destructive distillation of coal: When coal is heated at a high temperature in an iron retort and the distillate is bubbles in water, three substances are obtained:

(a) Tarry black pitch, (b) Liquor ammonia & (c) Coal gas

The liquor ammonia is a concentrated solution of ammonia and ammonium salts. When heated it gives out ammonia. When all the free NH₃ is obtained, the residual liquid is heated with Ca(OH)₂ when ammonium salts get decomposed to liberate further quantity of ammonia.

p-BLOCK ELEMENTS

(iii)	Cyanamide process: CaO + 2C + N ₂ $\xrightarrow{2000^{\circ}\text{C}}$ CaCN ₂ + CO [↑] ; CaCN ₂ + 3H ₂ O \longrightarrow CaCO ₃ + 2NH ₃ [↑]					
PROPF	CRTIES:					
(i) (ii) (iii)	Colourless gas lighter than air. Being basic in nature turns red litmus blue. It acts as a Lewis base Highly soluble in water. The solution is called ammonium hydroxide solution.					
(111)	$\operatorname{Na} + \operatorname{Nn}_3 \xrightarrow{\longrightarrow} \operatorname{Na}\operatorname{Nn}_2 + 1/2 \operatorname{n}_2$ Amides decompose back with water to form NH and NaOH					
(iv)	Annues decompose back with water to form M_{3} and					
(\mathbf{v})	When CL is hubbled in liquor ammonia, nitrogen gas is formed					
(\mathbf{v})	$8NH + 3Cl \longrightarrow 6NH Cl + N^{\uparrow}$					
	With excess of CL it is converted to an explosive substance nitrogen trichloride					
	$NH_{a} + 3Cl_{a} \longrightarrow NCl_{a} + 3HCl$					
(vi)	Cupric oxide and PbO are reduced to metal when NH _a is passed over heated CuO and PbO.					
. /	3^{3} CuO + 2NH ₂ \longrightarrow 3^{3} Cu + 3^{3} H ₂ O + N_{2}^{\uparrow} ; 3^{2} PbO + 2^{3} NH ₂ \longrightarrow 3^{2} Pb + 3^{2} H ₂ O + N_{2}^{\uparrow}					
(vii)	$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 \downarrow (blue) + (NH_4)_2SO_4$					
	$Cu(OH)_2 + (NH_4)_2SO_4 + 3NH_4OH (excess) \longrightarrow [Cu(NH_2)_4]SO_4 (deep blue solution) + 4H_2O$					
	$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 \downarrow (white) + (NH_4)_2SO_4$					
	$Zn(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH (excess) \longrightarrow [Zn(NH_3)_4] SO_4 (colourless solution) + 4H_2O$					
	Similar reactions occur with $CdSO_4$ solution also.					
(viii)	$M(NO_3)_2 + 2NH_4OH \longrightarrow M(OH)_2 \downarrow (white) + 2NH_4NO_3$					
	$MCl_2 + 2NH_4OH \longrightarrow M(OH)_2 \downarrow \text{ (white)} + 2NH_4Cl$					
	(M = Mg, Ca, Sr, Ba, Ra, Sn, Pb)					
(ix)	When NH_4OH solution is added to $AgNO_3$ solution, a brown ppt. is obtained					
	$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O\downarrow (brown) + 2NH_4NO_3 + H_2O$					
Ŧ	Brown ppt of silver oxide formed dissolves in excess ammonium hydroxide forming a soluble complex					
	$Ag_2O + 2NH_4OH \longrightarrow [Ag(NH_3)_2]OH (colourless solution) + 2H_2O$					
	Similarly with mercuric salts, NH ₄ OH forms a white precipitate					
	$HgCl_{2} (aq.) + 2NH_{4}OH \longrightarrow HgNH_{2}Cl \downarrow (white) + NH_{4}Cl + H_{2}O$					
(x)	When liquor ammonia is dropped on heated bleaching powder, nitrogen gas is formed $3Ca(OCl)Cl + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2\uparrow$					
(xi)	$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3 ; \qquad 2NH_3 + CO_2 \xrightarrow{highpressure} NH_2CONH_2 (urea) + H_2O$					
(xii)	When NH ₃ gas is passed into the colourless solution of Nessler's reagent a brown precipitate or coloration is					
	formed. This is a test for NH ₃ gas.					
	$2K_2HgI_4 + 3KOH + NH_3 \longrightarrow H_2N \cdot HgO \cdot HgI \downarrow (brown) + 7KI + 2H_2O$					
(xiii)	$H_2PtCl_6 + 2NH_4Cl \longrightarrow (NH_4)_2 [PtCl_6] \downarrow $ yellow + 2HCl					
USES:	(i) Used as a refrigeration fluid. (ii) For the production of ammonium fertilizers such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea etc. (iii) For removing grease because NH_4OH dissolves grease. (iv) For manufacture of MH_4OH dissolves MH_4OH dissolv					
	HNO_3 by the Ostwald process. (v) As a laboratory reagent. (vi) In the production of artificial rayon, silk, nylon etc.					

(2) OXIDES OF NITROGEN :

Nitrogen forms a number of oxides, N_2O , NO, N_2O_3 , NO₂ or N_2O_4 and N_2O_5 , and also very unstable NO₃ and N_2O_6 . All these oxides of nitrogen exhibit *pf-pf* multiple bonding between nitrogen and oxygen.

p-BLOCK ELEMENTS

Name	<u>Formula</u>	<u>Colour</u>	<u>Remarks</u>
Nitrous oxide	N ₂ O	Colourless (g)	Neutral,+1 oxidation state
Nitric oxide	ŇÔ	Colourless (g)	Neutral, + 2 oxidation state
Dinitrogen trioxide	N_2O_3	Dark blue (s)	Acidic ,+ 3 oxidation state
Nitrogen dioxide	NO ₂	Brown (g)	Acidic, + 4 oxidation state
Dinitrogen tetroxide	N ₂ O ₄	Colourless (s)	Extensively dissociated to NO_2 as
			gas and partly dissociated as liquid, acidic, + 4 oxidation state
Dinitrogen pentoxide	N ₂ O ₅	Colourless (s)	Unstable as gas; ionic solid NO_{2}^{+} ,
	2 5		NO_3^{-} , acidic, +5 oxidation state

PREPARATION:

(i) N_2O is obtained generally by heating NH_4NO_3 with caution.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$
; $2NO + H_2SO_3 \longrightarrow N_2O + H_2SO_4$

(ii) NO is best prepared by the reduction of 8 M HNO₃ with reducing agents like Cu or by reduction of nitrous acid or nitrites by Fe^{2+} or I⁻ ions.

 $\begin{array}{l} 3\mathrm{Cu}+8\mathrm{HNO}_{3} \longrightarrow 3\mathrm{Cu}(\mathrm{NO}_{3})_{2}+2\mathrm{NO}+4\mathrm{H}_{2}\mathrm{O}\\ 2\mathrm{NaNO}_{2}+2\mathrm{FeSO}_{4}+3\mathrm{H}_{2}\mathrm{SO}_{4} \longrightarrow 2\mathrm{NaHSO}_{4}+\mathrm{Fe}_{2}(\mathrm{SO}_{4})_{3}+2\mathrm{NO}+2\mathrm{H}_{2}\mathrm{O}\\ 2\mathrm{NaNO}_{2}+2\mathrm{NaI}+4\mathrm{H}_{2}\mathrm{SO}_{4} \longrightarrow 4\mathrm{NaHSO}_{4}+2\mathrm{NO}+\mathrm{I}_{2}+2\mathrm{H}_{2}\mathrm{O} \end{array}$

(iii) N_2O_3 is obtained as an intense blue liquid or a pale blue solid on cooling an equimolar mixture of NO and NO₂ to 250 K. NO + NO₂ \longrightarrow N_2O_3

On warming, its colour fades due to its dissociation into these two oxides.

(iv) NO₂ can be prepared by reduction of concentrated HNO₃ with Cu or by heating heavy metal nitrates.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O; \qquad 2Pb(NO_3)_2 \xrightarrow{673K} 2PbO + 4NO_2 + O_2$$

 N_2O_5 is an anhydride of HNO₃. It is best prepared by dehydrating HNO₃ by P_4O_{10} at low temperatures.

$$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_5 + 4\text{HPO}_3$$

PROPERTIES:

(v)

Oxides of nitrogen are all oxidizing agents, N_2O even supporting the combustion of S and P. NO which is thermally more stable, supports the combustion of Mg and P but not of S. Sulphur flame is not hot enough to decompose it.

N₂O is isoelectronic with CO₂ and also has a linear structure. However, unlike CO₂, N₂O has a small dipole moment.

NO has a total of 15 electrons. It is impossible for all of them to be paired and hence this is an odd electron molecule. In the gaseous state, it is paramagnetic. However, the liquid and the solid states are diamagnetic because loose dimmers are formed canceling out the magnetic effects of unpaired electrons.

The brown ring formed in the test for nitrates is due to the formation of a complex of iron, $[Fe(H_2O)_5NO]^{2+}$.

 NO_2 with 23 electrons is again an odd electron molecule. In the gaseous state it is paramagnetic. On cooling, the gas condenses to a brown liquid and eventually to a colourless solid both of which are diamagnetic due to dimerisation.

Liquid N_2O_4 undergoes self-ionization to form NO^+ and NO_3^- ions and therefore, it has been extensively studied as a non-aqueous solvent.

$$\begin{array}{ccc} & & N_2O: & (a) \ Reduction: Cu(hot) + N_2O \longrightarrow CuO + N_2 \\ & & (b) \ Oxidation: 2KMnO_4 + 3H_2SO_4 + 5N_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 10NO \\ & & (c) \ Supporter \ of \ combustion: Mg + N_2O \longrightarrow MgO + N_2 \\ \hline \\ & & \text{NO:} & (a) \ Supporter \ of \ combustion: S + 2NO \longrightarrow SO_2 + N_2 \end{array}$$

(b) Oxidising properties (Reduction of NO) : $5H_2 + 2NO \xrightarrow{Pt-black} 2NH_3 + 2H_2O$ $SO_2 + H_2O + 2NO \longrightarrow H_2SO_4 + N_2O$ $H_2S + 2NO \longrightarrow H_2O + N_2O + S$ (c) Reducing properties (oxidation of NO) : $2NO + X_2 \longrightarrow 2NOX$ $6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3$ $N_2O_3 + KOH \longrightarrow 2KNO_2 + H_2O$ Ø N_2O_3 : (a) (b) It is anhydride of HNO_2 : $\begin{array}{ccc} 2HNO_2 & \longrightarrow & N_2O_3 + H_2O \\ \mbox{(c) with concentrated acids, form nitrosyl salts} \end{array}$ $N_2O_3 + 2HClO_4 \longrightarrow 2NO[CIO_4] + H_2O$ Ŧ NO_2 : It behaves both like HNO₂ and HNO₃. It behaves like HNO₂ as a reducing agent and like HNO₃ as an oxidising agent according to following reactions respectively. $2KMnO_4 + 3H_2SO_4 + 10NO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 10HNO_3$ $SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO$ * N_2O_4 is mixed anhydride of HNO₃ and HNO₂ N_2O_5 : (a) $2N_2O_5 \xrightarrow{\Delta} 2N_2O_4 + O_2$ æ $N_2O_5 + 2NaOH \longrightarrow 2NaNO_3 + H_2O$ (b) $N_2O_5 + I_2 \longrightarrow 10 NO_2 + I_2O_5$ (c)

(3) Oxyacids of nitrogen : (A) NITROUS ACID (HNO₂) : PREPARATION:

N

(i) By acidifying an aqueous solution of a nitrite

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4$$

(ii) By passing an equimolar mixture of NO and NO₂ into water:

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2$$

PROPERTIES:

- (i) It is an unstable, weak acid which is known only in aqueous solution.
- (ii) On trying to concentrate, the acid decomposes as given below.

 $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$

(iii) Nitrous acid and nitrites are good oxidizing agents and convert iodides to iodine, ferrous salts to ferric, stannous to stannic and sulphites to sulphates eg.

 $2\text{KI} + 2\text{HNO}_2 + 2\text{HCl} \longrightarrow 2\text{H}_2\text{O} + 2\text{NO} + 2\text{KCl} + \text{I}_2$

- (iv) With strong oxidizing agents like $KMnO_4$ nitrous acid and nitrites function as reducing agents and get oxidized to NO_3^- ions: $2KMnO_4 + 5KNO_2 + 6HCl \longrightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCl$
- (iii) Nitrite ion is a good coordinating agent. Both nitrogen and oxygen have lone pairs capable of forming coordinate bond with metal ions. Nitrite ion can coordinate either through N or through O.(It is an ambidentate ligand) This generates linkage isomerism. Analogous organic derivatives are also known, the nitrites, RONO and the nitro compounds RNO₂ where R is any alkyl or aryl group.

(B) NITRIC ACID (HNO₃) : PREPARATION :

 $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

(ii) HNO_3 is now almost exclusively manufactured by the Ostwald process. In this process NH_3 is catalytically oxidized to NO over a Pt-Rh catalyst at 1200K.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O \Delta H = -904 \text{ kJ}$$

About 96 to 98% of NH_3 is converted into NO. The mixture is then diluted with air. NO combines with O_2 to give NO_2 which is absorbed in water to give HNO_3 and NO, which is then recycled.

 $2NO + O_2 \longrightarrow 2NO_2; \quad 3NO_2 + H_2O \longrightarrow 2HNO_3 + NO_3$

Nitric acid can be concentrated to 68 % by distillation, when a **constant boiling mixture** is formed. More concentrated acid can be made by distilling the mixture with concentrated sulphuric acid.

PROPERTIES:

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Pure nitric acid is colourless liquil (bp 359°C). It decomposes readily in light giving a yellow colour due to the formation of nitrogen dioxide. It is a strong acid and is almost completely dissociated into ions in solution.

(ii) Thermal stability

$$4\text{HNO}_3 \xrightarrow{\Delta} 2\text{H}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$

(iii) Oxidising properties

 $2\text{HNO}_3 \text{ (conc.)} \longrightarrow \text{H}_2\text{O} + 2\text{NO}_2 + [\text{O}] \quad ; \qquad 2\text{HNO}_3 \text{ (dilute)} \longrightarrow \text{H}_2\text{O} + 2\text{NO} + 3[\text{O}]$ (a) Oxidises H₂S to sulphur

 $\mathrm{H_2S} + 2\mathrm{HNO_3} \ (\mathrm{conc.}) \longrightarrow 2\mathrm{H_2O} + 2\mathrm{NO_2} + \mathrm{S} \downarrow \ ; \quad 3\mathrm{H_2S} + 2\mathrm{HNO_3} \ (\mathrm{dilute}) \longrightarrow 4\mathrm{H_2O} + 2\mathrm{NO} + 3\mathrm{S} + 2\mathrm{HNO_3} \ (\mathrm{H_2O} + 2\mathrm{HO} + 2\mathrm{HO$

(b) Oxidises SO_2 to H_2SO_4

 $SO_2 + 2HNO_3 \text{ (conc.)} \longrightarrow H_2SO_4 + 2NO_2 \uparrow;$ $3SO_2 + 2H_2O + 2HNO_3 \text{ (dilute)} \longrightarrow 3H_2SO_4 + 2NO_3 \text{ (similarly oxidises ferrous salts to ferric salts, halogen acids to respective halogens.$

(iv) Reaction with non-metals.

$$C + 4HNO_3 \longrightarrow H_2CO_3 + H_2O + 4NO_2$$
; $S + 6HNO_3 \longrightarrow H_2SO_4 + 2H_2O + 6NO_2$

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 4H_2O + 10NO_2$$
; $P + 5HNO_3 \longrightarrow H_3PO_4 + H_2O + 5NO_2$

These reactions are given with conc. HNO₃.

(v) Reaction with metals :(A) Metals that are more electropositive than hydrogen

(a) Action on zinc or Fe :

p-BLOCK ELEMENTS

- As concentrated nitric acid (80%) behaves as an oxidizing agent and metals such as Al, Fe, Cr etc are rendered passive due to the formation of a tenacious layer of insoluble oxide on the metal surface.
- [∞] Noble metals such as Au, Pt, Rh, and Ir are not attacked by nitric acid. However a 1:3 mixture of conc. HNO₃ and conc. HCl known as aqua regia dissolves Au and Pt as it contains free(atomic) chlorine: HNO₃ + 3HCl → 2H₂O + 2Cl + NOCl; Au + 3Cl + HCl → HAuCl₄; Pt + 4Cl + 2HCl → H₂PtCl₆ Brown ring test : 2HNO + 2H SO + 6EaSO → 2Ea (SO) + 2NO + 4H O

$$2\text{HNO}_3 + 3\text{H}_2\text{SO}_4 + 6\text{FeSO}_4 \longrightarrow 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O}$$

FeSO₄ + NO + 5H₂O \longrightarrow [Fe(H₂O)₅ NO]SO₄

2. PHOSPHORUS :

It is a very reactive non-metal. It catches fire in air. It occurs in nature in the form of stable phosphates. (Animal bones also contain calcium phosphate (58 %)). The important minerals are:

(i) Phosphorite, $Ca_3(PO_4)_2$ (ii) Chloraptite, $Ca_3(PO_4)_2CaCl_2$ (iii) Fluoraptite, $Ca_3(PO_4)_2CaF_2$ (iv) Vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$ (v) Redonda phosphate, $AlPO_4$

ALLOTROPIC FORMS OF PHOSPHORUS:

(i) White or yellow phosphorus (\mathbf{P}_4) : **PDFPA PATION**.

PREPARATION:

 $2Ca_3(PO_4)_2$ (From bone-ash) + 10C + 6SiO₂ $\xrightarrow{\Delta}$ 6CaSiO₃ + 10CO + P₄(s)

PROPERTIES:

It is white-to-transparent and soft waxy solid. Its density is 1.8 g/cc at 20°C . Its mp and bp are 44°C and 287°C respectively. It is soluble in CS₂ but insoluble in water. It glows in dark due to slow oxidation producing yellowish-green light. This phenomenon is called phosphorescence

 $P_4 + 5O_2 \rightarrow P_4O_{10}$

White phosphorus is poisonous. It turns yellow after some time; it is called yellow phosphorus. It undergoes oxidation in the presence of air which slowly raises its temperature and due to its low ignition temperature (~ 30°C) after a few moments it catches fire spontaneously. Due to this reason, it is strored under water.



As readily oxidised, acts as a reducing agent.

$$\begin{array}{l} P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O; \qquad 3CaO + 8P + 9H_2O \longrightarrow 3Ca(H_2PO_2)_2 + 2PH_3\\ P_4 + 3CuSO_4 + 6H_2O \longrightarrow Cu_3P_2 + 2H_3PO_3 + 3H_2SO_4\\ Cu_3P_2 + 5CuSO_4 + 8H_2O \longrightarrow 8Cu + 5H_2SO_4 + 2H_3PO_4 \end{array}$$

Colloidal solution of gold may be prepared by reducing a solution of gold chloride with phosphours dissolved in ether.(ii) Red phosphorus:

PREPARATION:

When white phosphorus is heated in the atmosphere of CO_2 or coal gas at 573 K red phosphorus is prodouced. This red phosphorus may still contain some white phosphorus which is removed by boiling the mixture with NaOH where white phosphorus is converted into PH₃ gas but red phosphorus remains inert.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3(g) + 3NaH_2PO_2$$

It is also prepared by heating white phosphorus with a few crystals of iodine catalyst at 250°C under high pressure in absence of air.

PROPERTIES :

It is a red crystalline solid having a density of 2.2 g/cc. It is less reactive than white phosphorus and does not dissolve in liquid CS₂. It does not catch fire at room temperature because its ignition temperature is 260° C.
It is a polymeric substance forming linear chains like this.



(iii) Black phosphorus:

It has two forms α -black phosphorus and β -black phosphorous (a) α -black phosphorous

$$P(red) \xrightarrow{\text{insulated}} P(\alpha\text{-black})$$

α-black phosphorous structure is not definite and is non conductor of electricity.

(b) β -black phosphorous

 $P(white) \xrightarrow[Highpressure]{473 \text{ K}} P(\beta\text{-black})$

 β -black phosphorous is an electrical conductor resembling graphite in this respect and also in its flakiness and luster. It is insoluble in CS₂. It has a layered structure like graphite.



(iv) Brown phosphorus:

Above 1600°C, P_4 molecules begin to dissociate into P_2 molecules. Rapid cooling of this vapour gives brown phosphorus which probably contains P_2 molecules.

CHEMICAL PROPERTIES OF PHOSPHORUS:

Reactivity of the various allotropic forms of phosphorus towards other substances decreases in the order:
 Brown > white > red > black, the last one being almost inert.

Apart from their reactivity difference, all the forms are chemically similar.

(i) Action of air :

White phosphorus burns in air to form phosphorus trioxide and pentoxide.

$$_{4} + 5O_{2} \longrightarrow 2P_{2}O_{5}$$
; $P_{4} + 3O_{2} \longrightarrow 2P_{2}O_{3}$

Red and other forms of phosphorus also burn in air or oxygen but on heating.

(ii) Action of non-metals:

Ρ

When heated with non-metals phosphorus forms compounds PX_3 , PX_5 , P_2S_3 and P_2S_5 .

$$2P + 3X_2 \longrightarrow 2PX_3$$
, $2P + 5X_2 \longrightarrow 2PX_5$ (where X = Cl, Br, and I.)

(iii) Action with metals:

Alkali metals when heated with white phosphorus in vacuum produce alkali metal phosphide, which react with water to form phosphine gas.

 $3M + P \xrightarrow{\Delta} M_3P \quad M_3P + 3H_2O \xrightarrow{\Delta} 3MOH + PH_3^{\uparrow} \{ where M = Na, K etc. \}$

(iv) Action of NaOH:

When white phosphorus is heated with NaOH solution, phosphine gas is evolved.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3\uparrow$$

(v) Action of conc. HNO_3 :

When heated with conc. HNO_3 , phosphorus is oxidized to H_3PO_4 .

 $P + 5NHO_{3} \longrightarrow H_{3}PO_{4} + 5NO_{2}\uparrow + H_{2}O$

(vi) Action of conc. H_2SO_4 :

When heated with conc. H₂SO₄ phosphorus is oxidized to H₃PO₄.

$$2P + 5H_2SO_4 \xrightarrow{\Delta} 2H_3PO_4 + 5SO_2\uparrow + 2H_2O$$

Conversion of white phosphorus to red phosphorus and red phosphorus to white phosphorus.

Heat in presence of I₂ catalyst at 250°C and high pressure in absence of air

White phosphorus Red phosphorus

Heat above 250°C in presence of inert gas and condense in water

COMPOUNDS OF PHOSPHORUS : (1) PHOSPHINE : PREPARATION:

(i) By heating white phosphorus with NaOH solution in presence of coal gas. Phosphine gas is collected by the downward displacement of water.

$$4P + 3NaOH + 3H_2O \xrightarrow{\Delta} 3NaH_2PO_2 + PH_2\uparrow$$

- Coal gas is used to prevent oxidation of phosphine. The phosphine gas is contaminated with a combustible gas P_2H_4 . It is separated from PH_3 by passing the gaseous mixture through a freezing mixture whereupon P_2H_4 condenses to a liquid and PH_3 is collected by the downward displacement of air. Pure PH_3 does not burn in air.
- (ii) By the action of alkalies on phosphonium salts:

$$PH_{4}I + NaOH \xrightarrow{\Delta} NaI + PH_{3}\uparrow + H_{2}O$$

(iii) By the action of dil. HCl or dil. H_2SO_4 on metal phosphides.

$$Na_{3}P + 3HCl \longrightarrow 3NaCl + PH_{3}\uparrow; \qquad AlP + 3HCl \longrightarrow AlCl_{3} + PH_{3}\uparrow$$
$$2Na_{3}P + 3H_{2}SO_{4} \longrightarrow 3Na_{2}SO_{4} + 2PH_{3}\uparrow$$

(iv) $H_3PO_2 + 4H \xrightarrow{Zn/HCl} PH_3 + 2H_2O$

PROPERTIES :

P

(i) It is a colourless gas with a smell of rotten fish and is neutral to litmus paper, It is heavier than air and only slightly soluble in water, It is a poisonous gas and acts as a Lewis base.

(ii) Action of chlorine:

It reacts with Cl₂ to form PCl₅.

 $PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

- Similar reaction occurs between heated phosphine and Br₂ and I₂ vapours.
- (iii) Reaction with hydrogen halides: When PH₃ is bubbled in solution of HX, phosphonium halides are formed.

$$PH_2 + HX \longrightarrow PH_4X$$

(iv) Action on $CuSO_4$ solution:

When PH₃ is bubbled in acidic solution of copper sulphate, a black precipitate of copper phosphide is formed.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 \downarrow \{black\} + 3H_2SO_4$$

(v) Reaction with $AgNO_3$ solution:

When PH_3 gas is bubbled in a solution of $AgNO_3$, a yellow precipitate of silver phosphide, Ag_3P , is first formed which later decomposes to black Ag.

$$\begin{aligned} &3\text{AgNO}_3 + \text{PH}_3 \longrightarrow \text{Ag}_3\text{P} \downarrow (\text{yellow}) + 3\text{HNO}_3 \\ &\text{Ag}_3\text{P} + 3\text{AgNO}_3 + 3\text{H}_2\text{O} \longrightarrow 6\text{Ag} \downarrow (\text{black}) + 3\text{HNO}_3 + \text{H}_3\text{PO}_3 \end{aligned}$$

(vi) Reaction with mercuric chloride solution:

When mercuric chloride solution is treated with PH₃ gas, a brownish black precipitate of mercuric phosphide is formed.

 $3\text{HgCl}_2 + 2\text{PH}_3 \longrightarrow \text{Hg}_3\text{P}_2 \downarrow \text{(brownish-black)} + 6\text{HCl}$

* Samples of PH_3 can be dried using quick lime, or NaOH sticks. It cannot be dried by conc. H_2SO_4 because of its reaction with it.

USES:

It is used in making smoke signals and producing smoke screens in battle-fields.

2. OXIDES OF PHOSPHORUS : (A) PHOSPHORUS TRIOXIDE (P₂O₃) :

PREPARATION:

It is prepared by burning phosphorus in a limited supply of oxygen when gaseous P_4O_{10} and P_4O_6 are formed. On lowering the temperature using a condenser, P_4O_6 remains in gaseous form whereas P_4O_{10} condenses as a solid which is stopped by glasswool. On passing the remaining gaseous mixture through freezing mixture, it converts into colourless crystals of P_4O_6 .

PROPERTIES:

(i) It is colourless crystalline solid having mp 23.8°C and bp 178°C.

(ii) It dissolves in cold water to form phosphorus acid. It is thus the anhydride of phosphorus acid.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$

(iii) It dissolves in hot water liberating PH_3

 $2P_2O_3 + 6H_2O \longrightarrow 3H_3PO_4 + PH_3$

(iv) It slowly gets oxidized in air to form
$$P_2O_5$$

 $P_2O_3 + O_2 \longrightarrow P_2O_5$

(v) It burns in Cl₂ gas forming phosphorus oxytrichloride (POCl₃) and phosphoryl chloride (PO₂Cl) $P_2O_3 + 2Cl_2 \longrightarrow POCl_3 + PO_2Cl$

(B) PHOSPHORUS PENTOXIDE (P_2O_5) :

PREPARATION :

It is obtained by burning phosphorus in air.

 $P_4 + 5O_2 \longrightarrow P_4O_{10}$

PROPERTIES:

- (i) It is a white powder acidic in nature and is the anhydride of orthophosphoric acid. Its empirical formula is P_2O_5 and its molecular formula is P_4O_{10} .
- (ii) It sublimes on heating at 250° C.
- (iii) Action of water:

It dissolves in water with hissing sound forming metaphosphoric acid and finally orthophosphoric acid.

$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3; HPO_3 + H_2O \longrightarrow H_3PO_4$$

(iv) Dehydrating power:

It dehydrates conc. H_2SO_4 and conc. HNO_3 to SO_3 and N_2O_5 respectively.

 $2HNO_3 + P_2O_5 \xrightarrow{\text{distillation}} 2HPO_3 + N_2O_5 ; H_2SO_4 + P_2O_5 \xrightarrow{\text{distillation}} 2HPO_3 + SO_3$

USES:

(i) For drying acidic gases

(iii) For the preparation of SO_3 and N_2O_5

(ii) As a dehydrating agent(iv) For the preparation of phosphoric acid

3. OXY-ACIDS OF PHOSPHORUS : (A) PHOSPHORUS ACID (H₃PO₃) : PREPARATION:

(i) By dissolving P_2O_3 in water:

$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3$$

(ii) By hydrolysis of PCl_3 with water:

 $PCl_3 + 3H_2O$ $H_3PO_3 + 3HCl$

The solution containing H_3PO_3 and HCl is heated to 180°C and HCl gas is driven out. The resulting solution on crystallization gives white crystals of H_3PO_3 .

(iii) By heating hypophosphorus acid :

 $3H_3PO_2$ (concentrated solution) $\xrightarrow{40^{\circ}or more} PH_3 + 2H_3PO_3$

PROPERTIES:

- (i) It is a white crystalline solid, soluble in water and having melting point of 74° C.
- (ii) It is a weak acid and a reducing agent
- (iii) When neutralized with bases or alkalies, it forms neutral salts called phosphites which are unstable.

 $H_3PO_3 + 3NaOH \longrightarrow Na_3PO_3 + 3H_2O$

Its basicity is 2 because it has only two replaceable H atoms. The third H atom is not replaceable because it is not connected to oxygen.

- (iv) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$ (Disproportionation)
- (v) $H_3PO_3 + 3PCl_5 \longrightarrow PCl_3 + 3POCl_3 + 3HCl_3$
- (vi) It is a strong reducing agent :

$$2AgNO_3 + H_3PO_3 + H_2O \longrightarrow 2Ag + 2HNO_3 + H_3PO_4$$

$$2\text{HgCl}_2 + \text{H}_3\text{PO}_3 + \text{H}_2\text{O} \longrightarrow \text{Hg}_2\text{Cl}_2 + 2\text{HCl} + \text{H}_3\text{PO}_4$$

(B) ORTHOPHOSPHORIC ACID (H_3PO_4) : PREPARATION:

(i) By heating calcium phosphate with conc. H_2SO_4

 $Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2CaSO_4 + 2H_3PO_4$

 $CaSO_4$ is insoluble. Solution of H_3PO_4 is separated from $CaSO_4$. It is then concentrated by evaporating it at 180°C and dehydrated by conc. H_2SO_4 placed in a vacuum dessicator cooled by freezing mixture. White crystals of H_3PO_4 are thus formed.

(ii) By hydrolysis of PCl₅:

Р

$$PCl_{\epsilon} + 4H_{2}O \longrightarrow H_{2}PO_{4} + 5HCl$$

(iii) By heating white phosphorus with conc. HNO₃:

$$+5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O_3$$

PROPERTIES :

(i) Pure orthophosphoric acid is a white crystalline solid highly soluble in water having melting point of 42°C. It is a weak acid. It forms two acid salts and one normal salt.NaH₂PO₄ is sodium dihydrogen phosphate,Na₂HPO₄ is disodium hydrogen phosphate & Na₃PO₄ is sodium orthophosphate.

(ii) Action of heat :

$$H_3PO_4 \xrightarrow{220^{\circ}C} H_4P_2O_7$$
 (pyrophosphoric acid); $H_4P_2O_7 \xrightarrow{316^{\circ}C} HPO_3$ (metaphosphoric acid)

(iii) Neutralization with alkalies or bases:

$$H_{3}PO_{4} \xrightarrow{\text{NaOH}} \text{NaH}_{2}PO_{4} \text{ (pri. phosphate)} \xrightarrow{\text{NaOH}} \text{NaHPO}_{4} \text{ (sec. phosphate)} \xrightarrow{\text{NaOH}} \text{Na}_{3}PO_{4} \text{ (tert. phosphate)}$$

USES:

It is used as a laboratory reagent and in manufacture of medicines.

GROUP SIXTEEN ELEMENTS : THE OXYGEN FAMILY

Oxygen, sulphur, selenium, tellurium and polonium constitute group 16 of the periodic table. This is sometimes known as group of chalcogens. The name is derived from the greek word for brass and points to the association of sulphur and its congeners with copper. Most copper minerals contain either oxygen or sulphur and frequently the other members of the group.

Occurrence :

Oxygen is the most abundant of all the elements on the earth. Oxygen forms about 46.6% by mass of earth's crust . Dry air contains 20.946% oxygen by volume.

However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as gypsum $CaSO_4.2H_2O$, epsom salt $MgSO_4.7H_2O$, baryta $BaSO_4$ and sulphides such as galena PbS, zinc blende ZnS, copper pyrites $CuFeS_2$. Traces of sulphur occur as hydrogen sulphide in volcanoes.

Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals.

Electronic Configuration :

The elements of group 16 have six electrons in the outermost shell and have $ns^2 np^4$ general electronic configuration.

Atomic and Ionic Radii :

Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small.

Ionisation Enthalpy :

Ionisation enthalpy decrease down the group. It is due to increase in size. However, the element of this group have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods. This is due to the fact that group 15 element have extra stable half-filled p orbitals electronic configurations.

Electron Gain Enthalpy :

Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However from sulphur onwards the value again becomes less negative upto polonium.

Electronegativity :

Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decrease with an increase in atomic number. This implies that the metallic character increase from oxygen to polonium.

Physical Properties :

Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). All these element exhibit allotropy. The melting and boiling points increase with an increase in atomic number down the group. The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exist as diatomic molecules (O_2) whereas sulphur exists as polyatomic molecule (S_o).

ATOMIC & PHYSICAL PROPERTIES :

Element		0	S	Se	Те
Atomic Number		8	16	34	52
Atomic Mass		16	32.06	78.96	127.6
Electronic configuration		[He] 2s ² 2p ⁴	[Ne] 3s ² 3p ⁴	[Ar] 3d ¹⁰ 4s ² 4p ⁴	[Kr] 4d ¹⁰ 5s ² 5p ⁴
Covalent Radius / pm		74	103	119	142
Ionic Radius X ⁻² / pm		140	184	198	221
lonization enthalpy / (kJ mol ⁻¹)	Ι	1314	1000	941	869
	II	3388	2251	2045	1790
Electronegativity		3.5	2.44	2.48	2.01
Density/[g cm ⁻³ (293 K)]		1.32	2.06	4.19	6.25
Melting point / K		54	393	490	725
Boiling point / K		90	718	958	1260

Chemical Properties :

Oxidation states and trends in chemical reactivity :

The elements of group 16 exhibit a number of oxidation states. The stability of -2 oxidation state decreases down the group. Polonium hardly shows -2 oxidation states. Since electronegativity of oxygen is very high, it shows only negative oxidation states as -2 except in the case of OF_2 where its oxidation states is + 2. Other elements of the group exhibit + 2 + 4 + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation in their compounds with oxygen and +6 oxidations state with fluorine. The stability of +6 oxidation state decreases down the group and stability of +4 oxidation state increases (inert pair effect). Bonding in +4 and + 6 oxidation states are primarily covalent.

Anomalous behaviour of oxygen :

The anomalous behaviour of oxygen, like other member of p-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not found in H_2S .

The absence of d orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two. On the other hand, in case of other elements of the group, the valence shell can be expanded and covalence exceeds four.

(i) **Reactivity with hydrogen :** All the elements of group 16 form hydrides of the type H_2E (E = S, Se., Te, Po). Some properties of hydrides are given in Table. Their acidic character increases from H_2O to H_2Te . The increase in acidic character can be explained in terms of decrease in bond (H-E) dissociation enthalpy down the group. Owing to the decrease in bond (H-E) dissociation enthalpy down the group, the thermal stability of hydrides also decreases from H_2O to H_2Po . All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te .

Table : Properties of Hydrides of Group 16 Elements

Property	H ₂ O	H₂S	H₂Se	H₂Te
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
∆ _f H/kJ mol ⁻¹	-286	-20	73	100
$\Delta_{diss} H (H-E)/kJ mol^{-1}$	463	347	276	238
Dissociation constant ^a	1.8 × 10 ⁻¹⁶	1.3 × 10 ⁻⁷	1.3 × 10 ⁻⁴	2.3 × 10 ⁻³

- (ii) **Reactivity with oxygen :** All these elements form oxides of the EO₂ and EO₃ types where E = S, Se, Te or Po. Ozone (O₃) and sulphur dioxide (SO₂) are gases while selenium dioxide (SeO₂) is solid. Reducing property of dioxide decreases from SO₂ to TeO₂; SO₂ is reducing while TeO₂ is an oxidising agent. Besides EO₂ type sulphur, selenium and tellurium also form EO₃ type oxide (SO₃, SeO₃, TeO₃). Both types of oxides are acidic in nature.
- (iii) Reactivity toward the halogens : Elements of group 16 form a larger number of halides of the type EX_6 , EX_4 and EX_2 where E is an element of the group and X is an halogen. The stabilities of the halides decrease in the order F > Cl > Br > l. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Shulphur hexafluoride SF_{16} is exceptionally stable for steric reasons.

Amongst terrafluorides, SF_4 is a gas, SeF_4 liquid and TeF_4 a solid These fluorides have sp^3d hybridisation and thus, have trigonal bipyramidal structure in which one of the equatorial position is occupied by a lone pair of electrons. This geometry is also regarded as see - saw geometry.

All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp³ hybridisation and thus have tetrahedral structure. The well known monohalides are dimeric in nature, Examples are S_2F_2 , S_2Cl_2 , S_2Br_2 , Se_2Cl_2 and Se_2Br_2 . These dimeric halides undergo disproportionation as given below :

$$2\text{Se}_2\text{Cl}_2 \rightarrow \text{SeCl}_4 + 3\text{Se}.$$

1. **DIOXYGEN** (O_{γ}) :

It differs from the remaining elements of the VIth group because of the following properties.

(A) small size (B) high electronegativity and (C) non-availability of d-orbitals.

PREPARATION :

(i) By thermal decomposition of oxides of metals.

$$2 \text{ HgO} \xrightarrow{450^{\circ}\text{C}} 2 \text{ Hg} + \text{O}_2; \qquad 2 \text{ Ag}_2\text{O} \xrightarrow{350^{\circ}\text{C}} 4 \text{ Ag} + \text{O}_2$$

$$3 \operatorname{MnO}_2 \xrightarrow{\Delta} \operatorname{Mn}_3 \operatorname{O}_4 + \operatorname{O}_2; \qquad 2 \operatorname{Pb}_3 \operatorname{O}_4 \xrightarrow{\Delta} 6 \operatorname{PbO} + \operatorname{O}_2$$

(ii) By thermal decomposition of oxygen rich compounds.

 $2 \text{ NaNO}_3 \xrightarrow{\Delta} 2 \text{ NaNO}_2 + \text{O}_2$; $2 \text{ KCIO}_3 \xrightarrow{\Delta} 2 \text{ KCl} + 3\text{O}_2$ (laboratory method)

$$4 \text{ } \text{K}_2 \text{Cr}_2 \text{O}_7 \xrightarrow{\Delta} 4 \text{ } \text{K}_2 \text{Cr} \text{O}_4 + 2 \text{ } \text{Cr}_2 \text{O}_3 + 3 \text{O}_2 \text{ ; } 2 \text{ } \text{KMn} \text{O}_4 \xrightarrow{\Delta} \text{ } \text{K}_2 \text{Mn} \text{O}_4 + \text{Mn} \text{O}_2 + \text{O}_2 \text{ } \text{O}_2 \text{ } \text{ }$$

(iii) By the action of conc. H_2SO_4 on MnO_2 .

$$2 \operatorname{MnO}_2 + 2\operatorname{H}_2 \operatorname{SO}_4 \longrightarrow 2 \operatorname{MnSO}_4 + 2\operatorname{H}_2 \operatorname{O} + \operatorname{O}_2$$

(iv) By the action of water on Na_2O_2 .

$$2 \operatorname{Na_2O_2} + 2 \operatorname{H_2O} \longrightarrow 4 \operatorname{NaOH} + \operatorname{O_2}$$

(v) By the action of conc. H_2SO_4 on $KMnO_4$ or $K_2Cr_2O_7$.

$$\mathrm{KMnO}_4 + 6 \mathrm{H}_2\mathrm{SO}_4 \longrightarrow 2 \mathrm{K}_2\mathrm{SO}_4 + 4\mathrm{MnSO}_4 + 6\mathrm{H}_2\mathrm{O} + 5\mathrm{O}_2$$

$$2 \operatorname{K}_2\operatorname{Cr}_2\operatorname{O}_7 + 8\operatorname{H}_2\operatorname{SO}_4 \longrightarrow 2 \operatorname{K}_2\operatorname{SO}_4 + 2\operatorname{Cr}_2(\operatorname{SO}_4)_3 + 8\operatorname{H}_2\operatorname{O} + 3\operatorname{O}_2$$

2

$$BaO + O_2(air) \xrightarrow{500^{\circ}C} 2BaO_2$$
; $2BaO_2 \xrightarrow{800^{\circ}C} 2BaO + O_2$

(vii) From air (mfg.) :

Oxygen is obtained by liquification of air and then its fractional distillation.

PROPERTIES:

Colourless, odourless and tasteless gas. It is paramagnetic and exhibits allotropy. Three isotopes of oxygen are ${}^{16}_{8}$ O, ${}^{17}_{8}$ O

and ${}^{18}_{8}$ O. Oxygen does not burn but is a strong supporter of combustion.

USE :

(i) Oxygen mixed with helium or CO₂ is used for artificial respiration. (ii) Liquid oxygen is used as oxidising agent in rocket fuels. (iii) Oxygen is used for production of oxy-hydrogen or oxy-acetylene flames employed for cutting and welding.

2. OXIDES :

(i) Acidic oxides

They dissolve in water forming oxyacids , e.g., CO_2 , SO_2 , SO_3 , N_2O_5 , N_2O_3 , P_4O_6 , P_4O_{10} , Cl_2O_7 , CrO_3 , Mn_2O_7 , V_2O_5 .

$$Cl_2O_7 + H_2O \longrightarrow 2 HClO_4; Mn_2O_7 + H_2O \longrightarrow 2 HMnO_4$$

(ii) Basic oxides

They either dissolve in water to form alkalies or combine with acids to form salts and water or combine with acidic oxides to form salts; e.g., Na₂O, CaO. CuO, FeO, BaO etc.

$$Na_2O + H_2O \longrightarrow 2 NaOH$$
; $CaO + H_2O \longrightarrow Ca(OH)_2$; $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$
Oxides

(iii) Neutral Oxides

They neither combine with acids nor with the bases to form salts e.g., CO, N₂O, NO etc.

(iv) Amphoteric Oxides

These can combine with acids as well as bases e.g., ZnO, Al₂O₃, BeO, Sb₂O₃, Cr₂O₃, PbO etc.

$$PbO + 2 NaOH \longrightarrow Na_2 PbO_2 + H_2O; PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$$

$$\operatorname{Cr}_2O_3 + 2 \operatorname{NaOH} \longrightarrow \operatorname{Na}_2\operatorname{Cr}_2O_4 + \operatorname{H}_2O; \quad \operatorname{Cr}_2O_3 + 3 \operatorname{H}_2SO_4 \longrightarrow \operatorname{Cr}_2(SO_4)_3 + 3 \operatorname{H}_2O_4$$

(v) Mixed Oxides

They behave as mixture of two simple oxides,

e.g., $Pb_3O_4 (2PbO + PbO_2)$, $Fe_3O_4 (FeO + Fe_2O_3)$, $Mn_3O_4 (2 MnO + MnO_2)$

(vi) Peroxides

They react with dilute acids and form H₂O₂, e.g., Na₂O₂, K₂O₂, BaO₂ etc.

 $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$ They react with water forming O_2 .

$$Na_2O_2 + H_2O \longrightarrow 2NaOH + 1/2O_2$$

(vii) Dioxides

Like peroxide, they contain excess of oxygen but do not yield H_2O_2 with dil. acids e.g. PbO_2 , MnO_2 etc. They evolve Cl_2 with conc. HCl and O_2 with conc. H_2SO_4 .

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O; \ 2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + O_2 + 2H_2O$$

er Oxides

(viii) Super Oxides

They contain O_2^- ion, e.g., KO_2 , RbO_2 and CsO_2 . These oxides react with water forming H_2O_2 and O_2

$$2 \operatorname{KO}_2 + 2 \operatorname{H}_2 O \longrightarrow 2 \operatorname{KOH} + \operatorname{H}_2 O_2 + O_2$$

(ix) Sub Oxides

They contain less oxygen than expected from the normal valency of the elements e.g., C₃O₂, N₂O, Pb₂O, Hg₂O etc.

$$\mathbb{C}^{\mathbb{P}}$$
 $C_3O_2 \longrightarrow O = \mathbb{C} = \mathbb{C} = \mathbb{C} = \mathbb{C}$

2. OZONE (O_3) :

PREPARATION:

It is prepared by passing silent electric discharge through pure and dry oxygen

$$O_2 \longrightarrow O + O$$

 $O_2 + O \longrightarrow O_3$; $\Delta H = 2845 \text{ kJ mol}^{-1}$

 $3O_2 \rightleftharpoons 2O_3$

Mixture obtained contains 5-10% ozone by volume and this mixture is called ozonised oxygen. The apparatus used for this is called as ozoniser ((i) Simen's and (ii) Brodie's ozonisers).

PROPERTIES:

Pale blue gas which forms a blue liquid on cooling and on solidification forms violet black crystals. It has a strong fish-like (i) smell and is slightly soluble in water but more in turpentine oil, glacial acetic acid or CCl₄. O_3 molecule is diamagnetic but O_3^- is paramagnetic.

(i) **Oxidising agent :**

 $O_3 + 2H^+ + 2\overline{e} \longrightarrow O_2 + H_2O$; SRP = + 2.07 v (In acidic medium)

 $O_3 + H_2O + 2\overline{e} \longrightarrow O_2 + 2OH^-$; SRP = + 1.24 v (In alkaline medium) Therefore, ozone is a strong oxidising agent in acidic medium.

(a) It oxidises I^- to I_2 (from neutral solution of KI)

$$O_{3} \longrightarrow O_{2} + [O]$$

$$2 \text{ KI} + \text{H}_{2}\text{O} + [O] \longrightarrow 2 \text{ KOH} + \text{I}_{2}$$

$$2 \text{ KI} + \text{H}_{2}\text{O} + [O] \longrightarrow 2 \text{ KOH} + \text{O}_{2} + \text{I}$$

Ŧ Alkaline KI is oxidised to potassium iodate & periodate.

> It oxidises moist S, P, As into their oxy acids.

(b)

$$O_{3} \longrightarrow O_{2} + [O] \times 3$$

$$S + 3 [O] \longrightarrow SO_{3}$$

$$SO_{3} + H_{2}O \longrightarrow H_{2}SO_{4}$$

$$S + 3O_{3} + H_{2}O \longrightarrow H_{2}SO_{4} + 3O_{2}$$

It oxidises H₂S to S (c)

$$H_2S + O_2 \longrightarrow H_2O + S \downarrow (yellow)$$

 $H_2S + O_3 \longrightarrow H_2O$ Reaction with dry I_2 : **(ii)**

$$2 I_2 + 9[O_3] \longrightarrow I_4O_9 + 9O_2$$

- I_4O_9 yellow solid has the composition $I^{+3} (IO_3^{-})_3$. Formation of this compound is a direct evidence in favour of basic nature P of I_2 (i.e. its tendency to form cations).
- (iii) **Reaction with moist iodine :**

$$O_{3} \longrightarrow O_{2} + [O] \times 5$$

$$I_{2} + 5[O] \longrightarrow I_{2}O_{5}$$

$$I_{2}O_{5} + H_{2}O \longrightarrow 2HIO_{3}$$

$$\overline{5O_{3}} + I_{2} + H_{2}O \longrightarrow 2HIO_{3} + 5O_{2}$$

(iv) **Reaction with Silver :**

Silver articles become black in contact with ozone.

$$Ag + O_3 \longrightarrow Ag_2O \downarrow (black) + O_2$$

(v) Reaction with
$$H_2O_2$$
:
 $2e^- + 2H^+ + O_3 \longrightarrow O_2 + H_2O$
 $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$
 $O_3 + H_2O_2 \longrightarrow 2O_2 + H_2O$
Oxidising Reducing
agent agent

It is supported by the fact that SRP of ozone is higher (+2.07) than SRP of hydrogen peroxide (+1.77). Therefore, ozone is stronger oxidising agent than hydrogen peroxide.

(vi) Bleaching Action :

 O_3 also bleaches coloured substances through oxidation

(vii) Ozonolysis :

Alkenes, alkynes react with ozone forming ozonides.

$$CH_{2} = CH_{2} + O_{3} \longrightarrow \bigcup_{\substack{i \in \mathcal{H}_{2} \\ i \in \mathcal{H}_{2}}}^{i \in \mathcal{H}_{2}} \xrightarrow{CH_{2}}_{i \in \mathcal{H}_{2}} \xrightarrow{Zn+H_{2}O}_{-ZnO} 2HCHO$$

(viii) Reaction with KOH :

Forms orange coloured compound, potassium ozonide.

$$2 \text{ KOH} + 5\text{O}_3 \longrightarrow 2\text{KO}_3^- + 5\text{O}_2 + \text{H}_2\text{O}_3^-$$

TESTS FOR OZONE

(i) A filter paper soaked in a alcoholic benzidine $\begin{bmatrix} H_2 N - \bigcirc - N H_2 \end{bmatrix}$ becomes brown when brought in contact with O_3

(this is not shown by H_2O_2)

(ii) Tailing of mercury

Pure mercury is a mobile liquid but when brought in contact with O_3 its mobility decreases and it starts sticking to glass surface forming a type of tail due to the dissolution of Hg_2O (mercury sub-oxide) in Hg.

 $2 \text{ Hg} + \text{O}_3 \longrightarrow \text{Hg}_2\text{O} + \text{O}_2$

USES:

(i)

- (i) As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.
- (ii) For detecting the position of double bond in the unsaturated organic compounds.
- (iii) In mfg. of artificial silk, synthetic camphor, $KMnO_4$ etc.

3. HYDROGEN PEROXIDE $(\mathbf{H}_2\mathbf{O}_2)$:

PREPARATION :

Laboratory method $BaO_2 \cdot 8H_2O + H_2SO_4 \text{ (cold)} \longrightarrow BaSO_4 \downarrow \text{ (white)} + H_2O_2 + 8H_2O$ $BaSO_4 \text{ is filtered to get aqueous hydrogen peroxide.}$

- $\overset{4}{\bigcirc} \qquad \text{Ba(OH)}_2 + \text{H}_2\text{O}_2 + 6\text{H}_2\text{O} \longrightarrow \text{BaO}_2 \cdot 8\text{H}_2\text{O}$
- $\textcircled{P} \qquad BaO_2 + 2HCl (ice cold) \longrightarrow BaCl_2 + H_2O_2$
- Not possible to isolate H₂O₂ from this solution as BaCl₂ is soluble in water
- The reaction between anhydrous BaO_2 and H_2SO_4 is slow and practically ceases after sometimes due to the formation of a protective layer of $BaSO_4$ on BaO_2 .
- Since H_2SO_4 can decompose H_2O_2 at a higher temperature, therefore, the reaction should be carried out at low temperature or H_3PO_4 can be used in place of H_2SO_4

$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3((PO_4)_2 \downarrow + 3H_2O_2; Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 \downarrow + 2H_3PO_4$$

H₂PO₄ can be used again.

(ii) By electrolysis of conc. H_2SO_4 at 0^0C using inert electrodes (platinum).

$$H_2SO_4 \longrightarrow H^{\oplus} + HSO_4^{\Theta}$$

at anode :
$$\rightarrow 2HSO_4^{\bigoplus} \longrightarrow S_2O_8^{2-} + 2H^+ + 2\overline{e}$$
; at cathode : $\rightarrow H^+ + \overline{e} \longrightarrow \frac{1}{2}H_2$

$$H_{2}S_{2}O_{8} + H_{2}O \xrightarrow{80-90^{0}C} 2H_{2}SO_{4} \xrightarrow{BaCl_{2}} BaSO_{4} \downarrow (white) + H_{2}O_{2} (aq)$$

 $BaSO_4$ is removed by filteration to get aqueous H_2O_2 . Industrial method (Auto oxidation):



2- Ethyl anthraquinol

2-Ehtylanthraquinone

 $K_2S_2O_8(s) + 2D_2O \longrightarrow 2KDSO_4(aq) + D_2O_2(\ell)$

PROPERTIES:

- (i) Colourless viscous liquid which appears blue in the larger quantity and is soluble in water (due to H- bonding) in all proportions and form a hydrate H₂O₂.H₂O (mp 221 K)
- (ii) Its boiling point 144^{0} C more than water but freezing point (-4) less than water. Density and dielectric constant are also higher than H₂O
- (iii) Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O_2 slowly on exposure to light.

 $2H_2O_2 \longrightarrow 2H_2O + O_2$

 H_2O_2 is not kept in glass containers because traces of alkali metal ions from the glass can catalyse the explosive decomposition of H_2O_2 Therefore, aqueous solution is stored in plastic or wax-lined glass containers and some urea or phosphoric acid or glycerol is added to that solution because these compounds have been found to behave as negative catalyst for the decomposition of H_2O_2

(iv) Acidic nature :

Behaves as a weak acid according to the following equation

$$H_2O_2$$
 (aq) $H^+ + HO_2^-$; $K_2 = 1.5 \times 10^{-12}$ at 25⁰ C

Aqueous solution of H₂O₂ turns blue litmus red which is then bleached by the oxidising property of H₂O₂

 $\begin{array}{l} \mathrm{Na_2CO_3} + \mathrm{H_2O_2} \longrightarrow \mathrm{Na_2O_2} + \mathrm{H_2O} + \mathrm{CO_2} \\ \mathrm{Ba(OH)_2} + \mathrm{H_2O_2} + \mathrm{6H_2O} \longrightarrow \mathrm{BaO_2} \cdot \mathrm{8H_2O} \downarrow \end{array}$

 \Im A 30% H₂O₂ solution has pH = 4.0

(v) Oxidising Agent :

 $2 \stackrel{\frown}{e} + 2H^+ + H_2O_2 \longrightarrow 2H_2O$; SRP = + 1.77 v (In acidic medium)

- $2 \overline{e} + H_2 O_2 \longrightarrow 2OH^-$; SRP = + 0.87 v (In alkaline medium)
- \bigcirc On the basis of the above potentials, we can say that H_2O_2 is strong oxidising agent in acidic medium but kinetically it is found that reactions are faster in basic medium.

(A) In acidic medium :

(a) It oxidises PbS to $PbSO_4$.

 $\begin{array}{c} H_2O_2 \longrightarrow H_2O + [O] \times 4 \\ PbS + 4[O] \longrightarrow PbSO_4 \end{array}$

 $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

This property is utilised in restoring the white colours in old paintings which turns black due to the formation of PbS by the action of atmospheric H_2S .

(iii)

(b) H_2O_2 oxidises H_2S to sulphur. $H_2O_2 \longrightarrow H_2O + [O]$ $H_2S + [O] \longrightarrow H_2O + S \downarrow$ $H_2O_2 + H_2S \longrightarrow 2H_2O + S \downarrow$ $H_2O_2 \text{ in acidic medium also oxidises } AsO_3^{3-} \rightarrow AsO_4^{3-}, SO_3^{2-} \rightarrow SO_4^{2-}, KI \rightarrow I_2, S^{2-} \rightarrow SO_4^{2-}, KI \rightarrow I_2, S^{2-} \rightarrow SO_4^{2-}, S$ C) $\operatorname{FeSO}_4 \to \operatorname{Fe}_2(\operatorname{SO}_4)_3 \& [\operatorname{Fe}(\operatorname{CN})_6]^{4-} \to [\operatorname{Fe}(\operatorname{CN})_6]^{3-}$ $NH_2 - NH_2$ (hydrazine) + $2H_2O_2 \longrightarrow N_2 + 4H_2O_2$ (c) $+ H_2O_2 \xrightarrow{FeSO_4} + H_2O$ (d) Benzene **(B)** In alkaline medium : $Cr(OH)_3$ (s) + 4 NaOH + $3H_2O_2 \longrightarrow 2Na_2CrO_4$ (aq.) + $8H_2O_2$ (a) $10 \text{ OH}^{-} + 3 \text{ H}_2\text{O}_2 + 2 \text{ Cr}^{3+} \longrightarrow 2 \text{ Cr}\text{O}_4^{2-} + 8\text{H}_2\text{O}$ $2\text{NaBO}_2 + 2\text{H}_2\text{O}_2 + 6\text{H}_2\text{O} \longrightarrow \text{Na}_2[(\text{OH})_2 \text{ B}(\text{O-O})_2 \text{ B}(\text{OH})_2] 6\text{H}_2\text{O} \text{ (sodium per oxoborate)}$ (b) Ŧ Used as a brightner in washing powder. (vi) **Reducing Agent :** It acts as a reducing agent towards powerful oxidising agnet. $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e$ Ŧ In alkaline solution, its reducing character is more than in acidic medium. $2 \text{ OH}^- + \text{H}_2\text{O}_2 \longrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}$ Ag₂O is reduced to Ag. (a) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$ It reduces O_3 to O_2 . **(b)** $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$ It reduces ferric cyanide to ferrous cyanide (basic medium). (c) $2 \text{ K}_3 [\text{Fe}(\text{CN})_6] + 2\text{KOH} \longrightarrow \text{K}_4 [\text{Fe}(\text{CN})_6] + \text{H}_2 \text{O} + \text{O}$ $H_2O_2 + O \longrightarrow H_2O + O_2$ $2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$ Ŧ It also reduces $MnO_4^- \rightarrow Mn^{2+}$ (acidic medium), $MnO_4^- \rightarrow MnO_2$ (basic medium), $OCl^- \rightarrow Cl^-, IO_4^- \rightarrow IO_3^- \& Cl_2 \rightarrow Cl^-$ TESTS FOR H_2O_2 : With K₂Cr₂O₇ (i) $K_2Cr_2O_7 + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + 2 CrO_5 + 5 H_2O_4$ $\operatorname{Cr}_2\operatorname{O}_7^{2-} + 2\operatorname{H}^+ + 4\operatorname{H}_2\operatorname{O}_2 \longrightarrow 2\operatorname{CrO}_5 + 5\operatorname{H}_2\operatorname{O}$ CrO₅ bright blue coloured compound soluble in ether. Ŧ $\operatorname{CrO}_5 + \operatorname{H}_2\operatorname{SO}_4 \longrightarrow 2\operatorname{Cr}_2(\operatorname{SO}_4)_3 + 6\operatorname{H}_2\operatorname{O} + 7\operatorname{O}_2$

(ii)
$$2 \text{ HCHO} + \text{H}_2\text{O}_2 \frac{\text{OH}^-}{\text{pyrogallol}} 2 \text{ HCOOH} + \text{H}_2$$

When this reaction is carried out in dark, it is accompanied by emission of light (yellow coloured). It is an example of chemiluminescene.

(iii) An acidified solution of titanium salt gives yellow or orange colour with H_2O_2 .

$$\text{Ti}^{+4} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{TiO}_4 \text{ (yellow/orange)} + 4\text{H}^+$$

USES :

- (i) In bleaching of delicate materials such as silk, wool, cotton, ivory etc.
- (ii) As a valuable antiseptic and germicide for washing wounds, teeth and ears under the name perhydrol.
- (iii) As 'antichlor' to remove traces of chlorine and hypochlorite.
- (iv) As oxidising agent in rocket fuels

4. SULPHUR (S) :

Sulphur Allotropic Froms :

Sulphur forms numerous allotropes of which the **yellow rhombic** (α - sulphur) and **monoclinic** (β - sulphur) forms are the most important. The stable forms at room temperature is rhombic sulphur, which transfroms to monoclinic sulphur when heated above 369 K.

Rhombic sulphur (r1- sulphur) :

This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2 . It is insoluble in water but dissolved to some extent in benzene, alcohol and ether. It is readily soluble in CS_2 .

Monoclinic sulphur (S - sulphur) :

Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS_2 . This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β - sulphur are formed. It is stable above 369 K and transforms into α - sulphur below it . Conversely, α - sulphur is stable below 369 K and transforms into β - sulphur above this. At 369 K both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have S_8 molecules these S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in figure.



Fig. : The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo- S_6 , the ring adopts the chair form and the moleculatr dimension are as shown in fig. (b) At elevated temperatures (~ 1000 K), S_2 is the dominant species and is paramagnetic like O_2 .

3. COMPOUNDS OF SULPHUR : (A) SODIUM THIOSULPHATE (Na₂S₂O₃.5H₂O) : PREPARATION :

(i) $Na_2SO_3 + S \xrightarrow{boiled} Na_2S_2O_3$ (ii) $Na_2CO_3 + 2SO_2 (excess) + H_2O \longrightarrow 2NaHSO_3 + CO_2; 2NaHSO_3 + Na_2CO_3 \longrightarrow 2Na_2S_2O_3 + H_2O + CO_2$ (iii) $2 NaHS + 4NaHSO_3 \longrightarrow 3Na_2S_2O_3 + 3H_2O$

$(iv) \qquad Na_2S + Na_2SO_3 + I_2 \longrightarrow Na_2S_2O_3 + 2 Nal$	
(V) $2Na_2S_2 + 3O_2$ (from air) $\xrightarrow{\Delta} 2Na_2S_2O_2 + 2S$	
PROPERTIES :	
(i) It is a colourless crystalline substance soluble in water which loses water of crystallisation on strong heating	ıg
(ii) As antichlor :	
It removes the chlorine from the surface of fibres (while dyeing) according to following reaction.	
$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$	
(iii) Departies with UCL.	
(iii) Keaction with HC1 : No S $O + HC1 \rightarrow 2N_2C1 + SO + S + H O$	
$\operatorname{Na}_2 \operatorname{So}_3 + \operatorname{HCI} \longrightarrow 2\operatorname{NaCI} + \operatorname{So}_2 + \operatorname{S} + \operatorname{H}_2 \operatorname{O}_2^2$ This test is used for distinction between S O_2^2 and SO So_2^2 ions as SO So_2^2 ions give only SO, with HCl	
This test is used for distinction between S_2O_3 and SO_3 four as SO_3 four give only SO_2 with field.	
(iv) Complex formation reactions :	
(a) Reaction with silver salts (AgNO ₃ , AgCl, AgBr or AgI):	
$Na_2S_2O_3 + 2AgNO_3 \longrightarrow Ag_2S_2O_3 \downarrow (white) + 2 NaNO_3$	
$Ag.S.O. + H.O \longrightarrow Ag.S \downarrow (Black) + H.SO.$	
If hypo is in excess, then soluble complex is formed.	
$2Na_{3}S_{2}O_{2} + AgNO_{2} \longrightarrow Na_{2}[Ag(S_{2}O_{2})_{2}]$ (soluble complex) + NaNO ₂	
This reaction is utilized in photography where hypo is used as fixer.	
(b) Reaction with FeCl ₃ :	
It develops a pink or violet colour which soon vanishes according to following reaction.	
$\operatorname{Fe}^{3+} + 2\operatorname{S}_2\operatorname{O}_3^{2-} \longrightarrow [\operatorname{Fe}(\operatorname{S}_2\operatorname{O}_3)_2]^-$ (Pink or violet)	
$[\operatorname{Fe}(\operatorname{S}_{2}\operatorname{O}_{3})_{2}]^{-} + \operatorname{Fe}^{3+} \longrightarrow 2\operatorname{Fe}^{2+} + \operatorname{S}_{4}\operatorname{O}_{6}^{2-}$	
(c) Reaction with AuCl ₃ (Soluble in water) :	
$AuCl_3 + Na_2S_2O_3 \longrightarrow AuCl \downarrow + Na_2S_4O_6 + 2HCl$	
$AuCl + Na_2S_2O_3 \longrightarrow Na_3 [Au(S_2O_3)_2] $ (soluble complex) + NaCl	
(d) Reaction with $CuCl_2$:	
$2 \operatorname{CuCl}_2 + 2\operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \longrightarrow 2\operatorname{CuCl} \downarrow + \operatorname{Na}_2\operatorname{S}_4\operatorname{O}_6 + 2 \operatorname{NaCl}$	
$CuCl + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 \downarrow + 2 NaCl$	
$3 \operatorname{Cu}_2 \operatorname{S}_2 \operatorname{O}_3 + 2 \operatorname{Na}_2 \operatorname{S}_2 \operatorname{O}_3 \longrightarrow \operatorname{Na}_4 [\operatorname{Cu}_6 (\operatorname{S}_2 \operatorname{O}_3)_5] \text{ (soluble complex)}$	
(e) Reaction with bismuth :	
$Bi^{3+} + 3 Na_2S_2O_3 \longrightarrow Na_3[Bi(S_2O_3)_3]$ (soluble complex) + $3Na^+$	
But it soon decomposes to give black ppt. of Bi_2S_3	
(v) Reaction with HgCl ₂ :	
$Na_2S_2O_3 + HgCl_2 \longrightarrow Hg_2S_2O_3 + 2NaCl$	
$\downarrow + H_2O$	
$HgCl_2$. $2HgS \leftarrow HgCl_2$ $HgS \downarrow (Black)$	
(vi) As reducing agent In iodometric titration :	
(a) $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	
(b) $2 \operatorname{KMnO}_4 + \operatorname{Na}_2 \operatorname{S}_2 \operatorname{O}_3 \longrightarrow \operatorname{K}_2 \operatorname{SO}_4 + \operatorname{Na}_2 \operatorname{SO}_4 + \operatorname{Mn}_2 \operatorname{O}_3$	
(viI) $4\operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3.5\operatorname{H}_2\operatorname{O} \xrightarrow{215^\circ\operatorname{C}} 4\operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \xrightarrow{220^\circ\operatorname{C}} 3\operatorname{Na}_2\operatorname{SO}_4 + \operatorname{Na}_2\operatorname{S}_5$	
LISES •	

U:

- (i) As an 'antichlor' to remove excess of chlorine from bleached fabrics.
- (ii) In photography as fixer.
- As a reagent in idometric and idiometric titrations. **(iii)**

yellow ammonium sulphide

(B) HYDROGEN SULPHIDE (H₂S) : **PREPARATION:**

(i) $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$ It is prepared in kipp's apparatus

(ii) Preparation of pure H₂S gas Sb_2S_3 (pure) + 6 HCl (pure) $\longrightarrow 2 SbCl_3 + 3 H_2S$

PROPERTIES:

- Colourless gas with rotten egg smell (i)
- (ii) Moderately soluble in water but solubility decreases with increasing temperature.

(iii) **Reducing Agent :** Acts as a strong reducing agent as it decomposes evolving hydrogen.

- $H_2S + X_2 \longrightarrow 2 HX + S;$ **(a)**
- $H_2S + SO_2 \xrightarrow{\text{moisture}} H_2O + S;$ **(b)**

(c)
$$H_2O_2 + H_2S \longrightarrow H_2O + S + O_2$$

(d)
$$2HNO_{3} \longrightarrow H_{2}O + 2NO_{2} + [O]$$
$$H_{2}S + [O] \longrightarrow H_{2}O + S$$
$$2HNO_{3} + H_{2}S \longrightarrow 2H_{2}O + NO_{2} + S$$

It also reduces $\text{KMnO}_4 \rightarrow \text{Mn}^{2+}$, $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_2$ & $\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{Cr}^{3+}$ P

Acidic Nature : (iv)

Its aquesous solution acts as a weak dibasic acid according to following reaction $H_2S \Longrightarrow HS + H^+ \Longrightarrow S^{2-} + 2H^+$ Therefore, It forms two series of salts as given below $NaOH + H_2S \longrightarrow NaHS + H_2O$; $NaOH + H_2S \longrightarrow Na_2S + 2H_2O$ **(v)** Formation of Polysulphides : They are obtained by passing H₂S gas through metal hydroxides. $Ca(OH)_{2} + H_{2}S \longrightarrow CaS + 2H_{2}O; CaS + 4H_{2}S \longrightarrow CaS_{5} + 4H_{2}$ $NH_{4}OH + H_{2}S \longrightarrow (NH_{4})_{2}S + 2H_{2}O; (NH_{4})_{2}S + H_{2}S (excess) \longrightarrow (NH_{4})_{2}S_{x+1} + xH_{2}$

TESTS FOR H_sS :

- Turns acidified lead acetate paper black **(i)**
- Gives violet or purple colouration with sodium nitropruside solution. (ii)

USES:

- As a loboratory reagent for the detection of basic radicals in qualitative analysis. (i)
- **(ii)** As reducing agnet.

(C) SULPHUR DIOXIDE :

PREPARATION:

- $S + O_2 \text{ or air } \xrightarrow{Burn} SO_2$ (i)
- $S + 2H_2SO_4$ (conc.) $\longrightarrow 3SO_2 + 2H_2O_4$ (ii)
- (iii) By heating Cu or Ag with conc. H_2SO_4 $Cu + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$
- By reaction of metal sulphites with dil.HCl (iv) $Na_2SO_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O$ Similarly bisulphites also give SO₂ with dil. HCl $NaHSO_3 + HCl \longrightarrow NaCl + SO_2 + H_2O$

(v)	By heating sulphides in excess of air
	$2 \operatorname{ZnS} + 3O_2 \longrightarrow 2\operatorname{ZnO} + 2\operatorname{SO}_2$
(vi)	$CaSO_4 (gypsum) + C \xrightarrow{\Delta} 2 CaO + SO_2 + CO_2$
<u>C</u>	By this method SO ₂ is obtained in large scale
PROP	ERTIES :
(i)	Colourless gas with burning sulphur smell.
(ii)	It is heavier than air and is highly soluble in water
(iii)	Neither burns nor helps in burning but burning magnesium and potassium continue to burn in its atmosphere. $3Mg + SO_2 \longrightarrow 2 MgO + MgS$; $4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$
(iv)	Acidic Nature : Acidic oxide and thus dissolve in water forming sulphurous acid.
	$SO_2 + H_2O \longrightarrow H_2SO_3$
(v)	Addition Reaction :
	$SO_2 + Cl_2 \xrightarrow{Sun \text{ light}} SO_2Cl_2$ (sulphuryl chloride)
	platinised
	$SO_2 + O_2 \xrightarrow{\frown} SO_3 ; PbO_2 + SO_2 \longrightarrow PbSO_4$
(vi)	Reducing Nature :
	$H_2O + SO_2 \longrightarrow H_2SO_3$; $H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H$
(P	Reducing character is due to the liberation of nascent hydrogen
(a)	Reduces halogens to corresponding halides
	$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$
	$2H + Cl_2 \longrightarrow 2HCl$
	$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$
(b)	Reduces acidified iodates to iodine
	$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H] \times 5$
	$2KIO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HIO_3$
	$2\text{HIO}_3 + 10\text{H} \longrightarrow \text{I}_2 + 6\text{H}_2\text{O}$
	$2\text{KIO}_3 + 5\text{SO}_2 + 4\text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4 + \text{I}_2$
¢°	It also reduces acidified $\text{KMnO}_4 \longrightarrow \text{Mn}^{2+}$ (decolourises),
	Acidified $K_2Cr_2O_7 \longrightarrow Cr^{3+}$ (green coloured solution) & Ferric Sulphate \longrightarrow Ferrous sulphate
(vii)	Oxidising nature :
	Acts as oxidising agent with strong reducing agent
(a)	$2H_2S + SO_2 \xrightarrow{\text{moisture}} 2H_2O + 3S$
(b)	$2\text{SnCl}_2 + \text{SO}_2 + 4\text{HCl} \longrightarrow 2\text{SnCl}_4 + 2\text{H}_2\text{O} + \text{S}$
(c)	$2Hg_2Cl_2 + SO_2 + 4HCl \longrightarrow 2HgCl_2 + 2H_2O + S$
(d)	$2CO + SO_2 \longrightarrow 2CO_2 + S$
(e)	$2 \text{ Fe} + \text{SO}_2 \longrightarrow 2 \text{FeO} + \text{FeS}$
(viii)	Bleaching Action :
	$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$
	This is due to the reducing nature of SO_2
	Coloured matter + H $\underbrace{-}_{\text{Air oridation}}$ colourless matter.
	Therefore, bleaching is temporary

USES:

- (i) Used in manufacture of H_2SO_4 & paper from wood pulp.
- (ii) As a bleaching agent for delicate articles like wool, silk and straw.
- (iii) Used in refining of petroleum and sugar.

(D) SULPHUR TRIOXIDE (SO₂) : **PREPARATION:**

- $6H_2SO_4 + P_4O_{10} \longrightarrow 6SO_3 + 4H_3PO_4$ (i)
- P P_4O_{10} is dehydrating agent

 $\operatorname{Fe}_2(\operatorname{SO}_4)_3 \xrightarrow{\Delta} \operatorname{Fe}_2\operatorname{O}_3 + 3\operatorname{SO}_3$ (ii)

(iii)
$$2SO_2 + O_2 \stackrel{\text{pt}}{\longleftarrow} 2SO_3$$

PROPERTIES:

- Acidic Nature : (i) Dissolves in water forming sulphuric acid $SO_3 + H_2O \longrightarrow H_2SO_4$
- $H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$ (oleum) **(ii)**
- $SO_2 + HCl \longrightarrow SO_2(OH) Cl$ (chlorosulphuric acid) (iii)
- **Oxidising Nature :** (iv)
- $2SO_3 + S \xrightarrow{100^{\circ}C} 3SO_2$ **(a)**
- **(b)**
- $\begin{array}{l} 5\mathrm{SO}_3 + 2\mathrm{P} \longrightarrow 5\mathrm{SO}_2 + \mathrm{P}_2\mathrm{O}_5\\ \mathrm{SO}_3 + \mathrm{PCl}_5 \longrightarrow \mathrm{POCl}_3 + \mathrm{SO}_2 + \mathrm{Cl}_2 \end{array}$ (c)
- $SO_3 + 2HBr \longrightarrow H_2O + Br_2 + SO_2$ (**d**)

USES:

- (i) Used in manufacture of H_2SO_4 and oleum.
- **(ii)** Used as a drying agent for gases.

(E) SULPHURIC ACID (H_2SO_4) : **PREPARATION:**

- $2\text{FeSO}_4.7\text{H}_2\text{O} \xrightarrow{\text{dist.}} \text{Fe}_2\text{O}_3 + \text{H}_2\text{SO}_4 + \text{SO}_2 + 13\text{H}_2\text{O}_2$ (i) Lead Chamber Process (Industrial method) : (ii) $2SO_2 + O_2$ (air) $+ 2H_2O + [NO]$ (catalyst) $\longrightarrow 2H_2SO_4 + [NO]$ (catalyst) Acid obtained is 80% pure and is known as brown oil of vitriol
- (iii) Contact process (Industrial method) :

$$O_2 + 2SO_2 \xrightarrow{catalyst} 2SO_3$$

The commonly used catalysts are platinum, ferric oxide or vanadium pentoxide. V₂O₅ is preferred as it is cheaper and is not poisoned by impurities

 $H_2SO_4 (58\%) + SO_3 \longrightarrow H_2S_2O_7 (oleum)$

Sulphuric acid of any desired concentration can be obtained from oleum by dilution with water.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Oxidation of sulphur dioxide is reversible and exothermic. According to Le-chatelier principle, the favourable conditions for the greater yield of sulphur trioxide are.

- (a) An excess of air- SO₂ and oxygen are taken in 2:3 molecular proportion
- Low tempt-optimum tempt. 450°C **(b)**
- Higher pressure-one atmosphere (c)



 $2 \text{ KI} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{HI}$ $\text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{SO}_2 + [\text{O}]$ $2 \text{ HI} + [\text{O}] \longrightarrow \text{I}_2 + \text{H}_2\text{O}$

2 KI + $2H_2SO_4 \longrightarrow K_2SO_4 + SO_2 + I_2 + 2H_2O$ Here HI is oxidised to I_2 . Similarly bromine is liberated from KBr

(d)
$$C_{10}H_8$$
 (naphthalene) + 9H₂SO₄ $\xrightarrow{\text{Hg as}} C_8H_6O_4$ (phthalic acid) + 10H₂O + 9SO₂ + 2CO₂

(vi) **Dehydrating agent :**

(b)

Sulphuric acid acts as a powerful dehydrating agent because it has a great affinity for water

(a)
$$C_{12}H_{22}O_{11}$$
 (cane sugar) $\xrightarrow{H_2SO_4}{-11}H_2O$ 12C

$$\begin{array}{c} & H_2 SO_4 \\ & OOOH \end{array} \xrightarrow{H_2 SO_4} CO + CO_2 + H_2 O \end{array}$$

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(vii) **Miscellaneous reactions :**

(a) Sulphonation of aromatic compounds

$$+ H_2SO_4 \longrightarrow + H_2O$$

Benzene Benzene sulphonic acid

Reaction with PCl₅: **(b)**



$$O_2S$$
 $OH + 2PCl_5 \longrightarrow O_2S$ $CI + 2POCl_3 + 2HCl$
OH CI

 $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$ (c)

(d)
$$3\text{KCIO}_3 + 3\text{H}_2\text{SO}_4 \xrightarrow{\Delta} 3 \text{ KHSO}_4 + \text{HCIO}_4 + 2\text{CIO}_2 + \text{H}_2\text{O}$$

(e) $\text{H}_2\text{SO}_4 + \text{P}_2\text{O}_5 \longrightarrow 2\text{HPO}_3 + \text{SO}_3$

(e)

USES:

- **(i)** For the manufacture of fertilizer such as ammonium sulphate and super phosphate of lime.
- (ii) As an important laboratory reagent.
- (iii) In storage batteries.
- In leather, textile, paper and dyeing industries. (iv)

GROUP 17 ELEMENTS : THE HALOGEN FAMILY

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17. These are collectively known as the halogens (Greek halo means salt and genes born i.e., salt producers). The halogens are highly reactive non-metallic elements.

Electronic Configuration :

All these elements have seven electrons in their outermost shell $(ns^2 np^5)$ which is one electron short of the next noble gas. Atomic and Ionic Radii :

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge . Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

Ionisation Enthalpy :

They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy dereases down the group.

Electron Gain Enthalpy :

Halogen have maximum negative electrons gain enthalpy in the corresponding period. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction.

Electronegativity :

They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table

Physical Properties :

Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. Their melting and boiling points steadily increase with atomic number. All halogen are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example, F_2 , has yellow, Cl_2 , greenish yellow, Br_2 , red and I_2 , violet colour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water. But are soluble in organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.Except the smaller enthalpy of dissociation of F_2 compared to that of Cl_2 whereas X-X bond dissocitation enthalpies from chlorine onwards show the expected trend: Cl - Cl > Br - Br > I - I. A reason for this anomaly is the relatively larger electrons- electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2 .

Element	F	CI	Br	I
Atomic Number	9	17	35	53
Atomic Mass	19	35.45	79.90	126.90
Electronic configuration	[He] 2s ² 2p ⁵	[Ne] 3s ² 3p ⁵	[Ar] 3d ¹⁰ 4s ² 4p ⁵	[Kr] 4d ¹⁰ 5s ² 5p ⁵
Covalent Radius / pm	64	99	114	133
Ionic Radius X [−] / pm	133	184	196	220
lonization enthalpy / (kJ mol ⁻¹)	1680	1256	1142	1008
Electron gain enthalpy /(kJ mol ⁻¹)	- 333	- 349	- 325	- 296
Distance X -X/pm	143	199	229	266
Enthalpy of dissociation $(X_2)/kJ \text{ mol}^{-1}$	158.8	242.6	192.8	151.1
Electronegativity	4	3.2	3.0	2.7
Melting point / K	54.4	172	265.8	386.6
Boiling point / K	84.9	239.0	332.5	458.2

ATOMIC & PHYSICAL PROPERTIES :

Chemical Properties

Oxidation states and trends in chemical reactivity

All the halogens exhibit -1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids.

The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.

All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. The decreasing oxidising ability of the halogen in aqueous solution down the group is evident from their standard electrode potentials. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reactions of iodine with water is non-spontaneous . Γ can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.

$$\begin{split} & 2F_2(g) + 2H_2O(\ell) \to 4H^+ \, (aq) + 4F^- \, (aq) + O_2(g) \\ & X_2(g) + H_2O \, (\ell) \to HX(aq) + HOX \, (aq) \\ & (\text{where } X = \text{Cl or Br}) \\ & 4I^- \, (aq) + 4H^+ \, (aq) + O_2(g) \to 2 \ I_2 \, \ (s) + 2H_2O \, (\ell) \end{split}$$

Standard Reduction Potential (SRP)

$$X_2 + 2e^- \longrightarrow 2X^-$$

$$F_{2} + 2e^{-} \longrightarrow 2F^{-} \qquad \epsilon^{\circ} = +2.87 \text{ V}; \quad Cl_{2} + 2e^{-} \longrightarrow 2Cl^{-} \qquad \epsilon^{\circ} = +1.36 \text{ V}$$

$$Br_{2} + 2e^{-} \longrightarrow 2Br^{-} \qquad \epsilon^{\circ} = +1.09 \text{ V}; \quad I_{2} + 2e^{-} \longrightarrow 2I^{-} \qquad \epsilon^{\circ} = +0.54 \text{ V}$$

More the value of the SRP, more powerful is the (algebraically) oxidising agent. Hence the order of oxidising power is $F_2 > Cl > Br > L$

$$\operatorname{Cl}_2 > \operatorname{Br}_2 > \operatorname{I}_2$$

Since SRP is the highest for F_2 (among all elements of P.T.), it is a strogenst oxidising agent.

 \mathbb{F}_2 is more powerful oxidising agent than O_3 [Inspite of 3 'O's in O_3]

Note: E.A. and I.E. values pertain to atoms in gas phase where as redox phenomena occurs in gaseous medium.

Hence properties in the gas phase cannot reflect parallely in solution phase.

Electrode potential values would be the monitoring parameter in solution phase because they are experimental (based on the correct situation).

Hydration energy of X⁻

Smaller the ion, higher is the hydration energy

-			
F^{-}	Cl ⁻	Br ⁻	I^-
515 kJ/mol	381	347	305

Anomalous behaviour of fluorine :

The anomalous behviour of fluorine is due to its small size, highest electronegativity, low F- F bond dissociation enthalpy, and non availability of d orbitals in valence shell. Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogen form a number of oxoacids. Hydrogen fluoride is liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

(i) Reactivity towards hydrogen:

They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. They dissolve in water to form hydrohalic acids. The acidic strength of these acids varies in the order : HF < HCl < HBr < HI. The stability of these halides dereases down the group due to decrease in bond (H–X) dissociation enthalpy in the order : H - F > H - Cl > H - Br > H - I.

(ii) Reactivity towards oxygen :

Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2 . However, only OF_2 is the thermally stable at 298 K. These oxide are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reactions is used in removing plutonium as PuF_6 from spent nuclear fuel.

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogen range from + 1 to + 7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability oxides formed by halogens, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones.

Chlorine oxides, Cl_2O , Cl_2O_6 , Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

The bromine oxides, Br_2O , BrO_2 , BrO_3 are the least stable halogen oxides and exist only at low temperature. They are very powerful oxidising agents.

The iodine oxides, I_2O_4 , I_2O_5 , I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is very good oxidising agent and is used in the estimation of carbon monoxide.

(iii) Reactivity towards metals:

Halogen react with metals to form metal halides. For e.g., bromine reacts with magnesium to give magnesium bromide.(iv) Reactivity of halogen towards other halogens :

Halogens combine amongst themselves to form a number of compounds known as interhalogen of the types AB, AB_3 , AB_5 and AB_7 where A is a larger size halogen and and B is smaller size halogen.

1. FLUORINE (\mathbf{F}_2) :

PREPARATION:

(i) Electrolytic method :

Electrolyte : Molten KHF₂ (1 part) + HF (5 part) Anode : Carbon Cathode : Steel Vessel : Monel metal

On Electrolysis

Cathode : $2H^+ + 2e^- \longrightarrow H_2(g)$

Anode : $2F^- \longrightarrow F_2 + 2e^-$

The F_2 gas thus evolved must be free from HF which is more corrosive than fluorine.

In order to make flourine free from HF, the gas is passed through NaF which absorbs HF.

Anode of carbon should be free from graphide because F_2 reacts with graphite easily to form a polymeric substance known as graphite fluoride.

There should be no moisture present in the vessel otherewise fluorine will react with water.

 $3H_2O + 3F_2 \longrightarrow 6HF + O_3$; $2F_2 + 2H_2O \longrightarrow 4HF + O_2$

It is not possible to prepare fluorine by electrolysis of aq. solution of NaF or KF. It is because when aq. solution of KF is subjected to electrolysis, there will be following two oxidation in competition at anode,

$$H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^-$$
 SOP = -1.23 v
and
 $F^- \longrightarrow 1/2F_2 + e^-$ SOP = -2.87v

As a matter of rule that substance will be oxidise whose SOP is higher therefore water gets oxidise at anode and not F^- . **Chemical method :** From K₂ [MnF₆] - potassium hexafluoromanganate (IV)

$$K_{2} [MnF_{6}] + 2 SbF_{5} \longrightarrow 2K [SbF_{6}] + MnF_{3} + \frac{1}{2} F_{2} ; \begin{cases} via \\ MnF_{4} \longrightarrow MnF_{3} + \frac{1}{2} F_{2} \end{cases}$$

 \checkmark In this reaction, the stronger Lewis acid SbF₅ displaces the weaker one, MnF₄ from its salt. MnF₄ is unstable and readily decomposes to give MnF₃ and fluorine.

PROPERTIES :

(ii)

- (i) Diatomic, Pale green-yellow gas which appears to be almost colourless. It is heavier then air. It condenses to yellow liquid at -188° C and yellow solute at -223° C. It has punged oddur and is highly poisonous.
- (II) Oxidising character : It is the most powerful oxidising agent.

$$F_2 + 2NaX \longrightarrow 2NaF + X_2$$

$$(X = Cl, Br, I)$$

- (a) It can oxidise all other halide ions into halogen molecules
- (b) It can oxidise CIO_3^- into CIO_4^- and IO_3^- to IO_4^-

$$F_2 + ClO_3^- + H_2O \longrightarrow 2F^- + ClO_4^- + 2H^+$$

(c) It can oxidise HSO_4^{-1} into $S_2O_8^{2-1}$

$$2HSO_4 + F_2 \longrightarrow 2F^- + \frac{(+6)}{S_2O_8^{2-}} + 2H^+$$

 \bigcirc Some of the O²⁻ changes to O⁻ in the persulphate ions (having the O⁻). Hence oxygen is getting oxidised.

(iii) Reaction with NaOH solution : With dilute alkali forms oxygen diffuoride and with concentrated alkali
$$O_{2^*}$$

 $2F_1 + 4$ NaOH ($\sin - \rightarrow OF_2(g) + 2$ NaF + H_2O
 $2F_1 + 4$ NaOH ($\cos z) \rightarrow O_1(g) + 4$ NaF + 2H_2O
 $2F_1 + 4$ NaOH ($\cos z) \rightarrow O_1(g) + 4$ NaF + 2H_2O
(iv) Reaction with NH : (Distinction from other halogens)
 $2NH_1 + 3F_2 \longrightarrow N_2 + 6$ HF
 G^* Other halogens form explosive NX₂, with conc. NH₂ (liquor ammonia)
(v) Reaction with HS^*
 $H_2S + F_2 \longrightarrow SF_6 + 2$ HF
 G^* H_2S burns
(vi) Reaction with HS^*
 $H_2S + F_2 \longrightarrow SF_6 + 2$ HF
 G^* H_2S burns
(vi) Reaction with HS^*
 $H_2S + F_2 \longrightarrow SF_6 + 2$ HF
 G^* H_2S burns
(vii) Reaction with HQ^*
 $2H_1Q + 2F_2(g) \longrightarrow SiF_1(g) + O_2(g)$
The reacton is slow with dry F_2 .
(viii) Reaction with HQ^*
 $2H_1Q + 2F_2 \longrightarrow 4$ HF + O_2
sometime a little amount of O_1 also forms
 $3H_2Q + 3F_2 \longrightarrow 2$ HF or H_2F_3
(viii) Reaction with H_2^*
 $Xe + F_1 \longrightarrow 2$ HF or H_2F_3
 XeF_4
(x) Reaction with H_2^*
 $SO_3 + F_2 \longrightarrow 2$ HF or H_2F_3
 G^* This reactions occurs even in dark
(x) Reaction with SO_1^*
 $SO_3 + F_2 \longrightarrow \frac{1600^2}{3illent electric discharge} O_2F_2$
(xi) Reaction with O_2^*
 $O_2 + F_2 \longrightarrow \frac{1600^2}{3illent electric discharge} O_2F_2$
(xii) Reaction with D_3^*
 $2A_2 + F_2 \rightarrow 2A_2F^*; 2A_1 + 3F_2 \rightarrow 2A_1F_3$
 $C + 2F_2 \rightarrow CF_4$; $SI + 2F_2 \rightarrow SIF_4$
2. CHLORINE (CI_2) :
PREPARATION:
(i) Common method (CI_3 , BF_2, T_2):
(ii) Common method (CI_3 , BF_2, T_2):

 $2 \operatorname{NaX} + 3\operatorname{H}_2\operatorname{SO}_4 (\operatorname{conc.}) + \operatorname{MnO}_2 (\operatorname{oxidising agent}) \xrightarrow{\Delta} X_2 + \operatorname{MnSO}_4 + 2\operatorname{NaHSO}_4 + 2\operatorname{H}_2\operatorname{O}$ $4\operatorname{H}^+ + \operatorname{MnO}_2 + 2\operatorname{X}^- \longrightarrow X_2 + \operatorname{Mn}^{+2} + 2\operatorname{H}_2\operatorname{O}$

(;;)

(ii) Only for
$$Cl_2$$
:
(a) NaCl + HNO₃ \longrightarrow NaNO₃ + HCl × 3

$$\frac{HNO_3 + 3HCl}{3} \longrightarrow NOCl + Cl_2 + 2H_2O}{3NaCl + 4 HNO_3} \longrightarrow 3 NaNO_3 + NOCl (nitrosyl chloride) + Cl_2 + 2H_2O}{3NaCl + 4 HNO_3} \longrightarrow 3 NaNO_3 + NOCl (nitrosyl chloride) + Cl_2 + 2H_2O}{2NOCl + O_2} \longrightarrow 2NO_2 + Cl_2 : NO_2 + H_2O \longrightarrow HNO_3 (to be recycled)
(b) When Cl_2 is used for the chlorination of hydrocarbon the byproduct is HCl. The HCl is catalytically oxidised into H_2O & Cl_2 using copper powder mixed with rare earth chlorides.
$$4 HCl + O_2 \frac{Cu powder + rare earth}{Chloride} 2H_2O + 2Cl_2$$
(c) $Ca \swarrow_{Cl} + 2HCl \longrightarrow CaCl_2 + Cl_2 + H_2O$
(d) $2KMnO_4 + 16 HCl \rightarrow 2 KCl + 2 MnCl_2 + 5 Cl_2 + 8 H_2O$
(e) $PbO_2 + 4 HCl \rightarrow PbCl_2, + Cl_2 + 2 H_2O$
(iii) Manufacture of chlorine :
(a) Deacon's process : By oxidation of hydrogen chloride gas by atmoshperic oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4 HCl + O_2 \frac{-GuCl_2}{2} \rightarrow 2 Cl_2 + 2 H_2O$$
(b) Electrolytic process : Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is also obtained as by-product in many chemical industries.
 $NaX (aq) \longrightarrow Na^+ (aq) + X^- (aq)$
Anode : $2X^- \longrightarrow X_2 + 2e^-$
PROPERTIES :
(i) It is a greenish-yellow gas with pungent and suffocating odour. It is about 2–5 times heavier than air. It can be liquefied into$$

Cl₂

into greenish-yellow liquid which boils at 239 K. It is soluble in water.

At low temperature it forms a hydrate with water having formula Cl_2 . $8H_2O$ which is infact a clathrate compound. (ii)

 $H_2 + Cl_2 \xrightarrow{} 2HCl(g), [H_2 + Br_2 \rightarrow 2HBr \text{ is not a zero order reaction}]$ (iii)

Reaction with NH_3 (common for $Cl_2 \& Br_2$): (iv)

(a) 8 NH₃ + 3 Cl₂
$$\longrightarrow$$
 N₂ + 6 NH₄ Cl
(b) NH₃ + 3Cl₂ \longrightarrow NCl₃ + 3 HCl
(excess)

(v) Reaction with alkali metal halides (KX) :

$$2 \text{ KBr} + \text{Cl}_2 \longrightarrow 2 \text{KCl} + \text{Br}_2$$

$$2 \text{ KBr} + \text{Cl}_2 \longrightarrow 2 \text{ KCl} + \text{Cl}_2$$
$$2 \text{KI} + \text{Cl}_2 \longrightarrow 2 \text{ KCl} + \text{I}_2$$

- ${\rm Cl}_2$ can oxidise both ${\rm Br}^-$ & ${\rm I}^-$ but ${\rm Br}_2$ can oxidise ${\rm I}^-$ only. P
- Ŧ F_2 is not used in aqueous reaction since it itself reacts with water.
- Oxidising & bleaching properties : Chlorine water on standing loses its yellow colour due to the formation of HCl and (vi) HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

(i) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

 $2 \operatorname{FeSO}_4 + \operatorname{H}_2 \operatorname{SO}_4 + \operatorname{Cl}_2 \rightarrow \operatorname{Fe}_2 (\operatorname{SO}_4)_3 + 2 \operatorname{HCl} \\ \operatorname{Na}_2 \operatorname{SO}_3 + \operatorname{Cl}_2 + \operatorname{H}_2 \operatorname{O} \rightarrow \operatorname{Na}_2 \operatorname{SO}_4 + 2 \operatorname{HCl} \\ \operatorname{SO}_2 + 2 \operatorname{H}_2 \operatorname{O} + \operatorname{Cl}_2 \rightarrow \operatorname{H}_2 \operatorname{SO}_4 + 2 \operatorname{HCl} \\ \end{array}$

$$I_2 + 6 H_2O + 5 Cl_2 \rightarrow 2 HIO_3 + 10 HCl$$

(ii) It is a powerful bleaching agent ; Bleaching action is due to oxidation.

$$Cl_2 + H_2O \rightarrow 2 HCl + O$$

Coloured substance $+ O \rightarrow$ Colourless substance

It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chloride is permanent.

 \square But the bleching action of SO₂ is temporary because it takes place through reduction.

 $SO_2 + 2 H_2O \longrightarrow H_2SO_4 + 2 H$

 SO_3^{2-} + Coloured material $\longrightarrow SO_4^{2-}$ + Reduced coloured material (colourless)

Reduced Coloured material (colourless) O_2 of air Coloured material

(vii) Reaction with NaOH :

Common to Br₂, I₂ & Cl₂ (but with F₂ it is different, OF₂ or O₂ is obtained)

- (a) 2 NaOH (cold & dilute) + $Cl_2 \longrightarrow NaCl + NaClO + H_2O$
- (b) 6 NaOH (hot & concentrated) + 3 $Cl_2 \longrightarrow 5 NaCl + NaClO_3 + 3 H_2O$

(viii) Reaction with Hypo solution :

This reaction is common with Cl₂ & Br₂ but with I₂ it is different.

$$Na_{2} \overset{(+2)}{S}_{2} O_{3} + H_{2} O + Cl_{2} \longrightarrow Na_{2} \overset{(+2)}{S}_{4} + 2HCl + \overset{(o)}{S} \downarrow (colloidal)$$

In this reaction thiosulphate ions undergo disproportionation into SO_4^{2-} and S. Cl_2 is reduced to Cl^- .

(ix) Reaction with dry slaked lime, $Ca(OH)_2$: It gives bleaching powder.

$$2 \operatorname{Ca(OH)}_2 + 2 \operatorname{Cl}_2 \longrightarrow \operatorname{Ca(OCl)}_2 + \operatorname{CaCl}_2 + 2 \operatorname{H}_2 O$$

(x) Reaction with metals & non–metals : Forms corresponding chlorides.

 $2 \text{Al} + 3 \text{Cl}_2 \rightarrow 2 \text{AlCl}_3$; $2 \text{Na} + \text{Cl}_2 \rightarrow 2 \text{NaCl}$

$$P_4 + 6 Cl_2 \rightarrow 4 PCl_3$$
; $S_8 + 4 Cl_2 \rightarrow 4 S_2Cl_2$

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \rightarrow 2 HCl; H_2S + Cl_2 \rightarrow 2 HCl + S; C_{10}H_{16} + 8 Cl_2 \rightarrow 16 HCl + 10 C$$

Uses : Cl_2 is used

(i) for bleaching woodpulp (required for the manufacture of paper and rayon). bleaching cotton and textiles,

(ii) in the manufacture of dyes, drugs and organic compounds such as CCl₄, CHCl₃, DDT, refrigerants, etc.

(iii) in the extraction of gold and platinum.

(iv) in sterilising drinking water and

(v) preparation of poisonous gases such as phosgene (COCl₂), tear gas (CCl₃NO₂), mustard gas (ClCH₂CH₂SCH₂CH₂Cl).

3. BROMINE (\mathbf{Br}_2) :

PREPARATION:

(i) Common method :

 $2 \text{ NaBr} + 3\text{H}_2\text{SO}_4 (\text{conc.}) + \text{MnO}_2 \xrightarrow{\Delta} \text{Br}_2 + \text{MnSO}_4 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O}$

(ii) From Sea-water :

NaCl is main component but NaBr is also present in some quantity in sea water. Cl_2 gas is passed through sea water when vapours of bromine are evolved.

 $2 \operatorname{Br}^{-}(\operatorname{aq}) + \operatorname{Cl}_{2} \longrightarrow 2\operatorname{Cl}^{-}(\operatorname{aq.}) + \operatorname{Br}_{2}$

PROPERTIES:

(i) Reddish brown liquid, fairly soluble in water. It also forms hydrate like Cl,

 $(Br_2 . 8H_2O) \leftarrow Clathrate compound$

(ii) Rest reactions are same as with Cl₂

4. **IODINE** (I_{1}) :

PREPARATION:

(i) **Common method :**

 $2\text{NaI} + 3\text{H}_2\text{SO}_4 \text{ (conc.)} + \text{MnO}_2 \xrightarrow{\Delta} \text{I}_2 + \text{MnSO}_4 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O}_4 + 2\text{H$

From Caliche or Crude chile salt petre : **(ii)**

> The main source of iodine is NaIO₃ (sodium iodate) which is found in nature with NaNO₃ (chile saltpetre). NaIO₃ is present in small amount. After crystallisation of NaNO₃, the mother liquor left contains NaIO₃ (soluble). To this solution NaHSO₃ is added where upon I_2 is precipitated.

$$2IO_3^- + 5HSO_3^- \longrightarrow 3HSO_4^- + 2SO_4^{2-} + I_2(s) + H_2O_4^{2-}$$

(iii) From sea-weeds :

Sea-weeds are dried and burnt in shallow pits, ash left is called kelp. Ash on extraction with hot water dissolves out chlorides, carbonates, sulphates and iodides of sodium and potassium. The solution on concentration seperates out all leaving behind iodide in the solution. Solution is mixed with MnO2 and concentrated H2SO4 in iron retorts. Liberated iodine is condensed in series of earthen-ware known as aludels.

 $2NaI + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + I_2 + 2H_2O_4$

$$\begin{array}{ll} (\mathbf{iv}) & 2\mathrm{KI} + \mathrm{Cl}_2 \longrightarrow 2\mathrm{KCl} + \mathrm{I}_2 & (\mathbf{v}) & 2\mathrm{KI} + \mathrm{H}_2\mathrm{O}_2 \longrightarrow 2\mathrm{KOH} + \mathrm{I}_2 \\ (\mathbf{vi}) & \mathrm{CuSO}_4 + 2\mathrm{KI} \longrightarrow \mathrm{K}_2\mathrm{SO}_4 + \mathrm{CuI}_2 \, ; & 2\mathrm{CuI}_2 \longrightarrow \mathrm{Cu}_2\mathrm{I}_2 + \mathrm{I}_2 \end{array}$$

- $2CuI_2 \longrightarrow Cu_2I_2 + I_2$
- This I_2 gets dissolved into KI forming KI_3 , since I_3^- ions are yellow, therefore solution develops yellow colour. P

PROPERTIES:

- It is a dark violet solid, undergoes sublimation, least soluble (among halogens) in water but much more soluble in KI(aq.) due (i) to formation of KI₃
- P KF₃ cannot be formed similarly since F does not have 'd' orbitals. So sp³d hybridisation is not possible with F.
- (ii) It is soluble in organic solvents like CHCl₃, CCl₄ etc. to get violet solutions.
- (iii) **Reaction with hypo :**

iodometric titrations

$$S_2 O_3^{2-}$$
 (thiosulphate ions) + $I_2 \longrightarrow S_4^{+2.5} O_6^{2-}$ (tetrathionate ions) + 2I

This reaction is the basis of iodometric (direct I_2 titration) titration, which is carried out for the estimation of iodine using starch indicator.

Reaction with NH₃: (iv)

$$NH_3(g) + I_2 \longrightarrow No Reaction$$

$$\begin{array}{c} \mathsf{NH}_3(\mathsf{aq}) + \mathrm{I}_2(\mathsf{s}) \\ (\mathsf{Ammonia\ liquor}) \end{array} \xrightarrow[]{A\ slurry\ is\ formed} \\ \begin{array}{c} \mathsf{A\ slurry\ is\ formed} \\ \mathsf{which\ can\ be\ dried} \\ \mathsf{an\ on\ hammering\ it} \\ \mathsf{explodes\ causing} \\ \mathsf{sound\ (crakers)} \end{array} \xrightarrow[]{NI}_3 \cdot \underbrace{\mathsf{NH}_3}_3 + 3\mathrm{HI} \\ (\mathsf{Nitrogentriiodide} \\ \mathsf{ammoniated} \end{array}$$

$$8NI_3$$
. $NH_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$

(v) Reaction with
$$KClO_3$$
 or $KBrO_3$:

$$2 \text{ KClO}_3 + \text{I}_2 \xrightarrow{\Delta} 2 \text{ KIO}_3 + \text{Cl}_2 \text{ ; } 2 \text{ KBrO}_3 + \text{I}_2 \xrightarrow{\Delta} 2 \text{ KIO}_3 + \text{Br}_2$$

Reaction with ozone (dry) : $2I_2(s) + 3O_3(g) \longrightarrow I_4O_9(s)$ I_4O_9 is an ionic compound consisting of I^{3+} & $(IO_3^{-})_3$ indicative of metallic character of I (low I.E, low E.N.) P With NaOH there is common reaction as with Cl₂ and Br₂. With H₂ there is reversible reaction. **OXIDES OF CHLORINE :** Chlorine dioxide (ClO_{γ}) : **PREPARATION:** $2 \operatorname{ClO}_{3}^{-}(\operatorname{aq}) + \operatorname{SO}_{2}(g) \xrightarrow{H^{+}} 2 \operatorname{ClO}_{2}(g) + \operatorname{SO}_{4}^{2-}(\operatorname{aq})$ (i) P Chlorates of sodium and potassium can be used $2\text{KClO}_3 + 2\text{ H}_2\text{C}_2\text{O}_4 \xrightarrow{90^\circ\text{C}} 2\text{ClO}_2(\text{g}) + 2\text{CO}_2 + \text{K}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}_2(\text{g}) + 2\text{CO}_2 + 2\text{K}_2\text{O}_2(\text{g}) + 2\text{CO}_2 + 2\text{K}_2\text{O}_2(\text{g}) + 2\text{CO}_2 + 2\text{K}_2\text{O}_2(\text{g}) + 2\text{CO}_2(\text{g}) + 2\text{CO}_2($ **(ii)** $2\text{AgClO}_3 + \text{Cl}_2 \xrightarrow{90^{\circ}\text{C}} 2\text{AgCl} \downarrow (\text{white}) + 2\text{ClO}_2 + \text{O}_2$ (iii) $Cl_2O_6 + N_2O_4 \longrightarrow ClO_2 + [NO_2^+] [ClO_4^-]$ (iv) **PROPERTIES:** Yellow gas at room temp, soluble in water and explosive substance. It also behaves as an oxidising agent. (It kill bacteria (i) better than Cl_2) **Reaction with ozone :** $2\text{ClO}_2 + 2\text{O}_3 \xrightarrow{H^+} \text{Cl}_2\text{O}_6$ (yellow solid) $+ 2\text{O}_2$ **(ii)** dichlorine hexa oxide In the reaction O_3 is behaving as an oxidising agent. F Cl_2O_6 (s) is a mixed anhydride of HClO₃ & HClO₄ because on dissolving in water it gives a mixture of these two acids. P In solid state, Cl_2O_6 exists as ClO_2^+ & ClO_4^- . (iii) **Reaction with alkaline H_2O_2:** In this reaction H₂O₂ acts as a reducing agent. It reduces ClO₂ into ClO₂⁻ $\mathrm{H_2O_2} \longrightarrow 2\mathrm{H^+} + \mathrm{O_2} + 2\mathrm{e^-} \ ; \quad \mathrm{e^-} + \mathrm{ClO_2} \longrightarrow \mathrm{ClO_2^-}] \times 2$ $H_2O_2 + 2ClO_2 \longrightarrow 2ClO_2^- + 2H^+ + O_2$ $H_2O_2 + 2CIO_2 + 2OH^- \longrightarrow 2CIO_2^- + 2H_2O + O_2$ or (iv) Reaction with HZ : In this reaction HI behaves as a reducing agent where it reduces CIO₂ into Cl⁻ and itself is oxidised to I₂. $[5e^{-} + 4 H^{+} + ClO_{2} \longrightarrow Cl^{-} + 2H_{2}O] \times 2$ $[2I^{-} \longrightarrow I_{2} + 2e^{-}] \times 5$ $2\text{ClO}_2 + 8\text{H}^+ + 10 \text{ I}^- \longrightarrow 5\text{I}_2 + 2\text{Cl}^- + 4\text{H}_2\text{O}$ HYDRA ACIDS (HALOGEN ACIDS) : HCl, HBr & HI: **PREPARATION:** By direct combination of elements : (i) $H_2 + Cl_2 \longrightarrow 2HCl$ $H_2 + Br_2 \xrightarrow{Pt} 2HBr$ $H_2 + I_2 \xrightarrow{Pt, 450 \circ C} 2HI$

(vi)

(ii) By heating a halide with acid :

 $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

 $NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$

For HCl we use H_2SO_4 as an acid, while for HBr and HI we use H_3PO_4 .

(a) HCl cannot be dried over $P_2O_5(P_4O_{10})$ or quick lime since they react with gas chemically.

 $CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

 $P_4O_{10} + 3HCl \longrightarrow POCl_3 + 3HPO_3$

HCl is, hence dried by passing through conc. H_2SO_4 .

(b) HBr (or HI) cannot be prepared by heating bromide (iodide) with conc. H_2SO_4 because HBr and HI are strong reducing agents and reduce H_2SO_4 to SO_2 and get themselves oxidised to bromine and iodine respectively. $KX + H_2SO_4 \longrightarrow KHSO_4 + HX$

$$H_2SO_4 + 2HX \longrightarrow SO_2 + X_2 + 2H_2O (X = Br \text{ or } I)$$

Hence, HBr and HI are prepared by heating bromides and iodides respectively with conc. H_3PO_4 .

3KBr(KI) + H_3 PO₄ $\longrightarrow K_3$ PO₄ + 3HBr (HI)

(iii) By reaction of P_4 (Laboratory Method) :

$$P_4 + 6Br_2 (6I_2) \longrightarrow 4PBr_3 (4PI_3)$$
 (product in situ)

$$PBr_{3}(PI_{3}) + 3H_{2}O \longrightarrow 3HBr(HI) + H_{3}PO_{3}$$

(iv) By passing H_2S/SO_2 into solutions of halogens :

$$\begin{array}{ccc} \mathrm{H_2S} + \mathrm{X_2} & \longrightarrow & \mathrm{2HX} + \mathrm{S} \\ \mathrm{SO_2} + \mathrm{2H_2O} + \mathrm{X_2} & \longrightarrow & \mathrm{2HX} + \mathrm{H_2SO_4} \end{array}$$

PROPERTIES :

(v)

- (i) These are colourless, pungent smelling gases with acidic tastes.
- (ii) It is heavier than air, can be liquified to colourless liquids.
- (iii) These are neither combustible nor supporter of combustion.
- (iv) When perfectly dry, they have no action on litmus, but in presence of moisture, they turn blue litumus red, showing acidic nature. Among HX, HI is the strongest and HF is the weakest acid.

(v) These are quite soluble in water.

HCl ionises as below.

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) K_a = 10^7$$

It aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water.

When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

Au + 4 H⁺ + NO₃⁻ + 4 Cl⁻ \rightarrow AuCl₄⁻ + NO + 2 H₂O 3 Pt + 16 H⁺ + 4 NO₃⁻ + 18 Cl⁻ \rightarrow 3 PtCl₆²⁻ + 4 NO + 8 H₂O Reaction with metals oxides, hydroxides and bicarbonates

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$
; $MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

$$NaOH + HCl \longrightarrow NaCl + H_2O; CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

(vi) Reaction with salts, HCl decomposes salts of weaker acids.

$$\begin{split} \text{NaHCO}_3 + \text{HCl} &\longrightarrow \text{NaCl} + \text{CO}_2^{\uparrow} + \text{H}_2\text{O}; & \text{Na}_2\text{S} + 2\text{HCl} &\longrightarrow 2\text{NaCl} + \text{H}_2\text{S}^{\uparrow} \\ \text{Na}_2\text{SO}_3 + 2\text{HCl} &\longrightarrow 2\text{NaCl} + \text{SO}_2^{\uparrow} + \text{H}_2\text{O}; & \text{Na}_2\text{S}_2\text{O}_3 + \text{HCl} &\longrightarrow 2\text{NaCl} + \text{SO}_2^{\uparrow} + \text{H}_2\text{O} + \text{S}_2\text{NaNO}_2 + 2\text{HCl} &\longrightarrow 2\text{NaCl} + \text{NO}^{\uparrow} + \text{NO}_2^{\uparrow} + \text{H}_2\text{O} \end{split}$$

(vii) Reducing property and stability of hydracids : It is quite stable and hence is oxidised by strong oxidising agents like MnO₂, KMnO₄, K₂Cr₂O₇, HCl: PbO_2, Pb_3O_4 . $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$ (i) $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$ (ii) $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_7$ (iii) $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$; (v) $Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$ (iv) Therefore, HCl is a weak reducing agent. HBr : It is not very stable and hence more easily oxidised or acts as a strong reducing agents. In addition to above reducing properties of HCl, it also reduces H_2SO_4 to SO_2 which is not done by HCl. $H_2SO_4 + HBr \longrightarrow SO_2 + Br_2 + 2H_2O$ Aqueous HBr on exposure to atmospheric oxygen is oxidised to bromine (yellow) $4HBr + O_2 \longrightarrow 2 Br_2 + 2H_2O$ **H**Z : It is least stable hydrogen halide. It is readily oxidised and thus acts as a powerful reducing agent. In addition to reaction shown by HCl, it shows following reactions also. (a) $H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + H_2O;$ $H_2SO_4 + 6HI \longrightarrow S + 3I_2 + 4H_2O;$ $H_2SO_4 + 8HI \longrightarrow H_2S + 4I_2 + 4H_2O;$ (c) $2HNO_2 + 2HI \longrightarrow 2NO + I_2 + 2H_2O$ (e) $K_2S_2O_8 + 2HI \longrightarrow K_2SO_4 + I_2 + H_2SO_4$ $2\mathrm{HNO}_3 + 2\mathrm{HI} \longrightarrow 2\mathrm{NO}_2 + \mathrm{I}_2 + 2\mathrm{H}_2\mathrm{O}$ (b) $HIO_3 + 5HI \longrightarrow 3I_2 + 2H_2O$ (d) $2\text{FeCl}_3 + 2\text{HI} \longrightarrow 2\text{FeCl}_2 + \text{I}_2 + 2\text{HCl}$ (f) C. Aqueous solution of acid, if exposed to O_2 is oxidised to iodine. $4\text{HI} + \text{O}_2 \longrightarrow 2\text{I}_2 + 2\text{H}_2\text{O}$ (viii) **Reaction with ammonia :** $NH_3 + HX \longrightarrow NH_4X \uparrow (white fumes) (where X = Cl, Br, I)$ (ix) Action of halogens : (a) Cl_2 is liberated from HCl by F_2 alone. $F_2 + HCl \longrightarrow 2HF + Cl_2$ (b) Br_2 is liberated from HBr by F_2 and Cl_2 (not by I_2) $2\text{HBr} + \text{F}_2/\text{Cl}_2 \longrightarrow 2\text{HF}(2\text{HCl}) + \text{Br}_2$ (c) I₂ is liberated from HI by F_2 , Cl₂ and Br₂ $2\text{HI} + \text{F}_2(\text{Cl}_2, \text{Br}_2) \longrightarrow 2\text{HF}(\text{HCl}, \text{HBr}) + \text{I}_2$ **(x) Detection of cation:** $AgNO_3 + HCl \longrightarrow AgCl \downarrow (white) + HNO_3$ HCl: $(CH_{3}COO)_{2}Pb + 2HCl \longrightarrow PbCl_{2}\downarrow (white) + 2CH_{3}COOH$ $Hg(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 \downarrow (white) + 2HNO_3$ **HBr**: $AgNO_3 + HBr \longrightarrow AgBr \downarrow (pale yellow) + HNO_3$ $(CH_{3}COO)_{2} Pb + 2HBr \longrightarrow PbBr_{2} \downarrow (white) + 2CH_{3}COOH$ $AgNO_3 + HI \longrightarrow AgI \downarrow (bright yellow) + HNO_3$ **H**Z1: $(CH_3COO)_2 Pb + 2HI \longrightarrow PbI_2 \downarrow (yellow) + 2CH_3COOH$ $HgCl_2 + 2HI \longrightarrow HgI_2 \downarrow (scarlet red) + 2HCl$

HI reacts with CuSO₄ liberating iodine via the formation of cupric iodide (not by HCl or HBr).

$$2\text{CuSO}_4 + 4\text{HI} \longrightarrow 2\text{CuI}_2 + 2\text{H}_2\text{SO}_4; \quad 2\text{CuI}_2 \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$$

(xi) Formation of aqua-regia :

3 parts of conc. HCl and 1 part of conc. HNO_3 is known as aqua-regia. This is used for dissolving noble metals like Au (Gold) and Pt (Platinum).

 $3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl (reactive); Au + 3Cl \longrightarrow AuCl_3$

USES:

- (i) HCl is used in preparation of Cl_2 , chlorides, aqua regia, glucose, (from corn starch), medicines, laboratory reagents, cleaning metal surfaces before soldering or electroplating. It is also used for extracting glue from bones and purifying bone black.
- (ii) HBr is used as laboratory reagent for preparing bromo derivatives like sodium bromides and potassium bromide. These are used in medicines as sedatives.
- (iii) HI is used as reducing agent in organic chemistry.

HYDROFLUORIC ACID $[H_2F_2, HF]$:

PREPARATION :

 H_2 and F_2 combine with each other very violently (even in dark) to form HF. So simple reaction cannot be used for its preparation, special methods are employed for its preparation.

(i) Laboratory Method :

Anhydrous HF is obtained by heating dry potassium hydrogen fluoride in a copper retort connected with copper condenser.

$$KHF_2 \longrightarrow KF + HF$$

(ii) Industrial Method :

HF is prepared by heating fluorspar (CaF₂) with conc H_2SO_4 .

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Aqueous HF being corrosive to glass, is stored in wax lined bottles or vessel made of copper or monel.

In glass or silica bottles, it attacks them as follows:

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O; CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$
; $SiF_4 + 2HF \longrightarrow H_2SiF_6$

This action of HF on silica (silicates) is used for etching glass. The glass surface to be etched is coated with wax, the design, is scratched on glass through wax coating this is then treated with 40% solution.

PROPERTIES:

- (i) It is colourless, corrosive liquid with pungent smell with high boiling point due to hydrogen bonding.
- (ii) Dry HF does not attack metals under ordinary conditions (except K), but in presence of water, it dissolves metals with liberation of hydrogen gas.
- (iii) It is a weak dibasic acid (due to strong HF bond) and forms two series of salt.

$$NaOH + H_2F_2 \longrightarrow NaHF_2 + H_2O$$
; $NaHF_2 + NaOH \longrightarrow 2NaF + H_2O$

(**Iv**) Concentrated acid reacts with oxides, hydroxides and carbonates.

$$2NaOH + H_2F_2 \longrightarrow 2NaF + 2H_2O : CaCO_3 + 2HF \longrightarrow CaF_2 + H_2O + CO_2$$

OXY-ACIDS OF CHLORINE : HYPO-CHLOROUS ACID [HCIO] : PREPARATION:

(i) The acid is known only in solution, It is obtained by shaking precipitate of HgO with chlorine water.

 $2HgO + 2Cl_2 + H_2O \longrightarrow Hg_2OCl_2$ (Oxychloride of mercury) + 2HClO

(ii) Commercially, it is obtained by passing CO₂ through suspension of bleaching powder and then distilling.

$$CaOCl_2 + H_2O + CO_2 \longrightarrow CaCl_2 + CaCO_3 + 2HClO$$

PROPERTIES:

- (i) It is a weak acid. Its concentrated solution is yellow in colour while dilute solution is colourless. It is unstable and decomposes. $2\text{HClO} \longrightarrow 2\text{HCl} + \text{O}_2$
- (ii) It dissolves magnesium with evolution of hydrogen. $Mg + 3HCIO \longrightarrow Mg(CIO)_2 + H_2$

- (iii) With alkalies, it forms salts called hypochlorites.
- (iv) It acts as a powerful oxidising and bleaching agent. This is due to release of nascent oxygen easily. HClO \longrightarrow HCl+ O

CHLOROUS ACID [HCIO₂] : PREPARATION:

It is obtained in aqueous solution when barium chlorite suspension in water is treated with H_2SO_4 . The insoluble barium sulphate is filtered off.

 $Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_2$

PROPERTIES:

(iii)

(i) The freshly prepared solution is colourless but it soon decomposes to ClO₂ which makes the solution yellow.

 $5 \text{ HClO}_2 \longrightarrow 4 \text{ ClO}_2 + \text{HCl} + 2\text{H}_2\text{O}$

(ii) The acid undergoes auto-oxidation.

$$2HClO_2 \longrightarrow HClO + HClO_2$$

The acid liberates iodine from KI.

$$4\text{KI} + \text{HClO}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{KOH} + \text{HCl} + 2\text{I}_2$$

CHLORIC ACID [HCIO₃] : PREPARATION:

This acid is only known in solution. The acid is preapred by the action of the dilute H_2SO_4 on barium chlorate.

 $Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2HClO_3.$

PROPERTIES:

Concentrated acid is colourless and pungent smelling liquid. It decomposes in light. However, it is stable in dark. It acts as a strong oxidising and bleaching agent in light. Organic substances like paper, cotton, wool, etc., catch fire in contact with the acid.

Per-Chloric Acid [HCIO₄]:

PREPARATION:

It is the most stable oxy-acid of chlorine. Anhydrous HClO_4 is obtained by doing distillation of KClO_4 (potassium perchlorate), with 96-97.5% H_2SO_4 under low pressure at 90-160°C.

 $\text{KCIO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{HCIO}_4$

An aqueous solution of the acid is obtained by reacting barium perchlorate with calculated quantity of dilute H_2SO_4 . The insoluble barium sulphate is removed by filtration.

$$Ba(CIO_4)_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2HCIO_4$$

PROPERTIES:

- (i) Anhydrous $HClO_4$ is a colourless liquid which turns dark on keeping. It fumes in moist air.
- (ii) It is one of the strongest acid and ionises as follows :

 $HClO_{4} \longrightarrow H^{+} + ClO_{4}^{-}$

(iii) It dissolves most of the metals.

$$Zn + 2HClO_4 \longrightarrow Zn(ClO_4)_2 + H_2$$

- It is an oxidising agent and explodes in contact with organic matter.
- (v) $2\text{HClO}_4 + \text{P}_2\text{O}_5 \longrightarrow 2\text{HPO}_3 + \text{Cl}_2\text{O}_7$

BLEACHING POWDER (CaOCI, H, O)

Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

Ca(OCl)Cl

PREPARATION:

$$Ca(OH)_2 + Cl_2 \xrightarrow{40^{\circ}C} Ca(OCl)Cl + H_2O$$

Properties

(iv)

- (i) It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.
- (ii) On long standing, it undergoes auto-oxidation into calcium chlorate and calcium chloride.

$$6 \operatorname{CaOCl}_2 \rightarrow \operatorname{Ca(CIO}_3)_2 + 5 \operatorname{CaCl}_2$$

(iii)
$$2 \operatorname{CaOCl}_2 \xrightarrow{\operatorname{CoCl}_2} 2 \operatorname{CaCl}_2 + O_2$$

(iv) In presence of a little amount of a dilute acid, it loses oxygen.

$$2 \operatorname{CaOCl}_2 + \operatorname{H}_2 \operatorname{SO}_4 \longrightarrow \operatorname{CaCl}_2 + \operatorname{CaSO}_4 + 2 \operatorname{HClO}_4$$

HClO \longrightarrow HCl + O

On account of the liberation of nascent oxygen, it shows oxidising and bleaching properties. (a) Oxidising properties

$$\begin{aligned} &\text{CaOCl}_2 + \text{H}_2\text{S} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{S} \\ &\text{CaOCl}_2 + 2 \text{ KI} + 2 \text{ HCl} \longrightarrow \text{CaCl}_2 + 2 \text{ KCl} + \text{H}_2\text{O} + \text{I}_2 \\ &\text{3 CaOCl}_2 + 2 \text{ NH}_3 \longrightarrow \text{3 CaCl}_2 + 3 \text{ H}_2\text{O} + \text{N}_2 \end{aligned}$$

It oxidises NO_2^- to NO_3^- , AsO_3^{3-} to AsO_4^{3-} and Fe^{2+} to Fe^{3+} (in acidic medium)

(b) Bleaching action

Coloured matter + $[O] \longrightarrow$ colourless product.

 (\mathbf{v}) When bleaching powder reacts with dilute acids or CO_2 it liberates chlorine which is known as available chlorine.

$$\begin{array}{c} \text{CaOCl}_2 + 2 \text{ HCl} & \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{Cl}_2\\\\ \text{CaOCl}_2 + \text{H}_2\text{SO}_4 & \longrightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{Cl}_2\\\\ \text{CaOCl}_2 + \text{CO}_2 & \longrightarrow \text{CaCO}_3 + \text{Cl}_2 \end{array}$$

P HNO₃ is a strong oxidising acid to be avoided, here.

ESTIMATION OF AVAILABLE CHLORINE :

Let the wt. of sample of B.P. = W gm.

Add into a beaker containing acetic acid solution and excess KI. A yellow brown solution is formed (I_3)

$$I_2 + I^- \longrightarrow I_3^-$$

Now few drops of starch solution is added into it. An intensive blue color is observed. Now hypo is used as the titrant. Note the volume where the blue colour disappear.



Ø Reaction involved

$$CaOCl_{2} + 2CH_{3}COOH \longrightarrow (CH_{3}COO)_{2}Ca + H_{2}O + Cl_{2}$$
$$Cl_{2} + 2KI \longrightarrow 2KCl + I_{2}$$
$$I_{2} + 2S_{2}O_{3}^{2-} \longrightarrow S_{4}O_{6}^{2-} + 2I^{-}$$

Calculation :

$$\%Cl = \frac{[M_{hypo} \times V_{hypo}] \times \frac{1}{2} \times 71}{W} \times 100$$

(vi) Bleaching powder converts acetone or ethyl alcohol into CHCl₃

 $\begin{array}{l} \text{CaOCl}_2 + \text{H}_2\text{O} & \longrightarrow & \text{Ca(OH)}_2 + \text{Cl}_2\\\\ \text{CH}_3\text{COCH}_3 + 3 \text{ Cl}_2 & \longrightarrow & \text{CCl}_3\text{COCH}_3 + 3 \text{ HCl}\\\\ 2 \text{ CCl}_3\text{COCH}_3 + \text{Ca(OH)}_2 & \longrightarrow & (\text{CH}_3\text{COO)}_2\text{Ca} + 2 \text{ CHCl}_3 \end{array}$

Ø Some important order

(a) Acid strength :

(i) HI > HBr > HCl > HF (ii) HOCl > HOBr > HOI

(iii) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

(b) Oxidising power : (i) $F_2 > Cl_2 > Br_2 > I_2$ (According to electrode potential)

(ii)
$$\operatorname{BrO}_4^- > \operatorname{IO}_4^- > \operatorname{ClO}_4^-$$
 (iii) $\operatorname{HClO}_4 < \operatorname{HClO}_3 < \operatorname{HClO}_2 \le \operatorname{HClO}_3$

(c) Order of disproportionation :

 $3 \text{ XO}^- \longrightarrow 2X^- + XO_3^-$ (hypohalite ion); $IO^- > BrO^- > CIO^-$

PSEUDO HALOGENS & PSEUDO HALIDES:

Some inorganic compounds like $(CN)_2$ cyanogen, $(SCN)_2$ thiocyanogen, $(SeCN)_2$ selenocyanogen, $(SCSN_3)_2$ azidocarbondisulphide have been found to behave like halogens & they are known as pseudo halogen solids. Similarly few ions are known, consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. They are therefore called pseudohalide ions, e.g. (CN^-) cyanide ion, (SCN^-) thiocyanate ion, $(SeCN^-)$ selenocyanate ion, (OCN^-) cyanate ion, (NCN^{2-}) cyanamide ion, (N_3^-) azide ion etc.

INTERHALOGEN COMPOUNDS :

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called interhalogen compounds. These are of four types.

AB	AB ₃	AB_5	AB_7
ClF	ClF ₃	ClF ₅	lF ₇
BrF	BrF ₃	BrF ₅	
ICl	ICl ₃	IF ₅	
IF	IF ₃	-	

PREPARATION:

(i) By the direct combination of halogens :

 $Cl_2 + F_2$ (equal volumes) $\xrightarrow{473K} 2ClF$; $Cl_2 + 3F_2$ (excess) $\xrightarrow{573K} 2ClF_3$;

 $I_2 + Cl_2 \longrightarrow 2ICl;$ (equimolar)

^{CP} Diluted with water.

 $Br_{2}(g) + 3F_{2} \longrightarrow 2BrF_{3}$

 $\mathbb{G}^{\mathbb{P}}$ F₂ is diluted with N₂

$$I_2 + 3F_2 \xrightarrow{-78^\circ C} 2IF_3$$

 \bigcirc F₂ is taken in freon.

$$Br_2 + 5F_2$$
 (excess) $\longrightarrow 2BrF_2$

 ${}^{\textcircled{C}}$ IF₇ can not be prepared by direct combination of I₂ & F₂.

(ii) From lower interhalogens :

 $ClF + F_{2} \longrightarrow ClF_{3}; \qquad ClF_{3} + F_{2} (excess) \xrightarrow{200^{\circ}C} BrF_{5}; IF_{5} + F_{2} \xrightarrow{270^{\circ}C} IF_{7}$

This method is generally applied for the preparation of halogen fluorides.

(iii) Other methods :

$$\begin{split} & 6\mathrm{HCl} + \mathrm{KIO}_3 + 2\mathrm{KI} \longrightarrow 2\mathrm{KCl} + 3\mathrm{H}_2\mathrm{O} + 3\mathrm{ICl} \\ & \mathrm{Cl}_2 + \mathrm{ClF}_3 \xrightarrow{250-350\,^{\circ}\mathrm{C}} 3\mathrm{ClF} \ ; \quad \mathrm{KCl} + 3\mathrm{F}_2 \xrightarrow{200\,^{\circ}\mathrm{C}} \mathrm{KF} + \mathrm{ClF}_5 \\ & 3\mathrm{I}_2 + 5\mathrm{AgF} \longrightarrow 5\mathrm{Agl} + \mathrm{lF}_5 \quad ; \quad 8\mathrm{F}_2 + \mathrm{PbI}_2 \longrightarrow \mathrm{PbF}_2 + 2\mathrm{lF}_7 \end{split}$$

PROPERTIES:

(i) These compounds may be gases, liquids or solids.

Gases : CIF, BrF, CIF₃, IF₇; Liquids : BrF_3 , BrF_5 ; Solids : ICl, IBr, IF₃, ICl₃.

(ii) Interhalogens containing fluorine are colourless but inter halogens consisting of heavier halogens are coloured. The intensity of colour increases with increase in the molecular weight of the compounds.

- (iii) All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.
- (iv) The boiling points increases with the increase in the electronegativity difference between A and B atoms.
- (v) Thermal stability of AB type interhalogen compounds decreases with the decrease in electronegativity difference between A and B atoms. IF > BrF > ClF > ICl > IBr > BrCl.
- \bigcirc More polar is the A B bond more is the stability of interhalogen.
- (vi) Interhalogen compounds are more reactive than the parent halogens but less reactive than F_{γ} .

 $ICl + 2Na \longrightarrow NaI + NaCl$

The order of reactivity of some interhalogens is as follows :

 $ClF_3 > BrF_3 > IF_7 > BrF_5 > BrF.$

(vii) Hydrolysis : All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when AB), halite (when AB₃), halate (when AB₅), and perhalate (when AB₇) anion derived from the larger halogen.

 $AB + H_2O \longrightarrow HB + HOA$

$$\begin{aligned} \text{BrCl} + \text{H}_2\text{O} &\longrightarrow \text{HCl} + \text{HOBr} ; & \text{ICl} + \text{H}_2\text{O} &\longrightarrow \text{HCl} + \text{HIO}_2 \\ \text{ICl}_3 + 2\text{H}_2\text{O} &\longrightarrow 3\text{HCl} + \text{HIO}_2 ; & \text{IF}_5 + 3\text{H}_2\text{O} &\longrightarrow 5\text{HF} + \text{HIO}_2 \\ \text{IF}_7 + 6\text{H}_2\text{O} &\longrightarrow 7\text{HF} + \text{H}_5\text{IO}_6 ; & \text{BrF}_5 + 3\text{H}_2\text{O} &\longrightarrow 5\text{HF} + \text{HBrO}_2 \end{aligned}$$

- Hydrolysis products are halogen acid and oxy-halogen acid. Oxy-halogen acid is of larger central halogen atom.
- Oxidation state of A atom does not change during hydrolysis.
- (viii) Reaction with non-metallic and metallic oxides :

 $4\mathrm{BrF}_3+3\mathrm{SiO}_2 \longrightarrow 3\mathrm{SiF}_4+2\mathrm{Br}_2+3\mathrm{O}_2 \hspace{3mm} ; \hspace{1.5mm} 4\mathrm{BrF}_3+3\mathrm{WO}_3 \longrightarrow 2\mathrm{WF}_6+2\mathrm{Br}_2+3\mathrm{O}_2$

(ix) Addition reaction (of AB type compounds) :

 $-CH = CH - + ICI \longrightarrow -CHI - CHCI - ; CH_2 = CH_2 + BrCI \longrightarrow CH_2Br - CH_2CI$

(**x**) Reaction with alkali metal halides :

 $\operatorname{IBr} + \operatorname{NaBr} \longrightarrow \operatorname{NaIBr}_2; \qquad \operatorname{ICl}_3 + \operatorname{KCl} \longrightarrow \operatorname{KICl}_4$

Uses : These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U .

 $U(s) + 3 \operatorname{ClF}_{3}(l) \longrightarrow UF_{6}(g) + 3 \operatorname{ClF}(g)$

(F)GROUP 18 ELEMENTS : (THE ZERO GROUP FAMILY)

Group 18 Consists of six elements: helium, neon, argon, krypton, xenon and radon. All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

Occurrence :

All the noble gases except radon occur in the atmosphere. Their atmospheric abundabce in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of 226 Ra.

$$^{226}_{88}$$
Ra \rightarrow^{222}_{86} Rn $+^{4}_{2}$ He

 \Im Most abundant element in air is Ar. Order of abundance in the air is Ar > Ne > Kr > He > Xe.

Electronic Configuration :

All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$. Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

Ionisation Enthalpy :

Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increases in atomic size.

Atomic Radii :

Atomic radii increase down the group with increase in atomic number.

Electron Gain Enthalpy :

Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have larger positive values of electron gain enthalpy.

Physical properties :

All the noble gases are monoatomic. They are colourless, and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces,. Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Element	He	Ne	Ar	Kr	Xe
Atomic Number	2	10	18	36	54
Atomic Mass	4	20.18	39.10	83.80	131.30
Electronic configuration	1s ²	[He] 2s ² 2p ⁶	[Ne] 3s ² 3p ⁶	[Ar] 3d ¹⁰ 4s ² 4p ⁶	[Kr] 4d ¹⁰ 5s ² 5p ⁶
Atomic Radius (pm)	120	160	190	200	220
Ionization enthalpy / $(kJ mol^{-1})$	2372	2080	1520	1351	1170
Density (at STP)/g cm ⁻³	1.8 × 10 ⁻⁴	9.0×10^{-4}	1.8 × 10 ⁻³	3.7 × 10 ⁻³	5.9 × 10 ⁻³
Melting point / K	-	24.6	83.8	115.9	161.3
Boiling point / K	4.2	27.1	87.2	119.7	165.0

ATOMIC & PHYSICAL PROPERTIES :

Chemical Properties

(i)

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

The noble gases expect helium $(1S^2)$ have completely filled ns² np⁶ electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy. The reactivity of noble gases has been investigated occasionally ever since their discovery, but all attempt to force them to react to form the compounds were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+ PtF_6^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kj mol⁻¹) was almost identical with that xenon (1170 kJ mol⁻¹). He made efforts to prepare same type of compound with Xe⁺ PtF₆⁻ by mixing Pt F₆ and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

- If Helium is compressed and liquified it forms He(I) liquid at 4.2 K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K, which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity. Compounds of inert gases are of following two types.
- Physical compounds (possess no proper bonding)
 Physical compounds may be (A) compounds whose existence is on the basis of spectroscopic studies (temporary phase not isolated) and (B) clatherate compounds.
Clatherate compounds :

Inert gas molecules get trapped in the cages formed by the crystal structure of water.

During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clatherate compounds.

There are no chemical bonds. They do not possess an exact chemical formula but approx it is 6 water molecules : 1 inert gas molecule. The cavity size is just smaller than the atom of the noble gas. Such compounds are also formed by the other organic liquids like dihydroxybenzene (for example quinol).



(ii) True chemical compounds (posses proper bonding).

COMPOUNDS OF XENON :

(a) XENON DIFLUORIDE (XeF₂): PREPARATION:

(i)
$$Xe + F_2 \xrightarrow{873K,1bar} XeF_2$$

Ni–Tube or monel metal (alloy of Ni)

Volume ratio should be 2:1 otherwise other higher fluorides tend to form.

(ii)
$$Xe + O_2F_2 \xrightarrow{118^{\circ}C} XeF_2 + O_2$$

(iii)
$$Xe + F_2 \xrightarrow{Hg(arc)} XeF_2$$

(iv) Recently discovered method :

 K^+ [AgF₄]⁻ [potassium tetrafluoroargentate (III)] is first prepared and this is reacted with BF₃.

$$K^{+} [AgF_{4}]^{-} \xrightarrow{BF_{3}} AgF_{3} (red solid) + KBF_{4}$$

2 AgF_{3} + Xe \longrightarrow 2 AgF_{2} (Brown solid) + XeF_{2}

PROPERTIES:

- (i) Colorless crystalline solid and sublimes at 298 K.
- (ii) Dissolves in water to give a solution with a pungent odour. Much soluble in HF liquid.
- (iii) This is stored in a vessel made up of monel metal which is a alloy of nickel.
- (iv) **Reaction with H**, : It reacts with hydrogen gas at 400° C

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

(v) Hydrolysis :

(a) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$ (slow)

The above is neither a cationic hydrolysis nor an anionic hydrolysis as seen in ionic equilibrium. It is a covalent compound and hydrolysis is like that of PCl_5 .

(b) Hydrolysis is more rapid with alkali.

$$XeF_2 + 2 NaOH \longrightarrow Xe + \frac{1}{2} O_2 + 2NaF + H_2O (fast)$$

The reaction (a) is slower probably due to dissolution of XeF_2 in HF.

p-BLOCK ELEMENTS

(vi) Oxidising properties :

Higher the value of SRP better is the oxidising property of the species.

The standard reduction potential for XeF_2 is measured to be + 2.64 V. Therfore it acts as a strong oxidising agent.

$$2e^{-} + 2H^{+} + XeF_{2} \longrightarrow Xe + 2HF; SRP = +2.64 V$$

This oxidises halides to their respective halogens.

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

It oxidises $2Br^- \longrightarrow Br_2 + 2e^-$ & $2I^- \longrightarrow I_2 + 2e^-$

 \bigcirc In this manner XeF₂ will oxidise halide ions (except F⁻) into free halogens.

Similarly it can oxidise BrO_3^- (bromate) which are themselves good oxidising agents to BrO_4^- (perbromate ions) and Ce^{+3} to Ce^{+4} ion.

(vii) Oxidising as well as fluorinating properties :

It can act as strong oxidising agent as well as fluorinating agent.

$$C_{6}H_{5}I + XeF_{2} \longrightarrow C_{6}H_{5}IF_{2} + Xe; \qquad CH_{3}I + XeF_{2} \longrightarrow CH_{3}IF_{2} + Xe$$

 \mathbb{C} CH₃ IF₂ exists as CH₃⁺ IF₂⁻, IF₂⁻ is analogous to I₃⁻



 \mathbb{F}_3^- can not be formed as it has no d-orbitals to attain sp³d hybridisation.

(viii) Reactions of $XeF_2 + HF$ (anhydrous) :

 $Pt + 3XeF_{2} \xrightarrow{\mathsf{HF}} PtF_{6} + 3Xe; \qquad S_{8} + 24 XeF_{2} \longrightarrow 8SF_{6} + 24 Xe$ $2CrF_{2} + XeF_{2} \longrightarrow 2CrF_{3} + Xe; 2MoO_{3} + 6XeF_{2} \longrightarrow 2MoF_{6} + 6Xe + 3O_{2}$ $Mo (CO)_{6} + 3 XeF_{2} \longrightarrow Mo F_{6} + 3 Xe + 6CO$ $2 \bigcirc + XeF_{2} \xrightarrow{\mathsf{HF}} 2 \bigcirc F + Xe$ $8 NH_{3} + 3 XeF_{2} \longrightarrow N_{2} + 6 NH_{4}F + 3 Xe$ $2NO_{2} + XeF_{2} \longrightarrow 2 NO_{2}F + Xe$ (nitronium fluoride)

(ix) Formation of addition compounds : XeF₂ reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

$$\begin{split} & XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^- \\ & IF_5 \quad (lewis \ acid) \ + \ \ XeF_2 \ \longrightarrow \ [XeF]^+ [IF_6]^- \ ; \ 2SbF_5 \quad (lewis \ acid) \ + \ \ XeF_2 \ \longrightarrow \ [XeF]^+ [SbF_6]^- \end{split}$$

Similar behaviour is shown by PF₅ and AsF₅
 Structure : Shape linear and geometry trigonal bipyramidal.



(b) XENON TETRAFLUORIDE (XeF_4) : PREPARATION:

$$\begin{array}{rrrr} Xe & + & 2F_2 & \xrightarrow{873K,} & XeF_4 \\ 1 & : & 5 & & Ni-tube \end{array}$$

PROPERTIES:

æ

- (i) It is a colorless crystalline solid and sublimes at 298 K.
- (ii) It undergoes sublimation, soluble in CF₃ COOH. It undergoes hydrolysis violently hence no moisture must be present during it's preparation.

(iii) Reaction with
$$H_2O$$
:

 $6 \operatorname{XeF}_4 + 12 \operatorname{H}_2 O \longrightarrow 4 \operatorname{Xe} + 2 \operatorname{XeO}_3 + 24 \operatorname{HF} + 3 \operatorname{O}_2$

- ^{CP} XeO₃ is white solid and explosive compound (dry), soluble in water (well behaved in water)
- XeO₃ reacts with NaOH forming sodium xenate

 $XeO_3 + NaOH \longrightarrow Na^+ [HXeO_4]^-$ (sodium xenate)

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It disproportionates into perxenate ion in basic medium.
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 $2 [HXeO_{4}]^{-} + 2OH^{-} \longrightarrow [XeO_{6}]^{4-} + Xe + O_{2} + 2H_{2}O$

Xenic acid $(H_2 XeO_4)$ is a very weak acid.

(i) $[XeO]_{6}^{4-} \xrightarrow{H^{+}} XeO_{3} + O_{2}$ (ii) $[XeO_{6}]^{4-} + Mn^{+2} \longrightarrow MnO_{4}^{-} + XeO_{3}$ (slow decomposition)

(slow decomposition)

 $[XeO_6]^{4-}$ is obtainable as $Na_4 XeO_6$. $8H_2O$ (sodium perxenate)

(iv) Oxidising properties of XeF_4 :

 $XeF_4 + 2 H_2 \longrightarrow Xe + 4 HF; XeF_4 + 2 Hg \longrightarrow Xe + 2HgF_2$

(v) Addition reactions : XeF_4 reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$$

(vi) Fluorinating angen :

$$XeF_4 + Pt \longrightarrow PtF_4 + Xe; XeF_4 + 4NO \longrightarrow Xe + 4NOF (nitrosyl Fluoride)$$

$$XeF_4 + 4 NO_2 \longrightarrow Xe + 4 NO_2F$$
 (nitronium fluoride); $XeF_4 + 2C_6H_6 \longrightarrow C_6H_5F + 2HF + Xe$

Structure : Shape square planar & geometry octahedral



p-BLOCK ELEMENTS

(c) XENON HEXAFLUORIDE (XeF_{6}) :

1:

PREPARATION:

(i)

$$\begin{array}{c} Xe + 3F_2 \xrightarrow{573K,60-70\text{ bar}} XeF_6 \\ 1: 20 \end{array} XeF_6 \end{array}$$

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

PROPERTIES:

- Colourless crystalline solid and sublimes at 298 K. (i)
- It gives yellow liquid on melting where as other form white liquids on melting (a point of difference) (ii)
- (iii) HF is a good solvent for all three fluorides.

(iv) Hydrolysis :

- (a) Complete hydrolysis : $XeF_6 + 3H_2O \longrightarrow XeO_3$ (white solid) + 2HF
- $XeF_6 + H_2O \longrightarrow XeOF_4$ (colorless solid) + 2HF (b) Partial hydrolysis :
- **(v)** Reaction with silica (SiO_{γ}) :

 $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$

(vi) Thermal decomposition (effect of heat) :

 $2XeF_6 \xrightarrow{\Delta} XeF_2 + XeF_4 + 3F_2$

P XeF₂ & XeF₄ do not undergo decomposition

(vii) Formation of addition compounds :

 $\mathrm{XeF}_6 + \mathrm{SbF}_5 \longrightarrow [\mathrm{XeF}_5]^+ [\mathrm{SbF}_6]^-; \qquad \mathrm{XeF}_6 + \mathrm{BF}_3 \longrightarrow [\mathrm{XeF}_5]^+ [\mathrm{BF}_4]^-$

Reaction With H, : (viii)

 $XeF_6 + 3H_2 \longrightarrow 6HF + Xe$

Reaction of XeF₆ with XeO₃: (ix)

 $XeO_3 + 2 XeF_6 \longrightarrow 3 XeOF_4$

F⁻ donating/ **F**⁻ accepting properties : **(x)**

XeF₆ reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

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

donation { $XeF_6 + PtF_5 \longrightarrow (XeF_5^+) (PtF_6^-)$

acceptance $\begin{cases} CsF + XeF_{6} \longrightarrow CsXeF_{7} \\ (alkali metal (caesium heptafluoroxenate) \\ fluoride) \\ 2CsXeF_{7} \longrightarrow XeF_{6} + Cs_{2}XeF_{8} \\ (caesium octafluoroxenate) \end{cases}$

Order of oxidising power :

 $XeF_2 > XeF_4 > XeF_6$

STRUCTURE : Shape caped octahedral (distorted oactahedral)

(d) XENON-OXYGEN COMPOUNDS :

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3 .

 $6 \operatorname{XeF}_4 + 12 \operatorname{H}_2 O \longrightarrow 4 \operatorname{Xe} + 2 \operatorname{XeO}_3 + 24 \operatorname{HF} + 3 \operatorname{O}_2$

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

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2 .

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2 HF$$

 $XeF_6 + 2 H_2O \longrightarrow XeO_2F_2 + 4 HF$

 XeO_3 is a colourless explosive solid and has a pyramidal molecular structure. $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.

Uses :

Helium is a non–inflammable and light gas. Hence, it is used in filling ballons for meterological observations. It is also used in gas–cooled nuclear reactors. Liquid helium (b.p.4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical process (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handing substances that are air–sensitive.

Xenon and Krypton are used in light bulbs designed for special purposes.

1. INTRODUCTION

1.1 Definition

"The elements in which the last differentiating electron enters into the d-orbitals of the penultimate shell i.e. (n-1) d where n is the last shell are called d-block elements". A transition element may also be defined as the element which partially filled d-orbital in their ground state or most stable oxidation state.

 $Cu(Z=29) = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

$$Cu^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$

(Cupric ion)

The properties of these elements are intermediate between the properties of s-block and p-block elements.

These elements represent a change or transition in properties from more electropositive elements (s-block) to less electropositive elements (p-block). Therefore these elements are called transition elements.

Position in the periodic table

The position of d-block element has been shown in periodic table as follows :

IA																	Zero
1																	18
	IIA											IIIA	IVA	VA	VIA	VIIA	
	2											13	14	15	16	17	
		₭				- d-	blo	ck ·			>						
		шв	IVE	VB	VIB	VIIE		VIII		IB	IIB						
		3	4	5	6	7	8	9	1Ò	11	12						
		21	22	23	24	25	26	27	28	29	30		n-h	lock			
		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		P	- vyn			
		39	40	41	42	43	44	45	46	47	48						
s-t	lock	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
		57	72	73	74	75	76	77	78	79	80						
		La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						
		89,	104	105	106	107	108	109	110	111	112						
		Ac*	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						
	→		_														
£ bl	*																
1-01	*					1	1					1				1	
	'⇒ *	L				1						L					

- d-block elements lie in between 's' and 'p' block elements, i.e. these elements are located in the middle of the periodic table.
- (2) d-block elements are present in,

4th period ($_{21}$ Sc to $_{30}$ Zn, 10 elements) \rightarrow 1st Transition series. 5th period ($_{39}$ Y to $_{48}$ Cd, 10 elements) \rightarrow 2nd Transition series. 6th period ($_{51}$ La, $_{72}$ Hf to $_{80}$ Hg, 10 elements) \rightarrow 3rd Transition series.

 7^{th} period (₈₉Ac, ₁₀₄Rf to ₁₁₂Uub, 10 elements) $\rightarrow 4^{th}$ Transition series.

1.2 Electronic configuration

 In d-block elements with increase in atomic number, the dorbitals of penultimate shell i.e. (n-1) d are gradually filled by electrons. The general electronic configuration of dblock element is,

 $(n-11) d^{1-10}, ns^{0-2}.$

- (2) Depending upon the d-orbitals of which penultimate shell i.e. n = 4, 5, 6, 7 are filled, four rows (called series) os ten elements each obtained. They correspond to 3d, 4d, 5d and 6d subshells.
- (3) Energy of '(n-1)d' subshell is slightly greater than 'ns' subshell, hence orbital is filled first then (n-1)d orbitals.
- (4) The general electronic configuration of d-block/d-series elements be shown as follows :

1. First (3d) Transition Series (Sc–Zn)

At. No.	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
E.C.	3d ¹ 4s ²	3d²4s²	² 3d ³ 4s ²	3d⁵4s	3d⁵4s²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²

2. Second (4d) Transition Series (Y-Cd)

At. No.	39	40	41	42	43	44	45	46	47	48
Element	Y	Zr	Nb	Мо	Tc*	Ru	Rh	Pd	Ag	Cd
E.C.	4d ¹ 5s ²	$4d^25s^2$	4d ⁴ 5s ¹	4d⁵5s¹	4d ⁶ 5s	4d ⁷ 5s	4d ⁸ 5s	¹ 4d ¹⁰ 5s ⁰	4d ¹⁰ 5s	¹ 4d ¹⁰ 5s ²

3. Third (5d) Transition Series (La–Hg)

At. No.	57	72	73	74	75	76	77	78	79	80
Element	La	Hf	Та	W	Re	Os	lr	Pt	Au	Hg
E.C.	5d ¹ 6s ²	5d ² 6s ²	5d ³ 6s ²	5d⁴6s ⁴	²5d⁵6s²	5d ⁶ 6s ²	5d ⁷ 6s	² 5d ⁹ 6s ¹	5d ¹⁰ 6s ¹	5d ¹⁰ 6s ²

4. Fourth (6d) Transition Series

At. No.	89	104	105	106	107	108	109	110	111	112	
Element	Ac	Ku	Ha	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	
		(Unh) (Uns)(Uno) (Une)									
E.C.	6d ¹ 7s ²	6d ² 7s ²	6d ³ 7s ²	6d ⁴ 7s ²	6d⁵7s²	6d ⁶ 7s ²	6d ⁷ 7s ² 6	6d ⁸ 7s ² 6	id ¹⁰ 7s ¹ 6	6d ¹⁰ 7s ²	

Exceptional configuration of Cr and Cu. The exceptions observed in the first series are in case of electronic configurations of chromium (Z = 24) and copper (Z = 29). It may be noted that unlike other elements, chromium and copper have a single electron in the 4s-orbital. This is due to the gain of additonal stability by the atom by either having half-filled configuration (i.e., containing 5 electrons in the d-sublevel) or completely filled configuration, (i.e., containing 10 electrons in the d-sublevel). The 3d-level in case of chromium gets excatly half-filled with configuration $3d^5 4s^1$ and that in case of copper, it gets completely filled with configuration $3d^{10} 4s^1$. This can be explained on the basis of exchange energy

Thus, the electronic configuration of chromium (Z = 24) and copper (Z = 29) are $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ and $1s^2 2s^2 2p^6 3s^6 3p^6 3d^{10} 4s^1$ respectively.

1.3 Properties

1. Atomic Raddii

- (i) The atomic radii of the transition metals lie in-between those of s- and p-block elements.
- (ii) Generally the atomic radii of d-block elements in a series decreas with increase in atomic number but the decrease in atomic size is small after midway.

Explanation

The atomic radius decreases with the increase in atomic number as the nuclear charge increases whereas the shielding effect of d-electron is small. After midway, as the electrons enter the last but one (penultimate) shell, the added d-electron shields (screens) the outermost electron. Hence, with the increase in the d-electrons, screening effect increases. This counterbalances the increased nuclear charge due to increase in atomic number. As a result, the atomic radii remain practically same after chromium. For example in Fe, the two opposing tendencies almost counterbalance and there is no change in the size from Mn to Fe.

(iii) At the end of the period, there is a slight increase in the atomic radii.

Explanation

Near the end of series, the increased electron-electron repulsions between added electrons in the same orbitals are greater than the attractive forces due to the increased nuclear charge. This results in the expansion of the electron cloud and thus the atomic radius increases.

(iv) The atomic radii increase down the group. This means that the atomic radii of second series are larger than those of first transition series. But the atomic radii of the second and third transition series are almost the same.

The atomic radii of the elements of the second and third transition metals are nearly same due to lanthanide contraction (or also called lanthanoid contraction) discussed later.

1.4 Ionic radii

- (i) The trend followed by the ionic radii is the same as that followed by atomic radii.
- (ii) Ionic radii of transition metals are different in different oxidation states.
- (iii) The ionic radii of the transition metals are smaller than those of the representative elements belonging to the same period.

1.5 Metallic character

Except for mercury which is a liquid, all the transition elements have typical metallic structure. They exhibit all the characteristics of metals. ductile, have high melting and boiling points, high thermal and electrical conductivity and high tensile strength.

Transition elements have relatively low ionization energies and have one or two electrons in their outermost energy level (ns¹ or ns²). As a result, metallic bonds are formed. Hence, they behave as metals. Greater the number of unpaired d electrons, stronger is the bonding due to the overlapping of unpaired electrons between different metal atoms.

1.6 Melting Point

Transition metals have high melting points which is due to their strong metallic bond. The metallic bond. The metallic bonding depends upon the number of unpaired e⁻. The melting point first increases (Sc-Cr), reaches a maximum value (Cr) and then decreases (Fe-Zn)

- * Tungsten (W) has the highest melting point.
- * Mercury (Hg) has the lowest melting point.
- * Mn has the lowest melting point in 3d series typicl transition elements.

1.7 Ionisation energies or Ionisation enthalpies

(i) The first ionisation enthalpies of d-block elements lie between s-block and p-block elements. They are higher than those of sblock elements and are lesser than those of p-block elements. The ionisation enthalpy gradually increases with increase in atomic number along a given transition series though some irregularities are observed

Explanation

- (i) The increasing ionization enthalpies are due to increased nuclear charge with increase in atomic number which reduces the size of the atom making the removal of outer electron difficult.
- (ii) In a given series, the difference in the ionisation enthalpies between any two successive d-block elements is very much less than the difference in case of successive s-block or pblock elements.

Explanation

The addition of d electrons in last but one [(n - 1) or penultimate] shell with increase in atomic number provides a screening effect and thus shields the outer s electrons from inward nuclear pull. Thus, the effects of increased nuclear charge and addition of d electrons tend to oppose each other.

- (iii) The first ionization enthalpy of Zn, Cd and Hg are, however, very high because of the fully filled $(n-1) d^{10} ns^2$ configuration.
- (iv) Although second and third ionization enthalpies also, in general, increase along a period, but the magnitude of increase for the successive elements is much higher.

- (v) The high values of 3rd ionization enthalpies for Cu, Ni and Zn explain why they show a maximum oxidation state of +2.
- (vi) The first ionisation enthalpies of 5d elements are higher as compared to those of 3d and 4d elements. This is because the weak shielding of nucleus by 4f electrons in 5d elements results in greater effective nuclear charge acting on the outer valence electrons.

1.8. Oxidation state

"The net numerical charge assigned to an atom of an element in its combined state is known as its Oxidation state or Oxidation number".

- With the exception of few elements, most of the d-block elements show more than one oxidation state i.e. they show variable oxidation states. The elements show variable oxidation state because of following reasons:
- (i) '(n-1) d' and 'ns' orbitals in the atoms of d-block elements have almost same energies and therefore electron can be removed from '(n-1)d' orbitals as easily as 's' orbitals electrons.
- (ii) After removing 's' electrons, the remainder is called Kernel of the metal cations. In d-block elements, the kernel is unstable and therefore it loses one or more electrons from (n-1)d electrons. This results in formation of cations with different oxidation states.
- (2) All transition elements show variable oxidation state except last element in each series.
- (3) Minimum oxidation state = Total number of electrons in 4s lost. Maximum oxidation state = (Total number of electrons in 4s + number of unpaired electrons in 3d lost).

In '3d' series all element contain 2 electrons in '4s' and hence they all give a common minimum oxidation state of +2. (Except 'Cr' and 'Cu' where minimum oxidation state is +1.] The maximum oxidation state is given by Mn i.e. Mn^{+7} in which two electrons are removed from 4s and five unpaired electrons are removed from 3d orbitals.

- (4) The highest oxidation state is shown by Ruthenium (Ru) and Osmium (Os) i.e. +8.
- (5) Across the period oxidation state increases and it is maximum at the centre and than decreases even if atomic number increases. The element which shows highest oxidation state occur in the middle or near the middle of the series and than decreases.
- (6) Transition metals also show zero oxidation states in metal carbonyl complex. (Nickel tetracarbonyl).

Example : Ni in Ni $(CO)_4$ has zero oxidation state.

- (7) The bonding in the compounds of lower oxidation state (+2, +3) is mostly ionic and the bonding in the compounds of higher oxidation state is mostly covalent.
- (8) The relative stabilities of some oxidation states can be explained on the basis of rule extra stability, according to which d⁰, d⁵ and d¹⁰ are stable configurations.

For example, the stability order of some ions is as follows:

 $Ti^{4+}(3d^0, 4s^0) > Ti^3(3d^1, 4s^0)$

 $Mn^{2+}(3d^5, 4s^0) > Mn^{3+}(3d^4, 4s^0)$

 Fe^{3+} , $(3d^5, 4s^0) > Fe^{2+} (3d^6, 4s^0)$

(9) Cu^{+2} is more stable than Cu^{+1} even when Cu^{+1} is $3d^{10}$ while Cu^{+2} is 3d due to high heat of hydration.

Variable oxidation states shown by 3d-series of d-block elements.

ELECTRONIC	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
CONFIGURATION	d ¹ s ²	d^2s^2	d^3s^2	d^4s^2	d^5s^2	d^6s^2	d^7s^2	d^8s^2	d^9s^2	$d^{10}s^2$
				d^5s^1					$d^{10}s^1 \\$	
Š				+1					+1	
ATE	+2	+2	+2	+2	+2	+2	+2	+2	+2	+2
LSN	+3	+3	+3	+3	+3	+3	+3	+3	+3	
IOII		+4	+4	+4	+4	+4	+4	+4		
IDA			+5	+5	+5	+5	+5			
X0				+6	+6	+6				
					+7					

Oxidation States

1.9 Standard electrode potentials (E°) and chemical reactivity

Thermodynamic stability of the compounds of transition elements can be evaluated in terms of the magnitude of ionisation enthalpies of the metals — smaller the ionisation enthalpy of the metal, stabler is its compound.

In solution, the stability of the compounds depends upon electrode potentials rather than ionization enthalpies. Electrode potential values depend upon factors such as enthalpy of sublimation (or atomisation) of the metal, the ionisation enthalpy and the hydration enthalpy, i.e.,

 $M(s) \xrightarrow{\Delta_{sub}H} M(g)$, $(\Delta_{sub}H \text{ is enthalpy of sublimation/} atomisation)$

 $M(s) \xrightarrow{\Delta_i H} M^+(g) + e^-, (\Delta_i H \text{ is ionisation enthalpy})$

 $M^{+}(g) + aq \xrightarrow{\Delta_{hyd}H} M^{+}(aq), (\Delta_{hyd} H \text{ is enthalpy of hydration})$

The total energy, Δ_{T} H, for the process involving sublimation, ionisation and hydration simultaneously, i.e.,

for the process, $M(s) \longrightarrow M^+(aq) + e^-$, will be the sum of the three types of enthalpies, i.e.,

$$\Delta_{\rm T} H = \Delta_{\rm sub} H + \Delta_{\rm i} H + \Delta_{\rm hvd} H.$$

Thus, $\Delta_T H$, is the total enthalpy change when solid meal, M is brought in the aqueous medium in the form of monovalent ion, M⁺ (aq).

Trends in the M²⁺/M Standard Electrode Potentials

- (i) There is no regular trend in the E° (M²⁺/M) values. This is because their ionization enthalpies (I₁ + IE₂) and sublimation enthalpies do not show any regular trend.
- (ii) The general trend towards less negative E° values along the series is due to the general increase in the sum of first and second ionization enthalpies.
- (iii) Copper shows a unique behaviour in the series as it is the only metal having positive value for E° . This explains why is does not liberate H_2 gas from acids. It reacts only with the oxidizing acids (HNO₃ and H_2SO_4) which are reduced. The reason for positive E° value for copper is that the sum of enthalpies of sublimation and ionization is not balanced by hydration enthalpy.

(iv) The values of E° for Mn, Ni and Zn are more negative than expected from the generall trend. This is due to greater stability of half-filled d-subshell (d⁵) in Mn²⁺, and completely filled d-subshell (d¹⁰) in Zn²⁺. The exceptional behaviour of Ni towards E° value from the regular trend is due to its high negative enthalpy of hydration.

Trends in the M³⁺/M²⁺ Standard Electrode Potentials

- A very low value for E^o (Sc³⁺/Sc²⁺) reflects the stability of Sc³⁺ ion which has a noble gas configuration.
- (ii) The highest value for Zn is on account of very high stability of Zn^{2+} ion with d^{10} configuration. It is difficult to remove an electron from it to change it into +3 state.
- (iii) The comparatively high value of E^o (Mn³⁺/Mn²⁺) shows that Mn²⁺ is very stable which is on account of stable d⁵ configuration of Mn²⁺.
- (iv) The comparatively low value of E° (Fe^{3+}/Fe^{2+}) is on account of extra stability of Fe^{3+} (d^5), i.e., low third ionization enthalpy of Fe.
- (v) The comparatively low value for V is on account of the stability of V²⁺ ion due to its half-filled t³_{2g} configuration (discussed in unit 9).

Chemical Reactivity and E° Values. The transition metals vary very widely in their chemical reactivity. Some of them are highly electropositive and dissolve in mineral acids whereas a few of them are 'noble', i.e., they do not react with simple acids. Some results of chemical reactivity of transition metals as related to their E° values are given below :

- (i) The metals of the first transition series (except copper) are relatively more reactive than the othr series. Thus, they are oxidized by H⁺ ions though the actual rate is slow, e.g., Ti and V are passive to dilute non-oxidizing acids at room temperature.
- (ii) As already explained, less negative E° values for M²⁺/M along the series indicate a decreasing tendency to form divalent cations.
- (iii) More negative E° values than expected for Mn, Ni and Zn show greater stability for Mn²⁺, Ni²⁺ and Zn²⁺.
- (iv) E° values for the redox couple M^{3+}/M^{2+} indicate that Mn^{3+} and Co^{3+} ions ar the strongest oxidizing agents in aqueous solution whereas Ti^{2+} , V^{2+} and Cr^{2+} are strongest reducing agents and can liberate hydrogen from a dilute acid, e.g., 2 $Cr^{2+}(aq) + 2 H^{+}(aq) \longrightarrow 2 Cr^{3+}(aq) + H_{2}(g)$

1.10 Catalytic Property

Most transition elements and their compounds have good catalytic properties because

(a) They possess variable oxidation state.

(b) They provide a large surface area for the reactant to be absorbed.

Catalysts	Uses
$\mathrm{TiCl}_{4} + \mathrm{Al}\left(\mathrm{C}_{2}\mathrm{H}_{5}\right)$	Ziegler-Natta catalyst, used in polymerisation of ethylene
V ₂ O ₅	Contact process $SO_2 \rightarrow SO$
Fe	Haber Bosch process
PdCl ₂	Wacker's process for CH CHO
	manufacturing
Pd	Hydrogenation of alkene, alkyne
	etc
Pt/PtO	Adam's catalyst for selective
	reduction
Pt	Catalytic convertor, for
	cleaning
	car exhaust fumes
Pt/Rh	Ostwald's process :
	$\rm NH \rightarrow \rm NO$
Cu	Oxidation of alcohols

1.11 Magnetic Behaviour

When a substance is placed in a magnetic field of strength H, the intensity of the magnetic field in the substance may be greater than or less than H. If the field in the substance is greater than H, the substance is a paramagnetic material and attracts line of force. If the field in the substance is less than H, the substance is diamagnetic. Diamagnetic materials tend to repel lines of force. The magnetic moment of a substance depends on the strength of magnetic field generated due to electronic spin, there is a change in electric flux which leads to induction of magnetic field. The electron is also under orbital angular momentum or orbital spin. It leads to generation of magnetic moment.

In first transition elements series the orbital angular magnetic moment is insignificant the orbital contribution is quenched by the electric fields of the surrounding atoms so magnetic moment is equal to the spin magnetic moment only.

 $\mu_{\rm eff} = \sqrt{n(n+2)} BM$

 $n \rightarrow no.$ of unpaired electron.

Maximum transition elements and compounds are paramagnetic due to presence of unpaired electrons.

2. COMPLEX FORMATION

(i) (ii)

(iii)

(i)

(ii)

(iii)

Transition metal ions form a large number of complex compounds. Complex compounds are those which have a metal ion linked to a number of negative ions (anions) or neutral molecules having lone pairs of electrons. These ions or molecules are called ligands. They donate lone pairs of electrons to the central transition metal ion forming coordinate bonds A few examples are given below : $[Fe(CN)_{6}]^{3-}$, $[Fe(CN)_{6}]^{4-}$, $[Cu(NH_{3})_{4}]^{2+}$, $[Zn(NH_{3})_{4}]^{2+}$, $[Ni(CN)_{4}]^{2-}$ and $[Ptcl_{4}]^{2-}$ Such complex compounds are not formed by s - and p block elements. Explanation. The transition elements form complexes because of the following reasons : Comparatively smaller size of their metal ions. Their high ionic charges. (Because of (i) and (ii), they have large charge/size ratio) Availability of vacant d-orbitals so that these orbitals can accept lone pairs of electrons donated by the ligands. 2.1 Interstitital Compounds The transition metals form a large number of interstitial compounds in which small atoms such as hydrogen, carbon, boron and nitrogen occupy the empty spaces (interstitial sites) in their lattices (Fig.). They are represented by formulae like TiC, TiH, Mn, N, Fe₃H, Fe₃C etc. However, actually they are nonstoichiometric materials, e.g., TiH₁₇, VH₀₅₆ etc. and the bonds present in them are neither typically ionic nor covalent. Some of their important characteristics are as follows: They are very hard and rigid, e.g., steel which is an interstitial compound of Fe and Cis quite hard. Similarly, some borides are as hard as diamond. They have high melting points which are higher than those of the pure metals. They show conductivity like that of the pure metal.

(iv) They acquire chemical inertness.

2.2 Alloy formation

Alloys are homogeneous solid solutions of two or more metals obtained by melting the components and then cooling the melt. These are formed by metals whose atomic radii differ by not more than 15% so that the atoms of one metal can easily take up the positions in the crystal lattice of the other (Fig.)

Now, as transition metals have similar atomic radii and

other characteristics, hence they form alloys very readily. Alloys are generally harder, have higher melting points and more resistant to corrosion than the individiual metals.

The most commonly used are the ferrous alloys the metals chromium, vanadium, molybdenum, tungsten and manganese are used in the formation of alloy steels and stainless steels. Some alloys of transition metals with non-transition metals are also very common. e.g., brass (Cu + Zn) and bronze (Cu + Sn)



Formation of interstitial compounds.



Formation of alloys.

3. COMPOUNDS OF TRANSITION ELEMENTS

3.1 Oxides

- (i) The metals of the first transition series form oxides with oxygen at high temperature.
- (ii) The oxides are formed in the oxidation, states +1 to +7 (as given in Table 8.10, page 8/14).

(iii) The highest oxidation state in the oxides of any transition metal is equal to its group number, e.g., 7 in Mn_2O_7 . Beyond group 7, no higher oxides of iron abov Fe₂O are known. Some metals in higher oxidation state stabilize by forming

oxocations, e.g., V^{V} as VO_{2}^{+} , V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+} .

(iv) All the metals except scandium form the oxides with the formula MO which are ionic in nature. As the oxidation number of the metal increases, ionic character decreases, e.g., Mn₂O₇ is a covalent green oil. Even CrO₃ and V₂O₅ have low melting points.

$$MnO = Mn_3O_4 = Mn_2O_3 = Mn_2O_7 + Mn_2O_7$$

(v) In general, the oxides in the lower oxidation states of the metals are basic and in their higher oxidation states, they are acidic whereas in the intermediate oxidation state, the oxides are amphoteric.

For example, the behaviour of the oxides of manganese may be represented as follows :

$$\underset{\text{Basic}}{\overset{+2}{\text{Mn}_{0}}} \quad \underset{\text{Amphoteric}}{\overset{+8/3}{\text{Mn}_{2}}O_{4}} \quad \underset{\text{Amphoteric}}{\overset{+3}{\text{Mn}_{2}}O_{3}} \quad \underset{\text{Amphoteric}}{\overset{+4}{\text{Mn}_{2}}O_{7}} \quad \underset{\text{Acidic}}{\overset{+7}{\text{Mn}_{2}}O_{7}}$$

Thus, Mn₂O₇ dissolves in water to give the acid HMnO₄.

3.2 KMnO₄ Potassium permanganate

It is prepared from the ore called chromite or ferrochrome or chrome iron, $FeO.Cr_2O_3$. The various steps involved are as follows :

Preparation of sodium chromate. The ore is finely powdered, mixed with sodium carbonate and quick lime and then roasted, i.e., heated to redness in a reverberatory furnace with free exposure to air when sodium chromate (yellow in colour) is formed and carbon dioxide is evolved. Quick lime keeps the mass porous and thus facilitates oxidation.

$$4\text{FeO.Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$

Chromite ore

Sod. chromate Ferric oxide

After the reaction, the roasted mass is extracted with water when sodium chromate is completely dissolved while ferric oxide is left behind. Ferric oxide is separated out by filtration.

 (ii) Conversion of sodium chromate into sodium dichromate. The filtrate containing sodium chromate solution is treated with concentrated sulphuric acid when sodium chromate is converted into sodium dichromate.

$$2Na_{2}CrO_{4} + H_{2}SO_{4} \longrightarrow Na_{2}Cr_{2}O_{7} + Na_{2}SO_{4} + H_{2}O_{Sod. dichromate}$$

Sodium sulphate being less soluble crystallizes out as decahydrate, Na_2SO_4 . $10H_2O$ and is removed. The clear solution is then evaporated in iron pans to a specific gravity of 1.7 when a further crop of sodium sulphate is formed. It is removed and the solution is cooled when orange crystals of sodium dichromate, $Na_2Cr_2O_7$. $2H_2O$ separate on standing.

(iii) Conversion sodium dichromate into potassium dichromate. Hot concentrated solution of sodium dichromate is treated with calculated amount of potassium chloride when potassium dichromate, being much less soluble than sodium salt, crystallizes out on cooling as orange crystals.

$$\begin{array}{ccc} Na_2Cr_2O_7 + 2KCl & \longrightarrow & K_2Cr_2O_7 & + 2NaCl \\ \hline \text{Sodium dichromate} & & Potassium dichromate \\ \end{array}$$

3.3 Properties

- 1. Colour and Melting point. It forms orange crystals which melt at 669 K.
- 2. Solubility. It is moderately soluble in cold water but freely soluble in hot water.
- **3.** Action of heat. When heated to a white heat, it decomposes with the evolution of oxygen.

$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

4. Action of alkalies. When an alkali is added to an orange red solution of dichromate, a yellow solution results due to the formation of chromate.

$$K_2Cr_2O_7 + KOH \longrightarrow 2K_2CrO_4 + H_2O$$

Pot. dichromate Pot. chromate

or $\operatorname{Cr}_2\operatorname{O}_7^{2-} + 2\operatorname{OH}^- \longrightarrow 2\operatorname{Cr}\operatorname{O}_4^{2-} + \operatorname{H}_2\operatorname{O}$

On acidifying, the colour again changes to orange red due to the reformation of dichromate.

$$2 K_2 CrO_4 + H_2 SO_4 \longrightarrow K_2 Cr_2 O_7 + K_2 SO_4 + H_2 O$$

or $2 \operatorname{CrO}_4^{2-} + 2 \operatorname{H}^+ \longrightarrow \operatorname{Cr}_2 \operatorname{O}_7^{2-} + \operatorname{H}_2 \operatorname{O}$

This interconversion is explained by the fact that in dichromate solution, the $Cr_2O_7^{2-}$ ions are invariably in equilibrium with CrO_4^{2-} ions at pH = 4, i.e.,

$$\begin{array}{c} Cr_2O_7^{2-} + H_2O \xrightarrow{pH=4} 2CrO_4^{2-} + 2H^+ \\ Orange red \\ (dichromate) \\ (chromate) \end{array}$$

On adding an alkali (i.e., increasing the pH of the solution), the H⁺ ions are used up and according to the law of chemical equilibrium, the reaction proceeds in the forward direction producing yellow chromate solution. On the other hand, when an when an acid is added (i.e., pH of the solution is decreased), the concentration of H⁺ ions is increased and the reaction proceeds in the backward direction producing an orange red dichromate solution.

5. Action of concentrated sulphuric acid

(a) In cold, red crystals of chromic anhydride (chromium trioxide) are formed.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2CrO_3 + 2KHSO_4 + H_2O$$

(b) On heating the mixture, oxygen is evolved.

6. Oxidising properties. It is a powerful oxidising agent. In the presence of dilute sulphuric acid, one molecule of potassium dichromate furnishes 3 atoms of available oxygen as indicated by the equation :

$$K_{2}Cr_{2}O_{7} + 4H_{2}SO_{4} \longrightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{3} + 4H_{2}O + 3O$$

or
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O^{3+}$$

Eq. wt. of
$$K_2 Cr_2 O_7 = \frac{Mol. wt.}{6} = \frac{294}{6} = 49$$

(i) It liberates I, from KI

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3$$

 $+3I_{2} + 7H_{2}O$

(ii) It oxidises ferrous salts to ferric salts

$$K_{2}Cr_{2}O_{7} + 7H_{2}SO_{4} + 6FeSO_{4} \longrightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{3}$$
$$+ 3Fe_{2}(SO_{4})_{3} + 2H_{2}O$$

$$K_{2}Cr_{2}O_{7} + 4H_{2}SO_{4} + 3H_{2}S \longrightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{3}$$
$$+ 7H_{2}O + 3S$$

(iv) It oxidises sulphites to sulphates and thiosulphates to sulphates and sulphur

$$K_2Cr_2O_7 + 4H_2SO_4 + 3Na_2SO_3 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3$$
$$+ 4H_2O + 3Na_2SO_4$$

(v) It oxidises nitrites to nitrates

$$K_{2}Cr_{2}O_{7} + 4 H_{2}SO_{4} + 3NaNO_{2} \longrightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{3}$$
$$+ 3 NaNO_{2} + 4 H_{2}O_{4} + 3 NaNO_{2} + 3 NaNO_{2} + 4 H_{2}O_{4} + 3 NaNO_{2} + 4 H_{2}O_{4} + 3 NaNO_{2} + 3 NaNO_{2} + 4 H_{2}O_{4} + 3 NaNO_{2} + 3 NaNO_{2} + 4 H_{2}O_{4} + 3 NaNO_{2} + 3 NaNO_{2} + 4 H_{2}O_{4} + 3 NaNO_{2} + 3 NaNO_{2}$$

(vi) It oxidises halogen acids to halogen

$$K_2Cr_2O_7 + 14 \text{ HCl} \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(vii) It oxidises
$$SO_2$$
 to sulphuric acid

(v

$$K_{2}Cr_{2}O_{7} + H_{2}SO_{4} + 3SO_{2} \longrightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{3} + 3H_{2}O$$

$$\operatorname{Cr}_2\operatorname{O}_7^2$$
 +14 H⁺ +3Sn²⁺ \longrightarrow 2 Cr³⁺ +3 Sn⁴⁺ +3 Sn⁴⁺ +7 H₂O

$$\mathrm{K_{2}Cr_{2}O_{7}}+4\mathrm{H_{2}SO_{4}}\longrightarrow\mathrm{K_{2}SO_{4}}+\mathrm{Cr_{2}}\left(\mathrm{SO_{4}}\right)_{3}+4\mathrm{H_{2}O}+3\mathrm{O}$$

$$\begin{array}{c} CH_2CH_2OH + O \longrightarrow CH_3CHO + H_2O \\ {}_{\text{Ethyl alcohol}} \end{array}$$

 $\begin{array}{c} CH_{3}CHO + O \longrightarrow CH_{3}COOH \\ Acetaldehyde & Acetic acid \end{array}$

Test for a drunken driver. The above reaction helps to test whether a driver has consumed alcohol or not. he is asked to breathe into the acidified $K_2Cr_2O_7$ solution taken in a test tube. If the orange colour of the solution changes into green colour (due to $Cr_2(SO_4)_3$ formed in the reaction), the driver is drunk, otherwise not.

7. Chromyl chloride test (Reaction with a chloride and conc. sulphuric acid). When heated with concentrated hydrochloric acid or with a chloride and strong sulphuric acid, reddish brown vapours of chromyl chloride are obtained.

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$$

Chromyl chloride
(Red vapour)

8. Reaction with hydrogen peroxide. Acidified $K_2Cr_2O_7$ solution reacts with H_2O_2 to give a deep blue solution due to the formation of peroxo compound, CrO $(O_2)_2$.

$$\operatorname{Cr}_2\operatorname{O}_7^{2-} + 2 \operatorname{H}^+ + 4 \operatorname{H}_2\operatorname{O}_2 \longrightarrow 2 \operatorname{CrO}_5 + 5 \operatorname{H}_2\operatorname{O}$$

The blue colour fades away gradually due to the decomposition of CrO_s into Cr^{3+} ions and oxygen.

The structure of CrO_5 is $\bigcup_{O}^{O} \xrightarrow{\operatorname{Cr}}_{O}^{O}$ in which Cr is in +6

oxidation state.

Uses.

 In volumetric analysis, it is used as a primary standard for the estimation of Fe²⁺ (ferrous ions) and I⁻ (iodides) in redox titrations.

Note

 $Na_2Cr_2O_7$ is not used in volumetric analysis because it is deliquescent.

(ii) In industry, it is used

(a) In chrome tanning in leather industry.

- (b) In the preparation of chrome alum K₂SO₄.Cr₂(SO₄)₃. 24H₂O and other industrially important compounds such as Cr₂O₃, CrO₃, CrO₂Cl₂, K₂CrO₄, CrCl₃ etc.
- (c) In calico printing and dyeing.
- (d) In photography and in hardening gelatine film.

(iii) In organic chemistry, it is used as an oxidising agent.

Structures of chromate and dichromate ions.



Dichromate ion-Two tetrahedra sharing one oxygen atom at one corner

3.4 Potassium Permanganate (KMnO₄)

Preparation

(i)

(ii)

On a large scale, it is prepared from the mineral, pyrolusite, MnO₂. The preparation involves the following two stesp:

Conversion of MnO_2 into potassium manganate. The finely powdered pyrolusite mineral is fused with potassium hydroxide or potassium carbonate in the presence of air or oxidising agent such as potassium nitrate or potassium chlorate when green coloured potassium manganate is formed.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

Potassium manganate
$$2MnO_2 + 2K_2CO_2 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$$

$$MnO_{2}+2KOH+KNO_{3} \longrightarrow K_{2}MnO_{4}+KNO_{2}+H_{2}O$$
$$3MnO_{2}+6KOH+KCIO_{3} \longrightarrow 3K_{2}MnO_{4}+KCI+2H_{2}O$$

Potassium manganate thus formed undergoes disproportionation in the neutral or acidic solution as follows, if allowed to stand for some time :

$$3 \underset{\text{Manganate ion}}{\text{MonO}_4^{2^-}} + 4 \text{ H}^+ \longrightarrow 2 \underset{\text{Permanganate ion}}{\text{VII}} + \underset{\text{MnO}_2}{\text{IV}} + 2 \text{ H}_2\text{O}$$

Oxidation of potassium manganate to potassium permanganate.

(a) Chemical oxidation. The fused mass is extracted with water and the solution after filtration is converted into potassium permanganate by bubbling carbon dioxide, chlorine or ozonised oxygen through the green solution.

$$3K_{2}MnO_{4} + 2CO_{2} \longrightarrow 2KMnO_{4} + MnO_{2} \downarrow + 2K_{2}CO_{3}$$
$$2K_{2}MnO_{4} + Cl_{2} \longrightarrow 2KMnO_{4} + 2KCl$$

 $2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$

The carbon dioxide process is uneconomical as one third of the original manganate is reconverted to manganese Lakshya Educare

dioxide. However, this process has the advantage that the potassium carbonate formed as a by-product can be used for the oxidative fusion of manganese dioxide. In the chlorine process, potassium chloride obtained as a by-product is lost.

PROPERTIES

- 1. **Colour.** Potassium permanganate exists as deep purple black prisms with a greenish lustre which become dull in air due to superficial reduction.
- 2. Solubility. It is moderately soluble in water at room temperature and it is more soluble in hot water.
- **3.** Action of heat. When heated to 513 K, it readily decomposes giving oxygen.

$$2KMnO_4 \xrightarrow{} K_2MnO_4 + MnO_2 + O_2$$

Pot. manganate

At red heat, potassium manganate formed decomposes into potassium manganite (K₂MnO₃) and oxygen.

 $2K_2MnO_4 \longrightarrow 2K_2MnO_3 + O_2$

4. Action of heat in current of hydrogen. When heated in a current of H₂, solid KMnO₄ gives KOH, MnO and water vapours.

2KMnO₄ + 5H₂ \longrightarrow 2KOH + 2MnO + 4H₂O

- 5. Oxidising property. Potassium permanganate is powerful oxidising agent. The actual course of reaction depends on the use of the permanganate in (a) neutral (b) alkaline or (c) acidic solution.
- (a) In neutral solution. Potassium permanganate acts as a moderate oxidising agent in neutral aqueous solution because of the reaction :

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3O$$

or $MnO_4^- + 2H_2O + 3 e^- \longrightarrow MnO_2 + 4OH^-$

Thus, MnO_4^- ion gains 3 electrons. Also, according to the above equation, in neutral medium, from two moles of permanganate, three oxygen atoms are available. In fact, during the course of reaction, the alkali generated renders the medium alkaline even when we start with neutral solutions. Hence, Eq. wt. of KMnO₄ in neutral or weakly alkaline medium

$$=\frac{\text{Mol. wt.}}{3}=\frac{158}{3}=52.67$$

Some oxidizing properties of $KMnO_4$ in the neutral medium. These are given below :

(i) It oxidises hot manganous sulphate to manganese dioxide.

 $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow K_2SO_4 + 2H_2SO_4 + 5MnO_2$

Presence of $ZnSO_4$ or ZnO catalyses the oxidation.

(ii) It oxidises sodium thiosulphate to sodium sulphate.

$$8KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 3K_2SO_4 + 8MnO_2 +$$
$$3Na_2SO_4 + 2KOH$$

(iii) It oxidises hydrogen sulphide to sulphur.

$$2KMnO_4 + 4H_2S \longrightarrow 2MnS + S + K_2SO_4 + 4H_2O$$

(b) In alkaline solution. In strongly alkaline solution,
$$MnO_4^{2-}$$
 (manganate) ion is produced

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O \quad or$$
$$MnO_4^{1-} + e^- \longrightarrow MnO_4^{2-}$$

:. Eq. wt. of KMnO₄ =
$$\frac{\text{Mol. wt.}}{1} = \frac{158}{1} = 158$$

Potassium manganate is also further reduced to MnO₂

when a reducing agent is present.

$$K_2MnO_4 + H_2O \longrightarrow MnO_2 + 2KOH + O$$

or
$$MnO_4^{2-} + 2H_2O + 2 e^- \longrightarrow MnO_2 + 4OH^-$$

So the complete reaction is :

$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3O$$

or $MnO_4^- + 2H_2O + 3 e^- \longrightarrow MnO_2 + 4OH^-$

which is the same as that for neutral medium. Hence, equivalent weight of $KMnO_4$ in weakly alkaline medium is same as that in the neutral medium, viz., 52.67

Some oxidizing properties of KMnO₄ in the alkaline medium. These are given below :

(i) It oxidises potassium iodide to potassium iodate.

$$2KMnO_4 + H_2O + KI \longrightarrow 2MnO_2 + 2KOH + KIO_3$$
Pot. iodate

or $I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6 e^-$

In this case, iodine is not liberated unlike the case of acidic medium.

Similar reaction takes place with KBr.

(ii) It oxidises olefinic compounds to glycols, i.e., when an olefinic compound is shaken with alkaline KMnO₄, pink colour of KMnO₄ is discharged.

$$\begin{array}{c} \mathrm{CH}_2\\ \|\\ \mathrm{CH}_2\\ \mathrm{CH}_2 \end{array} + \mathrm{H}_2\mathrm{O} \ + \ \mathrm{(O)} \xrightarrow{\mathrm{Alkaline}}_{\mathrm{KMnO_4}} \xrightarrow{\mathrm{CH}_2\mathrm{OH}}_{\mathrm{CH}_2\mathrm{OH}} \\ \end{array}$$
 Ethylene Ethylene glycol

Alkaline KMnO_4 used for this test is known as Baeyer's reagent. It is used for oxidation of a number of organic compounds.

(c) In acidic medium. Potassium permanganate in the presence of dil. sulphuric acid, i.e., in acidic medium, acts as a strong oxidising agent because of the reaction

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

or $MnO_4^- + 8H^+ + e^- \longrightarrow Mn^{2+} + 4H_2O$.

Since in the above reaction, MnO_4^- ion gains 5 electrons of five atoms of oxygen are available from two molecules of KMnO₄. Hence.

Eq. wt. of $\text{KMnO}_4 = \frac{\text{Mol. wt.}}{\text{Mol. wt.}} = \frac{158}{31.6} = 31.6$

Some oxidizing properties of $KMnO_4$ in the acidic medium. These are given below :

(i) It oxidises H_2S to S.

 $2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2O + 5O_4$

(ii) It oxidises sulphur dioxide to sulphuric acid.

 $2KMnO_4 + 5 SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(iii) It oxidises nitrites (NO_2^-) to nitrates (NO_3^-) , arsenites (AsO_3^{3-}) to arsentates (AsO_4^{3-}) and sulphites and thiosulphates to sulphates.

$$2KMnO_4 + 3H_2SO_4 + 5KNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 +$$

 $3H_2O + 5KNO_3$

(iv) It oxidises oxalates or oxalic acid to CO_2

 $2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10 CO_2$

(v) It oxidises ferrous sulphate to ferric sulphate (i.e., ferrous salt to ferric salt).

 $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 +$

 $5Fe_{2}(SO_{4})_{2} + 8H_{2}O$

(vi) It oxidises H_2O_2 to H_2O and O_2 . This is because acidified $KMnO_4$ is a stronger oxidising agent than H_2O_2 .

 $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 +$

 $8H_{2}O + 5O_{2}$

(vii) It oxidises potassium iodide to iodine

 $2KMnO_4 + 3H_2SO_4 + 10KI \longrightarrow K_2SO_4 + 2MnSO_4 +$

 $8H_{2}O + 5I_{2}$

(viii) It oxidises HX (where X = Cl, Br, l) to X,

$$2KMnO_4 + 3H_2SO_4 + 10 HX \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5X_2$$

(ix) It oxidises ethyl alcohol to acetaldehyde

$$2KMnO_4 + 3H_2SO_4 + 5CH_3CH_2OH \longrightarrow K_2SO_4 + 2MnSO_4 + 5CH_3CHO + 8H_2O.$$

Uses.

(i) It is often used in volumetric analysis for the estimation of ferrous salts, oxalates, iodides and hydrogen peroxide. However, it is not a primary standard because it is difficult to obtain it in the pure state and free from traces of MnO₂. It is, therefore, always first standardised with a standard solution of oxalic acid.

Remember that volumetric titrations inolving KMnO₄ are carried out only in presence of dilute H_2SO_4 but not in the presene of HCl or HNO₃. This is because oxygen produced from KMnO₄ + dill. H_2SO_4 is used only for oxidizing the reducing agent. Moreover, H_2SO_4 does not give any oxygen of its own to oxidiize the reducing agent. In case HCl is used, the oxygen produced from KMnO₄ + HCl is partly used up to oxidize Hcl to chlorine and in case HNO₃ is used, it itself acts as oxidizing agent and partly oxidizes the reducing agent.

- (ii) It is used as a strong oxidising agent in the laboratory as well as in industry. It is a favourite and effective oxidising agent used in organic synthesis Alkaline potassium permanganate is used for testing unsaturation in organic chemistry and is known as Baeyer's reagent.
- (iii) Potassium permanganate is also widely used as a disinfectant and germicide. A very dilute solution of permanganate is used for washing wounds and gargling for mouth sore. It is also used for purifying water of stinking wells.
- (iv) Because of its strong oxidizing power, it is also used for bleaching of wool, cottong, silk and other textile fibres and also for decolourisation of oils.

THE LANTHANIDE SERIES

1. INTRODUCTION

These elements are classified by the filling up of the antipenultimate 4f energy levels.

2. PHYSICAL PROPERTIES

Element		Electronic	Electronic	Oxidation States
		Configuration	Configuration of M ³⁺	
Lanthanum	Ia	[Xe] $5d^1 6s^2$	[Xe]	+3
Cerium	Ce	[Xe] $4f^1 5d^1 6s^2$	[Xe] $4f^1$	+3 (+4)
Praseodymium	Pr	$[Xe] 4f^3 = 6s^2$	[Xe] $4f^2$	+3 (+4)
Neodymium	Nd	$[Xe]4f^4$ $6s^2$	$[Xe] 4f^3$	(+2) +3
Promethium	Pm	[Xe]4f 6s ²	[Xe] 4f ⁴	(+2) +3
Samarium	Sm	$[Xe]4f^6$ $6s^2$	[Xe] 4f ⁵	(+2) +3
Europium	Eu	$[Xe]4f^7$ $6s^2$	[Xe] 4f ⁶	(+2) +3
Gadolinium	Gd	$[Xe] 4f^7 5d^1 6s^2$	[Xe] 4f ⁷	+3
Terbium	Tb	[Xe]4f ⁹ 6s ²	[Xe] 4f ⁸	+3 (+4)
Dysprosium	Dy	$[Xe] 4f^{10} 6s^2$	[Xe] 4f ⁹	+3 (+4)
Holmium	Но	$[Xe] 4f^{11} 6s^2$	[Xe] 4f ¹⁰	+ 3
Erbium	Er	$[Xe] 4f^{12} 6s^2$	[Xe] 4f ¹¹	+3
Thulium	Tm	$[Xe] 4f^{13} 6s^2$	[Xe] $4f^{12}$	(+2) +3
Ytterbium	Yb	$[Xe] 4f^{14} = 6s^2$	[Xe] $4f^{13}$	(+2) +3
Lutetium	Lu	$[Xe] 4f^{14} 5d^1 6s^2$	[Xe] $4f^{14}$	+3

Electronic Configuration and oxidation states

2.1 Oxidation state

The sum of the first three ionization energies for each element are low. Thus the oxidation state (+III) is ionic and Ln^{3+} dominates the chemistry of these elements. The Ln^{2+} and Ln^{4+} ions that do occur are always less stable than Ln^{3+} . Oxidation numbers (+II) and (+IV) do occur, particularly when they lead to :

1. a noble gas configuration e.g. $Ce^{4+}(f^{0})$

- 2. a half filled f shell, e.g. Eu^{2+} and $Tb^{4+}(f^7)$
- 3. a completely filled f level, e.g. $Yb^{2+}(f^{14})$.

NOTE

The 4f electrons in the antipenultimate shell are very effectively shielded from their chemical environment outside the atom by the 5s and 5p electrons. Consequently the 4f electrons do not take part in bonding. They are neither removed to produce ions nor do they take any significant part in crystal field stabilization or complexes. Crystal field stabilization is very important with the d-**block elements. The octahedral splitting of f orbitals** Δ_0 is only about 1kJ mol⁻¹. Whether the f orbitals are filled or empty has little effect on the normal chemical properties. However, it does affect their spectra and their magnetic properties.

2.2 Atomic radius

In lanthanide series, with increasing atomic number, there is a progressive decrease in the atomic as well as ionic radii of trivalent ions from La^{3+} to Lu^{3+} . This regular decrease in the atomic and ionic radii with increasing atomic number is known as lanthanide contraction. As we move along the lanthanide series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell (viz., 4f). As a result, the attraction on the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the f-subshell, there is imperfect shielding of one electron by another in this subshell due to the shapes of these f-orbitals. This imperfect shielding is unable to counterbalance the effect of the increased nuclear charge. Hence, the net result is a contraction in the size though the decrease is very small. It is interesting to note that in lanthanides, the decrease in the atomic radius for 14 elements [Ce (58) to Lu (71)] is only 11pm (from 183 to 172 pm). Similarly, decrease in ionic radii from Ce³⁺ to Lu³⁺ is only 17 pm (103 to 86 pm)

The contraction is similar to that observed in any transition series. The cause is also similar, just as in the transition series where the contraction is due to imperfect shielding of one d electron by another. But the shielding of one 4f electron by another is less than one d electron by another with increase in nuclear charge along the series.

Atomic and Ionic radii (pm) of lanthanum and lanthanoids.

Element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Atomic Radii (Ln)	187	183	182	181	181	180	199	180	178	177	176	175	174	173	172
Ionic Radii (Ln ³⁺)	106	103	101	99 [.]	98	96	95	94	92	91	90	89	88	87	86

2.3 Magnetic behaviour

Paramagnetism is shown by the positive ions of lanthanides except La^{3+} (lanthanum ion, f^0) and Lu^{3+} (lutetium ion, f^{14}). This property of the lanthanides is due to presence of unpaired electrons in the incomplete 4f subshell.

lanthanides differ from transition elements in the fact that their magnetic moments do not obey 'spin only' formula,

viz., $\mu_{eff} = \sqrt{n (n+2)}$ B.M. where n is the number of unpaired electrons. This because in case of transition elements, the orbital contribution is quenched by the electric field of the environment but in case of lanthanides, 4f orbitals lie to deep to be quenched. Hence, their magnetic moment is

calculated by considering spin as well as orbital contribution, i.e,

$$\mu_{eff} = \sqrt{4 S (S+1) + L (L+1)} B.M.$$

where S is spin quantum number and L is orbital quantum number.

NOTE

Separation of the Lanthanide Elements

Since the change in ionic radius is very small, the chemical properties are similar. This makes the separation of the element in pure state difficult. Separation is done by Ion Exchange methods which is based on the ionic size.

2.4 Colour

The Lanthanides are silvery white metals. However, most of the trivalent metal ions are coloured, both in the solid state and in aqueous solution. This is due to the partly filled-forbitals which permit f-f transition.

NOTE

Lanthanides ions with x f electrons have a similar colour to those with (14–x) f electrons e.g., La^{3+} and Lu^{3+} are colourless, Sm^{3+} and Dy^{3+} are yellow and Eu^{3+} and Tb^{3+} are pink.

2.5 Hydroxides

The hydroxides $Ln(OH)_3$ are precipitated as gelationous precipitates by the addition of NH_4OH to aqueous solutions. These hydroxides are ionic and basic. They are less basic than $Ca(OH)_2$ but more basic than $Al(OH)_3$ which is amphoteric. The metals, oxides and hydroxides all dissolve in dilute acids, forming salts. $Ln(OH)_3$ are sufficiently basic to absorb CO_2 from the air and form carbonates. The basicity decreases as the ionic radius decreases from Ce to Lu. Thus $Ce(OH)_3$ is the most basic, and Lu(OH_3), which is the least basic, is intermediate between Scandium and Yttrium in basic strength. The decrease in basic properties is illustrated by the hydroxides of the later elements dissolving in hot concentrated NaOH, forming complexes.

 $Yb(OH)_{3} + 3NaOH \rightarrow 3Na^{+} + [Yb(OH)_{6}]^{3-}$

 $Lu(OH)_3 + 3NaOH \rightarrow 3Na^+ + [Lu(OH)_6]^{3-}$

ACTINIDES SERIES

The elements and their Oxidation States

Atomic	Element	Symbol	Outer electronic	Oxidation states*
			structure	
89	Actinium	Ac	$6d^17s^2$	+3
90	Thorium	Th	$6d^2 7s^2$	+3,+4
91	Protactinium	Ра	$5f^2 6d^1 7s^2$	+3, +4, +5
92	Uranium	U	$5f^{3} 6d^{1} 7s^{2}$	+3,+4,+5,+6

93	Neptunium	Np	$5f^4 6d^1$	$7s^2$	+3, +4, +5, +6, +7
94	Plutonium	Pu	5f ⁶	$7s^2$	+3, +4, +5, +6, +7
95	Americium	Am	5f ⁷	$7s^2$	+2, +3, +4, +5, +6
96	Curium	Cm	$5f^7 6d^1$	$7s^2$	+3,+4
97	Berkelium	Bk	5f ⁹	$7s^2$	+3,+4
98	Californium	Cf	5f ¹⁰	$7s^2$	+2,+3
99	Einsteinium	Es	5f ¹¹	$7s^2$	+2,+3
100	Fermium	Fm	5f ¹²	$7s^2$	+2,+3
101	Mendelevium	Md	5f ¹³	$7s^2$	+2,+3
102	Nobelium	No	5f ¹⁴	$7s^2$	+2,+3
103	Lawrencium	Lr	5f ¹⁴ 6d ¹	$7s^2$	+3
104	Rutherfordium	Rf	4f ¹⁴ 6d ²	7s ²	

1. OXIDATION STATE

Unlike Lanthanides, Actinides show a large number of oxidation states. This is because of very small energy gap between 5f, 6d and 7s subshells. Hence, all their electrons can take part in bond formation. The dominant oxidation state of these element is +3 (similar to Lanthanides). Besides +3 state, Actinides also exhibit an oxidation state of +4. Some Actinides show still higher oxidation states. The maximum oxidation state first increases upto the middle of the series and then decreases, e.g., it increases from +4 from Th to +5, +6, and +7 for Pa, U and Np but decreases in the succeeding elements.

The Actinides resemble Lanthanides in having more compounds in +3 state than in the +4 state. However, the compounds in the +3 and +4 state tend to undergo hydrolysis.

Further, it may be noted that in case of Actinides, the distribution of oxidation states is so uneven that it is of no use to discuss their chemistry in terms of their oxidation states.

2. ATOMIC RADIUS

The Actinides show Actinide contraction (very much like Lanthanide contraction) due to poor shielding effect of the 5f-electrons. As a result, the radii of the atoms or ions of these metals decrease regularly across the series. The contraction is greater from element to element in this series due to poorer shielding by 5f electrons. This is because 5f orbitals extend in space beyond 6s and 6p orbitals whereas 4f orbitals are buried deep inside the atom.

3. MAGNETIC BEHAVIOUR

Like Lanthanides, the Actinides elements are strongly paramagnetic. The variation in magnetic susceptibility of Actinides with the increasing number of unpaired electrons is similar to that of Lanthanides but the values are higher for the Actinides than the Lanthanides.

4. COLOUR

These metals are silvery white. However, Actinide cations are generally coloured. The colour of the cation depends upon the number of 5f-electrons. The cations containing no 5f-electron or having seven 5f-electrons (i.e., exactly half-filled f-subshell) are colourless. The cations containing 2 to 6 electrons in the 5f-subshell are coloured both in the crystalline state as well as in aqueous solution. The colour arises due to f-f transition e.g. $Ac^{3+}(5f^0) =$ colourless, $U^{3+}(5f^3) =$ Red, $Np^{3+}(5f^4) =$ Blue, $Pu^{3+}(5f^5) =$ Voilet, $Am^{3+}(5f^6) =$ Pink, $Cm^{3+}(5f^7) =$ Colourless, $Th^{3+}(5f^0) =$ Colourless as so on.

COMPARISON OF LANTHANIDES AND ACTINIDES

Similarities :

As both Lanthanides and actinides involve filling of forbitals, they show similarities in many respects as follows :

- (i) Both show mainly an oxidation state of +3.
- (ii) Both are electropositive and very reactive.
- (iii) Both exhibit magnetic and spectral properties.
- (iv) Actinides exhibit Actinide contraction like Lanthanide contraction shown by Lanthanides.

Differences :

The show differences in some of their characteristics as follows :

	Lanthanides		Actinides
(i)	Besides + 3 oxidation state they show + 2 and +4 oxi- dation states only in few	(i)	Besides $+3$ oxidation state, they show higher oxidation states of $+4$, $+5$, $+6$, $+7$ also.
(ii)	cases.	(ji)	Most of their ions are
(11)	colourless	(11)	coloured
(iii)	They have less tendency	(iii)	They have greater tendency
	towards complex formation		towards complex formation.
(iv)	Lanthanides compounds are less basic.	(iv)	Actinides compounds are more basic
(v)	Do not form oxocation	(v)	From oxocations e.g.
			$\mathrm{UO}_2^{2+},\mathrm{PuO}_2^{2+}$ and UO^+
(vi)	Except promethium, they	(vi)	They are radioactive.
	are non-radioactive		
(vii)	Their magnetic properties can be explained easily.	(vii) Their magnetic properties cannot be explained easily, as they are more complex.

IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

П.

1. ZINC SULPHATE (ZnSO₄. 7H₂O - WHITE VITRIOL)

I. **PREPARATION**:

 $ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2$

II. REACTIONS:

(a)
$$ZnSO_4 + 2H_2O \longrightarrow Zn(OH)_2 + H_2SO_4$$

NaOH

$$\frac{Na_2ZnO_2}{(\text{sodium zincate})} + \frac{Na_2SO_4}{Na_2SO_4} + H_2O$$

(b)
$$\operatorname{ZnSO}_{4}.7\operatorname{H}_{2}O \xrightarrow{\text{below 70°C}} \operatorname{ZnSO}_{4}.6\operatorname{H}_{2}O \xrightarrow{280°C} \operatorname{ZnSO}_{4}$$

 $T > 760°C$

 $ZnO + SO_3$

(c)
$$\operatorname{ZnSO}_4 + \operatorname{NH}_4 \operatorname{OH} \rightarrow \operatorname{Zn} (\operatorname{OH})_2 + (\operatorname{NH}_4)_2 \operatorname{SO}_4$$

NH₄OH

 $[Zn(NH_3)_4]SO_4$

(d) Lithopone $(ZnS + BaSO_4)$ used as a white pigment.

2. ZINC OXIDE, ZNO (CHINESE WHITE OR PHILOSPHER'S WOOL)

It found in nature as zincite or red zinc ore.

- I. PREPARATION:
 - (a) $2Zn + O_2 \longrightarrow 2ZnO$

(b)
$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

(c)
$$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$$

REACTIONS:

- (a) $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$ (dil/conc.)
- (b) $ZnO + HNO_3 \longrightarrow Zn (NO_3)_2 + H_2O$ (dil/conc.)
- (c) $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$
- (d) $ZnO + 2KOH \longrightarrow K_2ZnO_2 + H_2O$

(e)
$$ZnO + CoO \longrightarrow CoZnO_2$$

(Rinmann's green)

III. USES :

- (i) As a white paint (It does not get tranished even in presence of H₂S because Zns is also white)
- (ii) For preparing Rinmann's green (Green Paint)
- (iii) As catalyst for preparation of methyl alcohol
- (iv) For making soft rubber
- (v) For making cosmetic powders, creams and in medicine

3. ZINC CHLORIDE ZnCl,.2H,O

Anhydride of zinc chloride cannot be obtained by heating its aqueous salt.

I. PREPARATION:

(a) $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

(b) $Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$

II. PROPERTIES:

- (a) $ZnCl_2 + H_2S \rightarrow ZnS + 2HCl$
- (b) $\operatorname{ZnCl}_2 + 2\operatorname{NaOH} \rightarrow \operatorname{Zn}(\operatorname{OH})_2 + 2\operatorname{NaCl}$ $\operatorname{Zn}(\operatorname{OH})_2 + 2\operatorname{NaOH} \rightarrow \operatorname{Na}_2\operatorname{ZnO}_2 + 2\operatorname{H}_2\operatorname{O}$
- (c) $ZnCl_2 + 2NH_4OH \rightarrow Zn(OH)_2 + 2NH_4Cl$

NH₄OH

 $[Zn(NH_3)_4]Cl_2 + 4H_2O$

4. FERROUS SULPHATE (FeSO₄. 7H₂O - GREEN VITRIOL)

I. PREPARATION:

- (a) $\operatorname{FeS} + \operatorname{H}_2 \operatorname{SO}_4 \to \operatorname{FeSO}_4 + \operatorname{H}_2 \operatorname{S}^{\uparrow}$
- (b) $\operatorname{Fe} + \operatorname{H}_2 \operatorname{SO}_4 \xrightarrow{\Delta} \operatorname{FeSO}_4 + \operatorname{H}_2 \uparrow$

 $2\text{FeS}_2 + \text{H}_2\text{O} + 7\text{O}_2 \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$

(Commercial preparation)

II. REACTIONS:

- (a) $2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$ (light green) (brown)
- (b) $\operatorname{Fe}^{+2} + [\operatorname{Fe} (CN)_6]^{3-} \longrightarrow \operatorname{Fe}_3[\operatorname{Fe} (CN)_6]_2$ Turmbull's blue (used as pigment in ink and paint)

Or $Fe_4 [Fe (CN)_6]_3$ (Prussian blue)

(c) NO_3^- detection :

$$\operatorname{FeSO}_4 + \operatorname{NO}_3^- + \operatorname{Conc.} \operatorname{H}_2\operatorname{SO}_4 \rightarrow \operatorname{[Fe}(\operatorname{H}_2\operatorname{O})_5\operatorname{NO}]^{\operatorname{SO}_4}$$
.

(d)
$$\operatorname{FeSO}_4 + 2\operatorname{KCN} \to \operatorname{Fe}(\operatorname{CN})_2 + \operatorname{K}_2\operatorname{SO}_4$$

brown

excess KCN K4[Fe(CN)6]

(e)
$$2\text{Hg}\text{Cl}_2 + 2\text{Fe}^{2+} \rightarrow \frac{\text{Hg}_2\text{Cl}_2}{\text{white}} + 2\text{Fe}^{3+} + 2\text{Cl}^{-1}$$

- (f) FeSO₄ + $H_2O_2 \rightarrow$ Fenton's reagent for oxidation of alcohols to aldehydes
- (g) FeSO_4 . $(\operatorname{NH}_4)_2 \operatorname{SO}_4$. $\operatorname{6H}_2 O \rightarrow \operatorname{Mohr's salt}$

5. FERRIC OXIDE, Fe₂O₃

I. **PREPARATION**:

(a)
$$2\text{FeSO}_4 \ \Delta \ \text{Fe}_2\text{O}_3 + \text{SO}_2 + 3\text{SO}_3$$

- II. REACTIONS:
 - (a) $Fe_2O_3 + 2NaOH$ Fusion $H_2O + 2NaFeO_2$

(sodium ferrite)

(b) $Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$

III. USES:

- (i) As a red pigment
- (ii) As abrasive polishing powder
- (iii) As catalyst

6. FERRIC CHLORIDE, FeCl₃

It is known in anhydrous and hydrated form. It is a red deliquiscent solid.

I. PREPARATION:

(a) $12\text{FeCl}_2(\text{anhydrous}) + 3O_2 \xrightarrow{\Delta} \text{Fe}_2O_3 + 8\text{FeCl}_3$

(anhydrous)

II. REACTIONS:

- (a) $2\text{FeCl}_3 \xrightarrow{\Delta} 2\text{FeCl}_2 + \text{Cl}_2$
- (b) $FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl$

(Reddish brown)

- (c) $4\text{FeCl}_3 + 3K_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12 \text{KCl}$ Prussian Blue
- (d) $2\text{FeCl}_3 + 6\text{NH}_4\text{CNS} \longrightarrow \text{Fe}[\text{Fe}(\text{CNS})_6] + 6\text{NH}_4\text{Cl}$ Deep red colour

Deep red colouration is produced due to formation of complex.

(e) Till 750°C it exists as its dimer Fe_2Cl_6 .



III. USES:

- (i) Its alcoholic solution is medicine, name (Tincture ferri perchloride)
- (ii) For detection of acetates and phenols
- (iii) For making prussion blue & as an oxidising agent

COPPER SULPHATE
 (CuSO₄. 5H₂O - BLUE VITRIOL)

- I. PREPARATION:
- (a) $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O_4$
- (b) $Cu(OH)_2.CuCO_3 + 2H_2SO_4 \rightarrow 2CuSO_4 + 3H_2O + CO_2$ Malachite Green

Copper scrape

 $Cu + H_2SO_4 + \frac{1}{2}O_2(air) \rightarrow CuSO_4 + H_2O$

(Commerical preparation)

II. REACTIONS:

(a) Effect of heat

$$CuSO_4.5H_2O \xrightarrow{100^{\circ}C} CuSO_4.H_2O \xrightarrow{230^{\circ}C}$$

pale blue.

$$CuSO_4 \xrightarrow{750^\circ} CuO + SO_3$$

(b)
$$[CuSO_4 + KI \rightarrow CuI_2 + K_2SO_4] \times 2$$

(Unstable

dirty white)

 $2\mathrm{CuI}_2 \rightarrow \mathrm{Cu}_2\mathrm{I}_2 + \mathrm{I}_2 \\ \underset{\text{white ppt.}}{}_{\mathrm{white ppt.}}$

$$2\mathrm{CuSO}_4 + 4\mathrm{KI} \rightarrow \mathrm{Cu}_2\mathrm{I}_2 + 2\mathrm{K}_2\mathrm{SO}_4 + \mathrm{I}_2$$

(c) Test of Cu^{2+}

$$CuSO_4 + NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$

NH₄OH

 $[Cu(NH_3)_4]SO_4$

Schwitzer's reagent (Deep blue solution)

(d) $CuSO_4 + KCN \rightarrow Cu(CN)_2 + K_2SO_4$

 $2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2 \uparrow_{\text{cyanogen gas}}$

 $Cu_2(CN)_2 + \underset{excess}{\text{KCN}} \rightarrow K_3[Cu(CN)_4]$

(e)
$$CuSO_4 + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6] + K_2SO_4$$

(f) $CuSO_4 + H_2S \rightarrow CuS_{(black ppt.)} + H_2SO_4$

(g) In Fehling's test & Benedict's test

Aldehyde + $Cu^{2+} \rightarrow Cu_2O \downarrow + acid$ (red ppt.)

III. USES:

(1) Bordeaux Mix \rightarrow CuSO₄+CaO

(to kill fungi)

8. CUPRIC OXIDE, CuO

It is called black oxide of copper and is found in nature as tenorite.

I. PREPARATION:

(a) By heating Cu₂O in air or by heating copper for a long time in air (the temperature should not exceed above 1100°C)

$$2Cu_2O + O_2 \longrightarrow 4CuO \text{ (black)}$$

$$2Cu + O_2 \longrightarrow 2CuO$$

- (b) $2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$
- (c) On a commercial scale, it is obtained by heating malachite which is found in nature.

 $CuCO_3$. $Cu(OH)_2 \longrightarrow 2CuO + CO_2 + H_2O$

II. REACTIONS:

(a) When heated to 1100–1200°C, it is converted into cuprous oxide with evolution of oxygen.

 $4CuO \longrightarrow 2Cu_2O + O_2$

(Black) (Red)

Uses : Used to impart blue and green colour to glazes and glass.

9. CUPRIC CHLORIDE, CuCl,.2H,O

(a)
$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$

 $Cu(OH)_2CuCO_3 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$
 $150^{\circ}C$

(b)
$$\operatorname{CuCl}_2 \cdot 2\operatorname{H}_2\operatorname{O} \xrightarrow{\operatorname{HCl}} \operatorname{Gas} \operatorname{CuCl}_2 + 2\operatorname{H}_2\operatorname{O}$$

II. REACTIONS:

(a) The anhydrous salt on heating forms Cu_2Cl_2 and Cl_2

$$3CuCl_2 \xrightarrow{} Cu_2Cl_2 + Cl_2$$
$$3CuCl_2 \cdot 2H_2O \xrightarrow{\Delta} CuO + Cu_2Cl_2 + 2HCl$$

 $+ Cl_2 + 5H_2O$

Dilute solution of $CuCl_2$ is blue but concentrated solution is green. Its dilute solution on adding HCl becomes yellow.

$$[Cu(H_2O)_4]^{2+} \rightarrow Blue$$

On adding HCl \rightarrow [CuCl₄]²⁻ \rightarrow green

10. AgNO₃ (LUNAR CAUSTIC)

I. Preparation :

(a)
$$3Ag + 4HNO_3 \xrightarrow{\Delta} 3AgNO_3 + NO + 2H_2O_{Colourless crystal}$$

- II. REACTION:
- (a) $2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$
- (b) $2\text{AgNO}_3 \xrightarrow{\text{T>212°C}} 2\text{AgNO}_2 + \text{O}_2$
- (c) $\operatorname{AgNO}_{3} \xrightarrow{\operatorname{KCN}} \operatorname{AgCN}_{\text{white ppts.}} \xrightarrow{\operatorname{KCN}} \operatorname{K} \begin{bmatrix} \operatorname{Ag(CN)}_{2} \end{bmatrix}$ soluble Potassium Dicyanidoargentate(I)

(d)
$$2AgNO_3 + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 + 2NaNO_3$$

(limited) white ppt.

White ppt. of Ag₂S₂O₃ which gracdually changes

$$Ag_{2}S_{2}O_{3} + H_{2}O \rightarrow Ag_{2}S + H_{2}SO_{4}$$

black
(e)
$$AgNO_{3} + Na_{2}S_{2}O_{3} \rightarrow Ag_{2}S_{2}O_{3} + 2NaNO_{3}$$
$$\bigcup_{\substack{Na_{2}S_{2}O_{3} \\ (excess)}} Na_{2}S_{2}O_{3}$$

$$\mathbf{v}$$
Na₃[Ag(S₂O₃)₂]

Sodium argentothic sulphate. It is used in photography.

(f)

$$AgNO_{3} \xrightarrow{S^{2^{-}}} Ag_{2}S \\
 PO_{4} \xrightarrow{3^{-}} Ag_{3}(PO_{4}) \\
 yellow \\
SO_{4} \xrightarrow{2^{-}} Ag_{2}SO_{4} \\
 white ppts. \\
 NaCl \qquad AgCl \\
 white ppts. \\
 NaBr \qquad AgBr \\
 (Pale yellow) \\
 Mal \qquad (Pale yellow) \\
 CrO_{4} \xrightarrow{2^{-}} Ag_{2}CrO_{4} \\
 (Red ppts.) \\
 \end{array}$$

(g) $\operatorname{AgNO}_3 + 2\operatorname{NH}_4\operatorname{OH} \rightarrow \operatorname{Ag}_2\operatorname{O}_{(brown \, ppt.)} + 2\operatorname{NH}_4\operatorname{NO}_3 + \operatorname{H}_2\operatorname{O}$

$$2[Ag(NH_3)_2]NO_3 + 3H_2O$$

- (h) Ammonical $AgNO_3 \rightarrow Tollen's reagent$ used to test aldehydes
- (i) It converts glucose to gluconic acid.

$$Ag_2O + C_6H_{12}O_6 \longrightarrow 2Ag + C_6H_{12}O_7$$

(j) It oxidises formaldehyde to formic acid

 $Ag_2O + HCHO \longrightarrow 2Ag + HCOOH$

Very dilute solution of AgNO₃ is used as dental antiseptic.

(k)
$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$$

11. SILVER BROMIDE, (AgBr)

I. PREPARATION:

It is prepared by the reaction of silver nitrate with a soluble bromide.

 $AgNO_3 + NaBr \longrightarrow AgBr + NaNO_3$

II. PROPERTIES

(a) It is a pale yellow solid. It is insoluble in water and concentrated acids. It is partially soluble in strong solution of ammonium hydroxide due to complex formation.

 $AgBr + 2NH_4OH \longrightarrow Ag(NH_3)_2Br + 2H_2O$

- (b) On heating, it melts to a red liquid.
- (c) It is most sensitive to light. It undergoes photoreduction.

 $2AgBr \xrightarrow{\text{Light}} 2Ag + Br_2$

(d) It dissolves in potassium cyanide.

$$AgBr + 2KCN \longrightarrow KAg(CN)_2 + KBr$$

Potassium argento-
cvanide (Soluble)

(e) It dissolves in sodium thiosulphate.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Sodium argento-
thiosubphate (Soluble)

(f) AgBr is reduced to silver, when treated with zinc and dilute H_2SO_4 .

 $Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$

$$2AgBr + 2H \longrightarrow 2Ag + 2HBr$$

All above reactions are also observed in the case of AgCl. However, it is white and fairly soluble in ammonium hydroxide. It is sensitive to light.

III. USES :

It is used for making photographic films and plates because it is sensitive to light.

12. MERCURY CHLORIDES

12.1 Mercurous Chloride (Hg₂ Cl₂ - Calomel)

I. PREPARATION:

 $2 HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

II. REACTIONS:

(a)

 $\mathrm{Hg}_{2}\mathrm{Cl}_{2} + \mathrm{SnCl}_{2} \xrightarrow{} 2\mathrm{Hg} + \mathrm{SnCl}_{4}_{\mathrm{black}/\mathrm{grey}}$

- (b) $Hg_2Cl_2 \xrightarrow{\Delta} HgCl_2 + Hg (grey deposit)$
- (c) $Hg_2Cl_2 + 2NH_3 \rightarrow \underbrace{Hg + Hg(NH_2)Cl}_{black} + NH_4Cl$

12.2 Mercuric Chloride (Hg Cl₂ - Corrosive sublimate)

I. PREPARATION:

It is highly corrosive, poisonous and hence is called as corrosive sublimate.

- (a) $\operatorname{Hg} + 2\operatorname{Cl}(\operatorname{aqua regia}) \rightarrow \operatorname{HgCl}_2$

 $Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$

II. REACTION:

(

(

a)
$$KI + HgCl_2 \rightarrow KCl + HgI_2$$

red ppts.

b)
$$HgI_2 + KI \rightarrow K_2HgI_4$$

colourless

Basic solution of K_2HgI_4 ($K_2HgI_4 + KOH$) is called as Nessler's Reagent.

(c) Test for ammonium ion

$$_{2}$$
HgI₄ + NH₄⁺Cl \rightarrow NH₂HgOHgI + KCl
Brown ppt.



Iodide of Millon's Base

(d)
$$\operatorname{HgCl}_2 + 2\operatorname{NH}_3 \rightarrow \underbrace{\operatorname{Hg}(\operatorname{NH}_2)\operatorname{Cl}}_{\text{white}} + \operatorname{NH}_4\operatorname{Cl}$$

- (e) $HgCl_2 + Cu \rightarrow CuCl_2 + Hg (grey deposit)$
- (f) HgCl₂ is sparingly soluble in cold H₂O but readily in hot water.

Chemistry Notes for class 12 Chapter 9 Coordination Compounds

Coordination compounds are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds, the central metal atom or ion is linked by ions or molecules with coordinate bonds, e.g., Potassium ferrocyanide, K_4 [Fe(CN)₆].

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Central metal atom Ligand $K_4[Fe(CN)_6] \leftarrow$ Coordination number Counter ion Coordinate sphere (entity)

Double Salts

These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g., Mohr'S salt, $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$ get dissociated into Fe²⁺, NH⁺₄ and SO²⁻₄ ions.

Terms Related to Coordination Compounds

1. Complex ion or Coordination Entity

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

(i) **Cationic complex entity** It is the complex ion which carries positive charge. e.g., $[Pt(NH_3)_4]^{2+}$

(ii) Anionic complex entity It is the complex ion which carries negative charge. e.g., $[Fe(CN)_6]^{4-}$

2. Central Atom or Ion

The atom or ion to which a fixed number of ions or groups are bound is .ned central atom or ion. It is also referred as Lewis acid. e.g., in $(NiCI_2(H_2O)_4]$. Ni is central metal atom. It is generally transition element or inner-transition element.

3. Ligands

Ligands is electron donating species (ions or molecules) bound to the Central atom in the coordination entity.

These may be charged or neutral. LIgands are of the following types :

(i) **Unidentate** It is a ligand, which has one donor site, i.e., the ligand bound to a metal ion through a single donor site. e.g., H_2O , NH_3 , etc.

(ii) **Didentate** It is the ligand. which have two donor sites.



(iii) **Polydentate** It is the ligand, which have several donor sites. e.g., [EDTA]⁴⁻ is hexadentate ligand.



(iv) **Ambidentate ligands** These are the monodentate ligands which can ligate through two different sites, e.g., NO⁻², SCN⁻, etc.

(v) **Chelating ligands** Di or polydentate ligands cause cyclisation around the metal atom which are known as chelate IS, Such ligands USes two or more donor atoms to bind a single metal ion and are known as chelating ligands.

More the number of chelate rings, more is the stability of complex.

The stabilisation of coordination compounds due to chelation is known as chelate effect.

 π – acid ligands are those ligands which can form π – bond and n-bond by accepting an appreciable amount of 1t electron density from metal atom to empty π or π – orbitals.

4. Coordination Number

It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

e.g., in $[PtCI_6]^{2-}$, Pt has coordination number 6.

In case of monodentate ligands,

Coordination number = number of ligands

In polydentate ligands.

Coordination number = number of ligands * denticity

5. Coordination Sphere

The central ion and the ligands attached to it are enclosed in square bracket which is known as coordination sphere. The ionisable group written outside the bracket is known as counter ions.

6. Coordination Polyhedron

The spatial arrangement of the ligands which are directly attached to the central atom or ion, is called coordination polyhedron around the central atom or ion.

7. Oxidation Number of Central Atom

The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom, is called oxidation number of central atom.

e.g., $[CU(CN_4)_{3-}, oxidation number of copper is +1, and represented as Cu(I).$

Types of Complexes

1. Homoleptic complexes

Complexes in which the metal atom or ion is linked to only one kind of donor atoms, are called homoleptic complexes e.g., $[Co(NH_3)_6]^{3+}$

2. Heteroleptic complexes

Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes e.g., $[Co(NH_3)_4CI_2]^+$

3. Labile and Inert complexes

Complexes in which the ligand substitution is fast are known as labile complexes and in which ligand substitution is slow, are known as inert complexes.

Effective Atomic Number (EAN)

This concept was proposed by Sidgwick. In a complex, the EAN of metal atom is equal to the total number of electrons present in it.

EAN = Z - ON of metal + 2 * CN

(where, Z = atomic number of metal atom

ON = oxidation number of metal

and CN = coordination number of complex)

An ion with central metal atom having EAN equal to next inert gas will be more stable.

IUPAC Naming of Complex Compounds

Naming is based on set of rules given by IUPAC.

1. Name of the compound is written in two parts (i) name of cation, and (ii) name of anion.

2. The cation is named first in both positively and negatively charged coordination complexes.

3. The dissimilar ligands are named in au alphabetical order before the name of central metal atom or ion.

4. For more then one similar ligands. the prefixes di, tri, tetra, etc are added before its name. If the di, tri, etc already appear in the complex then bis, tris, tetrakis are used.

5. If the complex part is anion, the name of the central metal ends with suffix 'ate'.

6. Names of the anionic ligands end in '0', names of positive ligands end with 'ium' and names of neutral ligands remains as such. But exception are there as we use aqua for H_2O , ammine for NH₃, carbonyl for CO and nitrosyl for NO.

7. Oxidation state for the metal in cation, anion or neutral coordination compounds is indicated by Roman numeral in parentheses.

8. The name of the complex part is written as one word.

9. If the complex ion is a cation, the metal is named same as the element.

10. The neutral complex molecule is named similar to that of the complex cation.

Some examples are

(i) [Cr(NH₃)₃(H₂O)₃]Cl₃

triamminetrichlorochromium (III) chloride

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(ii) [Co(H_2CH_2CH_2H_2)_3]_2(SO_4)_3
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tris (ethane-1,2-diamine) cobalt (III) sulphate

(iii) $[Ag(NH_3)_2] [Ag(CN)_2]$

diamminesilver (I) dicyanoargentate(I)

(iv) K_4 [Fe(CN)₆]

potassium hexacyanoferrate (II)

Isomerism in Coordination Compounds

Coordination compounds exhibit the following types of isomerism:

1.Structural Isomerism

In this isomerism. isomers have different bonding pattern. Different types of structural isomers are

(i) **Linkage isomerism** This type of isomerism is shown by the coordination compounds having ambidentate ligands. e.g.,

[Co(NH₃)₅(NO₂)]Cl and [Co(NH₃)₅(ONO)]Cl or pentaammine nitrito- N Cobalt (III) chloride and pentaammine nitrito-O'Cobalt (III) chloride.

(ii) **Coordination isomerism** This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex, e.g.,

[Cr(NH₃)₆) [CO(CN)₆]and [CO(NH₃)₆] [Cr(CN)₆]

(iii) **Ionisation isomerism** This isomerism arise due to exchange of ionisable anion with anionic ligand. e.g..

[Co(NH₃)₅SO₄]Br and [Co(NH₃)₅Br]SO₄ (red) (violet)

(iv) **Solvate isomerism** This is also known as hydrate isomerism. In this isomerism, water is taken as solvent. It has different number of water molecules in the coordination sphere and outside it. e.g..

 $[Co(H_2O)_6]CI_3, [Co(H_2O)_4C1_2]Cl \cdot 2H_2O, [Co(H_2O)_3Cl_3]. 3H_2O$

2. Stereoisomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. These are of two types :

(i) **Geometrical isomerism** Geometrical isomers are of two types i.e., cis and trans isomers. This isomensm is common in complexes with coordination number 4 and 6.

Geometrical isomerism in complexes with coordination number 4

(i) Tetrahedral complexes do not show geometrical isomerism.

(ii) Square planar complexes of formula $[MX_2L_2]$ (X and L are unidentate) show geometrical isomerism. The two X ligands may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer, e.g.,



(iii) Square planar complex of the type [MABXL] (where A, B, X, L, are unidentate ligands) shows three isomers, two cis and one trans.

e.g., [Pt(NH₃) (Br)(Cl)(Py)].

Geometrical isomerism in complexes with coordination number 6

Octahedral complexes of formula $[MX_2L_4]$, in which the two X ligands may be oriented cis or trans to each other, e.g., $[Co(NH_3)_4Cl_2)^+$.



Octahedral complexes of formula $[MX_2A_2]$, where X are unidentate ligands and A are bidentate ligand. form cis and trans isomers, e.g., $[CoC1_2(en)_2]'$

In octahedral complexes of formula $[MA_3X_3]$, if three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face. it is known as facial (fae) isomer, when the positions are around the meridian of the octahedron, it is known as meridional (mer) isomer. e.g., $[Co(NH_3)_3(NO_2)_3]$



(ii) **Optical isomerism** These are the complexes which have chiral structures. It arises when mirror images cannot be superimposed on one another. These mirror images are called enantiomers. The two forms are called dextro (d) and laevo (l) forms.

Tetrahedral complexes with formula $[M(AB)_2]$ show optical isomers and octahedral complexes (cis form) exhibit optical isomerism.

Bonding in Coordination Compounds

Werner's Theory

Metals exhibit two types of valencies in the formation of complexes.

These are primary valencies and secondary valencies.

1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.

2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.

Valence Bond Theory (VBT)

This theory was proposed by L. Pauling in 1930 s. According to this theory, when a complex is formed, the metal ion/atom provides empty orbitals to the surrounding ligands. Coordination number shows the number of such empty orbitals, i.e., number of empty orbitals is equal to the coordination number. These empty orbitals hybridised

before participation in bonding and the nature of hybridisation depends on the nature of metal and on the nature of approaching ligand.

Inner orbital complexes or outer orbital complexes

When outer d-orbital are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak field ligands or high spin ligands and hybridisation is sp^3d^2 . They have octahedral shape.

When d-orbitals of (n - 1) shell are used, these are known as inner orbital complex, they are formed due to strong field ligands or low spin ligands and hybridisation is d^2sp^3 . They are also octahedral in shape.

1. 6 – ligands (unidentate), octahedral entity.

(i) Inner orbital complex $[Co(NH_3)_6]^{3+}$



All electrons are paired, therefore complex will be diamagnetic in nature.

(ii) Outer orbital complex, $[CoF_6]^{3-}$



Complex has unpaired electrons, therefore, it will be paramagnetic in nature.

2. 4-ligands (unidentate) tetrahedral entity.

S.No.	Inner orbital complexes	Øuter orbital complexes
(a)	Strong field or low spin ligands	Weak field or high spin ligands
(b)	Hybridisation is dsp^2 (where one orbital of 3d, one orbital of 4s and two orbitals of 4p)/	Hybridisation is sp^3 (where one orbital of 4s and three orbitals of 4p)
(c)	Square planar shape	Tetrahedral shape

(i) Inner orbital complex, $[Ni(CN)_4]^{2-}$



All electrons are paired so complex will be diamagnetic in nature.

(ii) Outer orbital complex, [CoCI₄]⁻



Since, complex has unpaired electrons. so it will be paramagnetic in nature.

Limitations of VBT

This theory could not explain the quantisation of the magnetic data, existence of inner orbital and outer orbital complex, change of magnetic moment with temperature and colour of complexes.

Crystal Field Theory (eFT)

This theory was proposed by H. Bethe and van Vleck. Orgel. in 1952, applied this theory to coordination compounds. In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

The five d-orbitals are classified as

(i) Three d-orbitals i.e., d_{xy} , d_{yz} and d_{zx} are oriented in between the coordinate axes and are called t_{2g} – orbitals.

(ii) The other two d-orbitals, i.e., $d_x^2 - y^2$ and d_z^2 oriented along the x - y % axes are called e_g - orbitals.

Due to approach of ligands, the five degenerate d-orbitals split. Splitting of d-orbitals depends on the nature of the crystal field.

[The energy difference between t_{2g} and e_g level is designated by Δ and is called **crystal field splitting energy.**]

By using spectroscopic data for a number of coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

Spectrochemical series

$$\label{eq:scn} \begin{split} I^- < Br^- < SCN^- < CI^- < S^{2-} < F^- < OH^- \\ < C_2 O_4^{2-} < H_2 O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO. \end{split}$$

Crystal field splitting in octahedral complexes

In case of octahedral complexes, energy separation is denoted by Δ_o (where subscript 0 is for octahedral).

In octahedral complexes, the six-ligands approach the central metal ion along the axis of d x^2 and d z^2 orbitals.

Energy of e_g set of orbitals > energy of t_{2g} set of orbitals. The energy of e_g orbitals will increase by (3/5) Δ_o and t_{2g} will decrease by (2/5) Δ_o .

If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e^o_g$. (where, P = energy required for e⁻ pairing in an orbital). Ligands which produce this effect are known as strong field ligands and form low spin complexes.



Crystal field splitting in tetrahedral complexes

In tetrahedral complexes, four ligands may be imagined to occupy the alternate comers of the cube and the metal ion at the center of the cube.

Energy of t_{2g} set of orbitals > Energy of e_g set of orbitals.

In such complexes d – orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Orbital splitting energies are so low that pairing of electrons are not possible so these are high spin complexes.



Colour in Coordination Compounds

The crystal field theory attributes the colour of the coordination compounds to dod transition of the electron, i.e., electron jump from t_{2g} level to higher e_g level.

In the absence of ligands, crystal field splitting does not occur and hence the substance is colourless.

 $[Ti(H_2O]_6]^{3+}$ — Violet in colour $[Cu(H_2O)_4]^{2+}$ — Blue in colour, etc.

Limitations of CFT

1. It does not consider the formation of 7t bonding in complexes.

2. It is also unable to account satisfactorily for the relative strengths of ligands e.g., it does not explain why H_2O is stronger ligand than OH^- .

3. It gives no account of the partly covalent nature of metal-metal bonds.

Ligand Field or Molecular Orbital Theory
This theory was put forward by Hund and Mulliken. According to this theory, all the atomic orbitals of the atom participating in molecule formation get mixed to give rise an equivalent number of new orbitals, called the molecular orbitals. The electrons are now under the influence of all the nuclei.

Stability of Coordination Compounds

The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium. It is expressed as stability constant (K).

e.g.,
$$M^+ + nL^{x-} \rightleftharpoons [ML_n]^{y-}; \qquad K = \frac{[(ML_n)^{y-}]}{[M^+] [L^{x-}]^n}$$

The factors on which stability of the complex depends :

(i) **Charge on the central metal atom** As the magnitude of charge on metal atom increases, stability of the complex increases.

(ii) Nature of metal ion The stability order is 3d < 4d < 5d series.

(iii) Basic nature of ligands Strong field ligands form stable complex.

The instability constant or the dissociation constant of compounds is defined as the reciprocal of the formation or stability Constant.

Importance and Applications of Coordination Compounds

1. They are used in many qualitative and quantitative analysis.

2. Hardness of water is estimated by simple titration with Na₂ EDTA.

3. Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

4. They have great importance in biological systems.

5. They are used as catalyst for many industrial processes.

6. In medicinal chemistry, there is a growing interest of chelating therapy.

Organometallic Compounds

They contain one or more metal-carbon bond in their molecules. They are of the following types:

1. Sigma (σ) bonded compounds

Metal-carbon bond is sigma bond, e.g., $(C_2H_5)_4$ Pb, $Zn(C_2H_5)_2$ R – Mg – X, etc.

2. $Pi(\pi)$ bonded compounds

In which molecules/ions containing π bonds act as a ligand. e.g., Ferrocene, Dibenzene chromium and Zeise's salt.

Zeise's salts is K[PtCI₃($\eta^2 - C_2H_4$)] In which ethylene acts as a ligand which do not have a lone pair oi electron.

In ferrocene, $Fe(\eta^5 - C_5H_5)_2$ represents the number of carbon atoms with which metal ion is directly attached.

3. σ and π bonded compounds

Metal carbonyls are their examples. Metal-carbon bond of metal carbonyls have both σ and π – bond character. They have CO molecule as ligand, e.g.,



Wilkinson's catalyst (Rh(PPh₃)₃CI] is used as homogeneous catalyst in the hydrogenation of alkenes. Zeigler-Natta catalyst

[Ti CI₄ + ($C_2H_5>_3Al$] acts as heterogeneous catalyst in the polymerisation of ethylene

Chemistry Notes for class 12 Chapter 10 Haloalkanes and Haloarenes

The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Classification of Halogen Derivatives

On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,



On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1° , 2° , 3° , allylic, benzylic, vinylic and aryl derivatives, e.g.,



L.

General Methods of Preparation of Haloalkanes

1. From Alcohols

$$R = OH$$
alcohol
$$R = OH$$

$$R$$

In Groove's method, $ZnC1_2$ is used to weaken the C-OH bond. In case of 3° alcohols, $ZnC1_2$ is not required.

The reactivity order of halogen acids is HI > HBr > HCl.

Darzen procedure is the best method for preparing alkyl halides from alcohols since both the by products (SO₂ and HCl) are gaseous and escape easily.

2. Free Radical Halogenation of Alkanes



Addition of Hydrogen Halides on Alkenes



1. Finkelstein Reaction

$$\begin{array}{c} R \xrightarrow{} X + \operatorname{NaI} \xrightarrow{\operatorname{Acetone}} R \xrightarrow{} I + \operatorname{NaX} \\ (X = \operatorname{Cl}, \operatorname{Br}) \end{array}$$

2. Swarts Reaction

 $H_3C-Br+AgF \rightarrow H_3C-F+AgBr$

 Hg_2F_2 , COF_2 and SbF_3 can also be used as a reagent for Swarts reaction.

3. Hunsdiecker Reaction

 $\mathrm{CH}_3\mathrm{COOAg} + \mathrm{Br}_2 \xrightarrow[]{\mathrm{CCl}_4} \mathrm{CH}_3\mathrm{Br} + \mathrm{AgBr} + \mathrm{CO}_2$

Physical Properties of Haloalkanes

1. Boiling point orders

- 1. R I > R Br > R CI > R F
- 2. $CH_3 (CH_2)_2 CH_2Br > (CH_3)_2 CHCH_2Br > (CH_3)_3CBr$
- 3. $CH_3CH_2CH_2 > CH_3CH_2X > CH_3X$

2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is

 $CH_3F > CR_3Cl > CR_3Br > CH_3I$

3. Dipole moment decreases as the electronegativity of the halogen decreases.

4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is

RI > RBr > RCl > RF (For the same alkyl group)

 $CH_{3}I > C_{2}H_{5}I > C_{3}H_{7}I$

Chemical Reactions of Haloalkanes

1. Nucleophilic Substitution Reactions (S_N reactions)



kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO₂ form R-ONO while AgNO₂ produces R-NO₂ as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types

(a) $S_N 1$ type (Unimolecular nucleophilic reactions proceed in two steps:



Rate, r = k [RX). It is a first order reaction.

Reactivity order of alkyl halide towards S_N1 mechanism

 $3^{\circ} > 2^{\circ} > 1^{\circ}$

Polar solvents, low concentration of nucleophiles and weak nucleophiles favour $S_N 1$ mechanism.

In S_N1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



(b) $S_N 2$ type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with r = k[RX] [Nu].

During $S_N 2$ reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,



Reactivity of halides towards S_N2 mechanism is

 $1^{\circ} > 2^{\circ} > 3^{\circ}$

Rate of reaction in $S_N 2$ mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

 $:CN^{-} > : I^{-} > : OR^{-} > : OH^{-} > CH^{3}COO : > H_{2}O > F^{-}$

Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour $S_N 2$ mechanism.

Relative rates of some alkyl halides in S_N1 and S_N2 reactions are in the order



> CH_3CH_2X > $(CH_3)_2CHX$ > $(CH_3)_3CX$

Resonating structure of benzyl carbocations are



Relative reactivity of alkyl halides for same alkyl group is

RI > RBr > RCI > RF

2. Elimination Reactions

Dehydrohalogenation is a β – elimination reaction in which halogen is from α -carbon atom and the hydrogen from the α -carbon according to Saytzeff rule, e.g.,

$$\begin{array}{c} & \operatorname{Br} & & \operatorname{Alc. \ KOH} \\ & \operatorname{CH}_{3} - \operatorname{CH}_{2} - \operatorname{CH} - \operatorname{CH}_{3} & \xrightarrow{\operatorname{Alc. \ KOH}} & \operatorname{CH}_{3} - \operatorname{CH} = \operatorname{CH}_{-\operatorname{CH}_{3}} \\ & \xrightarrow{\operatorname{but-2-ene}} \\ & & \operatorname{but-2-ene} \\ & & \operatorname{(major)} \\ & + \operatorname{CH}_{3} \operatorname{CH}_{2} \operatorname{CH} = \operatorname{CH}_{2} \\ & & \operatorname{butene-1} (\operatorname{minor}) \end{array}$$

Ease of dehydrohalogenation among halides

$$3^{\circ} > 2^{\circ} > 1^{\circ}$$

i.e.,
$$(CH_3)_3 CCl > (CH_3)_2 CHCl > CH_3 CH_2 Cl$$

3. Reduction

1

$$C_{2}H_{5} \longrightarrow Br + H_{2} \xrightarrow{Ni, 575 \text{ K}} C_{2}H_{6} + HBr$$

$$C_{2}H_{5}I + HI \xrightarrow{\text{Red P, 420 K}} C_{2}H_{6} + I_{2}$$

4. Reaction with Metals



Grignard reagent is never isolated in the solid state as it explodes in dry state. So it is used as ethereal solution.

5. Isomerisation



General Methods of Preparation of Aryl Halides

1. By Halogenation of Aromatic Hydrocarbons



It is an electrophilic substitution reaction.

2. By Side Chain Halogenation



(It involves free radical mechanism.)

3. From Benzene Diazonium Salt

$$\frac{CuCl/HCl}{CuBr/HBr} = \frac{C_{6}H_{5}Cl + N_{2}}{C_{6}H_{5}Br + N_{2}}$$
Sandmeyer reaction

$$\frac{N_{2}^{+}Cl}{Cu/HCl} = \frac{C_{6}H_{5}Br + N_{2}}{C_{6}H_{5}Br + N_{2}}$$
Gattermann reaction

$$\frac{HBF_{4}}{C_{73}K} = \frac{C_{6}H_{5}N_{2}^{+}BF_{4}}{C_{6}H_{5}N_{2}^{+}BF_{4}} = \frac{\Delta}{-N_{2}, -BF_{3}} = C_{6}H_{5}F$$
(Balz Schiemann reaction)

$$\frac{KI, \Delta}{C_{6}H_{5}I + N_{2} + KCl}$$

4. From Phenol



Physical Properties of Aryl Halides

1. Aryl halides are colourless liquids or colourless solids with characteristic odour.

2. Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order

Ar - I > Ar - Br > Ar - Cl > Ar - F

3. The melting point of p -isomer is more than 0- and m-isomer.

This is because of more symmetrical nature of p-isomer.

4. Due to resonance in chlorobenzene, C-CI bond is shorter and hence, its dipole moment is less than that of cyclohexylchloride.

Chemical Properties of Aryl Halides

1. Nucleophilic Substitution Reaction

Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

- 1. Due to resonance, C-X bond has partial double bond character.
- 2. Stabilisation of the molecule by delocalisation of electrons.
- 3. (Instability of phenyl carbocation.

However, aryl halides having electron withdrawing groups (like $-NO_2$, $-SO_3H$, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.



Presence of electron withdrawing group (-NO₂) increases the reactivity.



2. Electrophilic Substitution Reactions

Halogens are deactivating but O, p-directing. Thus, chlorination, nitration, sulphonation and Friedel Craft's reaction give a mixture of o- and P- chloro substituted derivatives.

(i) Halogenation



(iii) Sulphonation



3. Reaction with Metals

(i) Wurtz Fittig reaction



(ii) Fitting reaction



(iii) Ullmann reaction





Dichloromethane (CH_2Cl_2) is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and milk redness of the skin.

Trihalogen Derivatives

1. Chloroform [Trichloromethane, CHCl₃]

Methods of preparation



Properties

1. Oxidation of CHCl₃ gives poisonous gas phosgene (carbonyl chloride).



To avoid this oxidation $CHCl_3$ iI .toreci in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

2. CHCl₃ is widely used in the production of freon refrigerant R-22.

3. On nitration, it gives tear producing insecticide substance chloropicrin.

 $\begin{array}{c} \mathrm{CHCl}_{8} + \mathrm{HONO}_{2} \left(\mathrm{conc.} \right) &\longrightarrow \mathrm{NO}_{2} \cdot \mathrm{CCl}_{8} + \mathrm{H}_{2}\mathrm{O} \\ \mathrm{chloropicrin} \end{array}$ $\begin{array}{c} \mathrm{4. \ On \ dehalogenation, \ it \ gives \ C_{2}\mathrm{H}_{2} \left(\mathrm{acetylene} \right). \\ \mathrm{CHCl}_{8} + 6\mathrm{Ag} + \mathrm{CHCl}_{8} &\longrightarrow \mathrm{CH} \Longrightarrow \mathrm{CH} + 6\mathrm{Ag}\mathrm{Cl} \end{array}$ $\begin{array}{c} \mathrm{5. \ When \ subjected \ to \ hydrolysis, \ it \ gives \ formate.} \\ \mathrm{OH} \end{array}$

$$CHCl_{3} + 3NaOH \longrightarrow CH \xrightarrow{OH} OH \xrightarrow{-H_{2}O} HCOONa$$

2. Iodoform (tri-iodornethane, CHl₃)

Iodoform is prepared by iodoform reaction.

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow$$

 $CHI_3 + 3NaI + CH_3COONa + 3H_2O$

Compounds containing either CH_3CO - or $CH_3CH(OH)$ group form yellow colour iodoform with I_2 and NaOH.

Iodoform when comes in contact with organic matter, decomposes easily to free iodine, an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Polyhalogen Derivatives

1. Tetrachloromethane (Carbon Tetrachloride, CCl₄)

Preparation



CCI₄ is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.

Uses

Carbon tetrachloride is used

- 1. as a solvent for oils, fats, resins
- 2. in dry cleaning
- 3. as fire extinguisher under the name 'pyrene'.

2. Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Carbon tetra chloride when reacts with antimony trifluoride in the presence of SbCl₅ as catalyst, dichlorofluromethane (freon) is obtained.

3. DDT (p, p'-Dichlorodiphenyltrichloroethane)



2,2- bis (4-chlorophenyl) -1,1,1- trichloroethane

DDT is the first chlorinated organic insecticide. Its stability and fat solubility'is a great problem.

It is prepared from chloral and chlorobenzene in the presence of conc. H_2SO_4 .

4. Perchloroethane (C₂Cl₆)

It is used as moth repellant and is also known as artificial camphor.

Chemistry Notes for class 12 Chapter 11 Alcohols, Phenols and Ethers

Alcohols and Phenols

Alcohols and phenols are formed when a hydrogen atom in hydrocarbon, aliphatic and aromatic respectively, is replaced by hydroxyl group (-OR group).

Classification of Alcohols and Phenols

In alcohols, -OR group is attached to Sp3 hybridised carbon. These alcohols are usually classified as primary, secondary and tertiary alcohols.



Alcohols may be

(i) monohydric-containing one – OR group,

(ii) dihydric-containing two - OR groups and

(iii) polyhydric-containing three or more -OR groups.

In phenols, -OR group is attached to Sp^2 hybridised carbon. These may also be monohydric, dihydric, etc. The dihydric phenol further rosy be ortho, meta' or para derivative.



In allylic alcohols, - OH group is attached to sp³ hybridised carbon but next to C=C bond.

e.g., $CH_2 = CH - CH_2OH$, Benzylic alcoho1($C_6H_5CH_2OH$)

Structure of Alcohols and Phenols

The oxygen atom of alcohols is Sp^3 hybridised and they have tetrahedral position of hybrid atomic orbitals .



The value of LROH bond angle depends upon the R group. For methyl alcohol, it is $(\angle C - O - H)$ 108.9° due to repulsion of lone pairs.

In phenols, the – OH group is attached to Sp^2 hybridised carbon and thus, the C – O bond acquires a partial double bond character.



Nomenclature of Alcohols and Phenol

In IUPAC, system, alcohol or alkanols are named by replacing the last word 'e' of the corresponding alkane by 'ol'. e.g.,





2-methyl phenol



2,4-dimethylcyclopentanol

Preparation of Alcohols

(i) From alkenes

(a) By acid catalysed hydration in accordance with Markownikoff's rule.



Mechanism

Step I Protonation of alkene by attack of H_3O^+



Step II Nucleophilic attack



Step III Deprotonation to form an alcohol



(b) By hydroboration-oxidation



(ii) From carbonyl compounds

(a) By reduction of aldehydes and ketones



Aldehydes yield primary alcohols whereas ketones give secondary alcohols, when subjected to reduction.

(b) By reduction of carboxylic acids and ester



Reduction of aldehyde, ketones and esters with No Alcohol is called Bouveault-blanc reduction.



The reaction produces a primary alcohol with methanol, a secondary alcohol with aldehydes (except methanal) and tertiary alcohol with ketones

$$HCHO + RMgX \longrightarrow RCH_{2}OMgX \xrightarrow{H_{2}O} RCH_{2}OH + Mg \xrightarrow{X}OH$$

$$RCHO + R'MgX \xrightarrow{H_{2}O} R \xrightarrow{H_{2}O} CH \longrightarrow OMgX \xrightarrow{H_{2}O} R \xrightarrow{R'}OH$$

$$RCHO + R'MgX \longrightarrow R \xrightarrow{H_{2}O} R \xrightarrow{H_{2}O} R \xrightarrow{H_{2}O} R \xrightarrow{H_{2}O} R \xrightarrow{H_{2}O} R \xrightarrow{H_{2}O} OH$$

$$RCOR + R'MgX \longrightarrow R \xrightarrow{R'}OMgX \xrightarrow{H_{2}O} R \xrightarrow{R'}OH$$

$$RCOR + R'MgX \xrightarrow{R'}R \xrightarrow{R'}R \xrightarrow{R'}R$$

(iv) Hydrolysis of alkyl halides

 $R - X + KOH(aq) \rightarrow ROH + KX$

To avoid dehydrohalogenation of RX, mild alkalies like moist

Ease of hydrolysis of alkyl halides RI > R - Br > RCI > and t > s > p alkyl halides.

(v) Hydrolysis of ethers

$$R \longrightarrow R + H_2O \longrightarrow ROH$$

(vi) From primary amines By treatment with nitrous acid.

 $RNH_2 + HONO \xrightarrow{(NaNO_2 + HCI)} ROH + N_2 + H_2O$

Methylamine does not give methyl alcohol when treated with HNO₂. It gives CH₃OCH₃ and CH₃ONO.

(vii) By alcoholic fermentation

 $\begin{array}{cccc} C_{12}H_{22}O_{11} + H_2O & \xrightarrow{\text{Invertase}} & C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{sucrose} & glucose & \text{fructose} \\ \hline & C_6H_{12}O_6 & \xrightarrow{\text{Zymase}} & 2C_2H_5OH + 2CO_2(g) \\ \text{glucose and fructose} & \text{ethyl alcohol} \end{array}$

Preparation of Phenols

(i) From haloarenes



(ii) From benzene sulphonic acid



(iii) From diazonium salts



(iv) From cumene



Physical Properties of Alcohols

1. Lower alcohols are colourless liquids, members from $C_5 - C_{11}$ are oily liquids and higher members are waxy solids.

2. The hydroxyl groups in alcohols can form H-bonds with water, so alcohols are miscible with water. The solubility decreases with increase in molecular mass.



3. Boiling points of alkanes are higher than expected because of the presence of intermolecular hydrogen bonding in the polar molecules.

[The boiling point decreases in the order $1^{\circ} > 2^{\circ} > 3^{\circ}$ as the van der Waals' forces of attraction decreases]

Physical Properties of Phenols

1. These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.

2. Phenol is also called carbolic acid.

3. Because of the presence of polar -OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.

Chemical Reactions of Alcohols and Phenols

(i) Reactions involving cleavage of O – H Bond

(a) Acidity of alcohols and phenols



Alcohols are weaker acids than water due to +1 group present in alcohols, which decreases the polarity of -O-H bond.

Acid strength of alcohols



Electron releasing group increases electron density on oxygen to decrease the polarity of – OH bond.

Order of acidity is

 $RCOOH > H_2CO_3 > C_6H_5OH > H_2O > R - OH.$

Phenol is more acidic than alcohols due to stabilisation of phenoxide ion through resonance. Presence of electron withdrawing group increases the acidity of phenol by , stabilising phenoxide ion while presence of electron releasing group decreases the acidity of phenol by destabilising phenoxide ion.

Thus. increasing acidic strength is

o-cresol < p-cresol < m-cresol < phenol < o-nitrophenol < 2, 4. 6.trinitrophenol (picric acid)

Higher K_a and lower pK_a value corresponds to the stronger acid.

(b) Esterification

$Ar/R - O - H + R'COOH \stackrel{H^+}{\rightleftharpoons} Ar/R - OCOR' + H_2O$ $Ar/R - OH + (R'CO)_2O \stackrel{H^+}{\rightleftharpoons} Ar/R - OCOR' + R'COOH$

 $R/Ar \rightarrow OH + R'COCl \longrightarrow R/Ar - OCOR' + HCl$ Pyridine

The reaction with R'COOH and $(R' CO)_2O$ is reversible, so cone, H_2SO_4 is used to remove water.

The reaction with R' COCI is carried out in the presence of pyridine so as to neutralise HCI which is formed during the reaction.

The introduction of acetyl (CH₃CO-) group in phenols is known as acetylation.

Acetylation of salicylic acid produces aspirin.



(ii) **Reaction involving cleavage of C-O bond in alcohols** In these reactions, the reactivity order of different alcohols :



Alkyl group due to +1 effect increases the electron density on the carbon and oxygen atom of C-OH bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present, more will be the reactivity of alcohol. Thus, the relative order of reactivity of the alcohols is justified.

(a) **Reaction with halogen acids** Alcohols can be converted into haloalkanes by the action of halogen acids.

 $R - OH + HX (HCI, HBr, HI) \rightarrow R-X + H_2O$

For a given alcohol order of reactivity of HX is

H-1 > H-Br > H-Cl

For a given halogen acid order of reactivity of alcohols

Tertiary > Secondary > Primary

Lucas test

Primary alcohols	Secondary alcohols	Tertiary alcohols	
RCH2OH Conc HCI	R2CH OH Conc HCI Anhy.ZnCl2	R3C-OH Conc HCI	
No reaction and hence,	R ₂ CHCI	R ₃ CCI	
no white cloudiness or turbidity at room temperature.	White cloudiness or turbidity appears with in about 5 minutes.	White cloudiness or turbidity appears immediately.	

(b) Reaction with phosphorus halides

 $ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$ $3ROH + PBr_3 \xrightarrow{P/Br_2} 3RBr + H_3PO_3$ $J_{3ROH} + PI_3 \xrightarrow{P/I_2} 3RI + H_3PO_3$

(c) Reaction with thionyl chloride

 $ROH + SOCl_2 \longrightarrow RCl + SO_2^{\uparrow} + HCl^{\uparrow}$

d) **Dehydration of alcohols** It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group.

Since, the rate determining step is the formation of carbocation, the ease of dehydration is



Mechanism

Step I Formation of protonated alcohol



Step II Formation of carbocation



Step III Formation of ethene by elimination of a proton



In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product. (Saytzeff's rule).

(iii) Oxidation reactions Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$.

Primary alcohols	Secondary alcohols	Tertiary alcohols
CH3CH2OH	CH ₃ CHOH-CH ₃	(CH3)3C-0H
↓ [0]	↓[0]	1(O)
CH3CHO	CH3COCH3	$CH_{3}COCH_{3} + CO_{2}^{3} + H_{2}O$
1[0]	↓[0]	10J
CH3COOH	$CH_{3}COOH + CO_{2} + H_{2}O$	$CH_{3}COOH + CO_{2} + H_{2}O$

A common reagent that selectively oxidises a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate (pCC).

CH₃CH=CH−CH₂OH − CH₃CH=CH−CHO

(iv) **Dehydrogenation**

$\begin{array}{c} RCH_2OH \xrightarrow{Cu/300^{\circ}C} \\ 1^{\circ} alcohol \end{array}$	$RCHO + H_2 \uparrow$ aldehyde
$\begin{array}{c} R \\ \hline R \\ 2^{\circ} \text{ alcohol} \end{array} \longrightarrow \begin{array}{c} Cu/300^{\circ} C \\ \hline \end{array}$	$R \cdot \mathrm{CO} \cdot R + \mathrm{H}_2 \uparrow$ ketone
$(CH_3)_3COH \xrightarrow{Cu/300^\circ C} 3^\circ alcohol$	H_{3C} C=CH ₂ + H ₂ O
	alkene (iso-butylene)

Distinction among $1^{\circ}, 2^{\circ}$ and 3° Alcohols

1°, 2° and 3° alcohols are distinguished by Lucas test, oxidation and reduced copper.

Victor Meyer's test is also used to distinguish them.

In this test, primary (1°) alcohols give red colour, secondary (2°) alcohols give blue colour and tertiary (3°) alcohols give no colouration.



Reactions of Phenols

(i) **Electrophilic substitution reactions** The -OH group attached to the benzene ring activates it towards electrophilic substitution at ortho and para positions .

(a) Halogenation



With calculated amount of Br₂ in CS₂ or CHCI₃ it gives ortho and para product.



(b) SuLphonation



(c) Nitration



The ortho and para isomers can be separated by steam distillation. This is because onitrophenol is steam volatile due to intramolecular hydrogen bonding while p nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



(d) Reimer-Tiemann reaction



This reaction is an electrophilic substitution reaction and electrophile is dichlorocarbene. Similarly with carbon tetrachloride and alkali, c- and p-hydroxybenzoic acid are obtained



(ii) Kolbe's reaction



(iii) Reaction with zinc dust



Terms Related to Alcohols

(a) **Rectified spirit** It contains 95% ethyl alcohol and 45% water. It is an azeotrope (constant boiling mixture) and boils at 74° (.

(b) Absolute alcohol Alcohol containing no water, i.e; 100% C_2H_5OH is known as absolute alcohol. It is prepared as follows.

(i) Quick lime process

(ii) Azeotropic method

(c) **Methylated spirit** The rectified spirit rendered poisonous by addition of 4-5% methyl alcohol, traces of pyridine and some copper sulphate and is known as methylated spirit or denatured alcohol.

(d) **Power alcohol** Alcohol mixed with petrol or fuel and used In internal combustion engines Is known as power alcohol.

(e) **Wood spirit** Methyl alcohol (CH₃OH) is also called wood spirit. It is obtained by destructive distillation of wood. Pyroligneous add, the product of destructive distillation of wood, contains acetic acid (10%), methyl alcohol (25%) and acetone (05%). Drinking of methanol causes blindness.

(f) **Grain alcohol** Ethyl alcohol C_2H_5OH is also called grain alcohol. It is used In the preparation of various beverages containing different percentages.

Dihydric Alcohols

These are generally called glycols because of their sweet taste. Ethylene glycol ($CH_2OH - CH_2OH$) is the first and most important member of dihydric alcohol series.

Methods of Preparation

(i) From ethylene

$$CH_2 = CH_2 + [0] + H_2O \xrightarrow{Baeyer's reagent} CH_2OH - CH_2OH$$

(1% alkaline KMnO4 is called Baeyer's reagent)

$$CH_2 = CH_2 \xrightarrow{OsO_4/pyridine} CH_2OH - CH_2OH$$

(ii) By reduction of glyoxal

CHO		LiAIH4	CH ₂ OH
CHO + (H)	,	Сн₂он	
glyoxal			ethylene glycol

Physical Properties

1. It is a colourless, syrupy liquid with sweet taste.

2. Because of its tendency of formation of H-bonds, it is miscible with H_2O and ethanol but not with ether.

Chemical Properties

It gives all the general reactions of -OH group.



The per-iodic acid cleavage of 1,2-g1ycols is sometimes called Malaprade reaction.

Trihydric Alcohols

Glycerol or glycerine, $CH_2OH - CH(OH)$ - CH_2OH is the first member of this group. Its IUPAC name is propane-1,2,3-triol.

Method of Preparation
It is obtained as a by product in saponification reaction.



Physical Properties

- 1. It is a colourless, odourless, viscous and hygroscopic liquid.
- 2. It is sweet in taste and steam volatile.
- 3. It is soluble in water but insoluble in ether.
- 4. Due to excessive H-bonding, it is highly viscous and has high boiling point.

Chemical Properties

It gives all the general reactions given by -OR group but 2° OR is less reactive as compared to 1° .

Some of its specific reactions are :



Glyceryl trinitrate or tri nitroglycerine, when adsorbed on Kieselguhr is known as dynamite. Mixture of TNG and cellulose trinitrate is called blasting gelatin.



Cone HNO₃ gives II; dil HNO₃ gives II and III; $Bi(NO_3)_3$ or NaNO₃ gives VI; Fenton's reagent or NaOBr or Br₂ water in Na₂CO₃ gives a mixture of I and IV.

Solid KMnO₄ oxidises glycerol to VII and CO₂ and H₂O.

With HIO₄ (periodic acid). glycerol gives HCOOH and HCHO.

Ethers

Ethers are the organic compounds in which two alkyl or aryl groups are attached to a divalent oxygen. known as ethereal oxygen. These are represented by the general formula R–O-R" where R may be alkyl or aryl groups. e.g.,

	CH ₃ -O-CH ₃ , dimethyl ether	C ₂ H ₅ -O-C ₂ H ₅ diethyl ether
Mixed ethers	CH3-O-C2H5,	CH ₃ -O-C ₃ H ₇
	ethyl methyl ether	methyl n-propyl ether

These are the functional isomers of alcohols. These also exhibit chain isomerism and metamerism.

Nomenclature of Ethers

In the IUPAC system, ethers are regarded as 'alkoxy alkanes' in which the ethereal oxygen is taken along with smaller alkyl group while the bigger alkyl group is regarded as a part of the alkane.

Preparation of Ethers



(ii) **Williamson's synthesis** Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.



Physical Properties of Ethers

Ethers are polar but insoluble inH20 and have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.

Structure of Ether

The hybridisation of 0 atom in ethers is sp^3 (tetrahedral) and its shape is V-shape.



Chemical Reactions of Ether

(i) Reaction with HX



Ethers with two different alkyl groups are also cleaved in the same manner and results in the formation of a primary halide (or smaller and less complex alkyl halide) by S_N^2 mechanism.

R-O-R' + HX \rightarrow RX + R'OR

The order of reactivity of hydrogen halides is as follows

HI > HBr > HCl

In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiary halide by S_N^1 mechanism.



(ii) Halogenation



(v) Electrophilic 8ublititutioD reactions In ethers,-OR is ortho, para directing group and activate. the aromatic ring towards electrophilic substitution reaction.



Ethyl phenyl ester $C_6H_5OC_2H_5$ is also, known as phenetole.

Uses of Ethers

- 1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
- 2. Diethyl Ether is used as an anaesthesia in surgery .

Chemistry Notes for class 12 Chapter 12 Aldehydes, Ketones and Carboxylic Acids

In aldehydes, the carbonyl group ()C=O) is bonded to carbon and hydrogen, while in the ketones, it is bonded to two carbon atoms

Nature of Carbonyl Group

The carbon and oxygen of the carbonyl group are Sp^2 hybridised and the carbonyl double bond contains one o-bond and one π -bond.



The electronegativity of oxygen is much higher than that of the carbon, so there electron cloud is shifted towards the oxygen. Therefore, C-O bond is polar in nature.

Nomenclature

(i) **Nomenclature of aldehydes** In IUPAC system, the suffix "e" of alkane is replaced by the suffIX "al". e.g.,

Compound	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH3CHO	Acetaldehyde	Ethanal

(ii) **Nomenclature of ketones** In IUPAC system, the suffix "e" of alkane is replaced by "one". e.g.,

Compound	Common name	IUPAC name
H ₃ C · COCH ₃	Dimethyl ketone (acetone)	Propanone
H3C · COC2H5	Ethyl methyl ketone	Butanone

Preparation of Aldehydes and Ketones

(i) **By oxidation of alcohols** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.



(ii) **By dehydrogenation of alcohols** In this method, alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones.



(iii) By ozonolysis of alkenes



(iv) **By hydration of alkynes** Acetylene on hydration gives acetaldehyde and other alkynes on hydration give ketones.



(v) By heating Ca salt of acid

 $(RCOO)_2Ca \xrightarrow{\Delta} RCOR + CaCO_3$

To obtain aldehyde, calcium formate and any other Ca salt of acid are heated.

 $(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} RCHO + CaCO_2$

(vi) By decarboxylation and dehydration of aromatic acids

 $\begin{array}{c} C_{\theta}H_{5}COOH + HCOOH & \xrightarrow{MnO} & C_{\theta}H_{5}CHO + H_{2}O + CO_{2} \\ \hline C_{\theta}H_{5}COOH + HOOCH_{3} & \xrightarrow{MnO} & C_{\theta}H_{5}COCH_{3} + H_{2}O + CO_{2} \end{array}$

Preparation of Aldehydes



Formaldehyde cannot be prepared by this method as HCOCl is highly unstable.

(ii) From nitriles

 $RCN + SnCl_2 + HCl \longrightarrow RCH \Longrightarrow NH \xrightarrow{H_3O^+} RCHO$ This reaction is called **Stephen reaction**.

Alternatively, nitriles are selectively reduced by disobutylaluminium hydride, [DiBAL-H] to imines which on hydrolysis give aldehydes.

$$\frac{\text{(i) AlH(iBu)_2}}{\text{(ii) H_2O}} RCHO$$

Similarly, esters can also reduced to aldehydes with DiBAL-H.



(iv) Side chain halogenatiohn followed by hydrolysis of toluene





Preparation of Ketones

(i) From acyl chlorides

$$2R - Mg - X + CdCl_2 \longrightarrow R_2Cd + 2Mg \xrightarrow{X}_{Cl} \\ 2R' - C - Cl + R_2Cd \longrightarrow 2R' - C - R + CdCl_2 \\ 0 & 0 \\$$

(ii) From nitriles

(iii) Friedel-Crafts acylation



(iv) Oppenauer oxidation

 $\begin{array}{c} R_2 \text{CHOH} + (\text{CH}_3)_2 \text{C} = 0 \xrightarrow{[(\text{CH}_3)_3 \text{ CO}]_3 \text{ Al}} & R_2 \text{C} = 0 + (\text{CH}_3)_2 \text{CHOH} \\ \xrightarrow[\text{ketone}]{\text{ketone}} & \xrightarrow[\text{iso-propyl}]{\text{alcohol}} \end{array}$

Physical Properties of Aldehydes and Ketones

1. Methanal (HCHO) is a gas at room temperature. and its 40% aqueous solution is known as formalin. It is a reducing agent in silvering of mirrors and decolourising vat dyes.

2. Ethanal (CH_3CHO) is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.

3. The boiling point of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular mass due to high magnitude of dipole-dipole interactions.

4. Aldehydes and ketones have lower boiling point than those of alcohols of similar molecular

masses due to absence of intermolecular hydrogen bonding.

5. The lower members of aldehydes and ketones are miscible with water due to the formation of hydrogen bond with water. However, the solubility decreases with increase in length of alkyl chain.

6. Acetophenone is a hypnotic (sleep producing drug) so used as a medicine under the name hypnone.

Chemical Reactions of Aldehydes and Ketones



It is due to + I effect of alkyl groups which decreases the positive charge on carbonyl carbon and steric hinderance (The bulky alkyl group hinder the approach of nucleophile).

Addition of hydrogen cyanide

100



Addition of sodium hydrogen sulphite

$$>$$
C=O + NaHSO₃ \Rightarrow $>$ C $<$ OSO₂Na
OH
white crystalline solid

This reaction is used for the separation and purification of aldehydes and ketones. This is because the addition compound formed, is water soluble and can be converted back to the original carbonyl compound by treating with dilute mineral acid or alkali. Addition of lower alcohols



(ii) Addition of ammonia and its derivatives Reaction with ammonia



Some N-substituted Derivatives of Aldehydes and Ketones

Z	Reagent name	Carbonyl derivative	Product name
R	Amine	>C=N-R	Substituted imine (Schiff's base)
-OH	Hydroxyl amine	C=N-OH	oxime
-NH ₂	Hydrazine	C=N-NH2	Hydrazone
	Phenyl- hydrazine	>c=n_NH	Phenylhydrazone
	2,4-dinitro- phenyl hydrazine		2,4-dinitro- phenyl hydrazone
-NH-C-NH2	Semi- carbazide		Semi-carbazone

(iii) **Reduction** Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH₄) or lithium aluminium hydride [LiAlH₄].



(iv) **Oxidation** Aldehydes get easily oxidised to carboxylic acids by HNO₃, KMnO₄, K₂Cr₂O₇, etc., or even by mild oxidising agent.

$RCHO \xrightarrow{[O]} RCOOH$

Ketones are generally oxidised under vigorous conditions, *i.e.*, strong oxidising agents and at elevated temperature.



During oxidation of unsymmetrical ketones the point of cleavage is such that keto group stays preferentially with the smaller alkyl group popoff's rule).

(a) **Tollen's test** Aldehydes give bright silver mirror with Tollen's reagent (ammoniacal silver nitrate). $RCHO + 2[Ag(NH_{a})_{2}]^{+} + 3OH \longrightarrow RCOO + 2Ag \downarrow$ silver mirror $+ 2H_{2}O + 4NH_{a}$

(b) Fehling's test Fehling solution gives a reddish brown precipitate with aldehydes. (except benzaldehyde)

$$R \longrightarrow CHO + 2Cu^{3+} + 5OH \longrightarrow RCOO^{-} + Cu_{3}O \downarrow + 3H_{2}O$$

[Fehling solution is a mixture of Fehling solution A and Fehling solution B in 1: 1 ratio. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartrate which is also called, Rochelle salt.]

(c) **Benedict solution** With it, aldehydes (except benzaldehyde) also give red ppt. of CU_2O .

(d) **Schiff's reagent** It is an aqueous solution of magenta or pink coloured rosaniline hydrochloride which has been decolourised by passing SO_2 , Aldehydes give pink colour with this reagent but ketones do not.

Haloform reaction Aldehydes and ketones having at east one methyl group $[3-\alpha$ hydrogen] linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform.

$$\begin{array}{c} O \\ R - -C - CH_3 \end{array} \xrightarrow{NaOX} R - C - ONa + CHX_3 \\ [X = Cl, Br, I] \end{array}$$

This oxidation does not affect a carbon-carbon double bond, if present in the molecule.



Iodoform reaction with sodium hypoiodite is also used for the detection of CH_3 – group or $CH_3CH(OH)$ - group by producing yellow solid CHI_3 .

(v) Aldol condensation



Its further condensation gives phorone,

This reaction is exhibited by those aldehydes and ketones which have at least one a-hydrogen.

(vi) **Cross aldol condensation** Base catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called **Claisen-Schmidt condensation or Claisen reaction**.



The above reaction is called Benzoin condensation, not the cross aldol condensation.

(vii) **Cannizzaro reaction** Aldehydes which do not have any α – hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.



(viii) **Electrophilic substitution reaction** Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group shows + R effect, therefore acts as a deactivating and meta directing group.



(ix) **Baeyer- ViLLiger oxidation** With Caro's acid (H_2SO_5) or per benzoic acid ($C_6H_5CO_3H$) or peracetic acid (CH_3CO_3H) aliphatic ketones give ester.

$$R_2CO + R'CO_3H \longrightarrow RCOOR + RCOOH$$

per acid

(x) Tischenko's reaction It is a modified form of Cannizzaro reaction.

 $2CH_{3}CHO \xrightarrow{(C_{2}H_{5}O)_{3}Al} CH_{3}COOH + C_{2}H_{5}OH$ $\longrightarrow CH_{3}COOC_{2}H_{5}$ ethyl acetate

(xi) **Knoevenagel reaction** It involves condensation between active methylene group and ,carbonyl groups in the presence of base.



(xii) Schmidt reaction

$$RCHO + N_{3}H \xrightarrow{\text{Conc. H}_{2}SO_{4}} \xrightarrow{\Delta}$$

R—CN + HCONHR + N₂ alkyl cyanide N-alkyl formamide

(xiii) Refomatsky reaction



OH β-hydroxy ester

(xiv) Perkin's reaction



(xv) Wittig reaction

>C=O + PPh₃=CH₂ - \rightarrow >C=CH₂ + Ph₃P=O

(xvi) Polymerisation

 $n\text{HCHO} \longrightarrow (\text{CH}_2\text{O})_n$ paraformaldehvde

3HCHO - (HCHO)₃ meta formaldehyde or trioxane

 $3CH_3CHO \longrightarrow (CH_3CHO)_3$ paraldehyde (hypnotic, sleep producing)

4CH₃CHO DryHCl gas Or ionic H₂SO₄ (CH₃CHO)₄ metaldehyde

Carboxylic Acids

These are the compounds which have -C—OH group [carboxy] group]. The word carboxyl is a combination of two words carbonyl C = 0 and hydroxyl (-OH).

Classification

Depending upon the number of -COOH groups, they are classified as

(i) monocarboxylic acids; containing one -COOH group

(ii) dicarboxylic acids: containing two -COOH groups.

Sources of carboxylic acids

Formula	Common name	Source
HCOOH	Formic acid	Red ant (formica)
CH3COOH	Acetic acid	Vineger (acetum)
C3H7COOH	Butyric acid	Butter (butyrum)

Nomenclature

Their IUPAC names have been derived from the corresponding alkanes by replacing the letter 'li of the alkane with 'oic' and adding suffix 'acid' at the end, Thus, monocarboxylic acids are called alkanoic acids.



Methods of Preparation of Monocarboxylic Acids

(i) From primary alcohols and aldehydes

 $\begin{array}{c} RCH_{2}OH \xrightarrow{(i) Alkaline \ KMnO_{4}} \\ \hline \\ \hline \\ (ii) \ H_{3}O^{+} \end{array} \xrightarrow{(ii) H_{3}O^{+}} R-COOH \\ CH_{3}(CH_{2})_{8}CH_{2}OH \xrightarrow{CrO_{3} \cdot H_{2}SO_{4}} CH_{3}(CH_{2})_{8}COOH \\ \hline \\ decanoic \ acid \end{array}$

(ii) **From alkyl benzenes** Alkyl benzene when treated with strong oxidising agent like H_2CrO_4 (chromic acid), acidic or alkaline KMnO₄ gives benzoic acid.



(iii) **From acid derivatives** All acid derivatives like amides (RCONH₂), acid halides (RCOCl), esters (RCOOR'), acid anhydrides (RCO-O-COR) on hydrolysis give carboxylic acids. All acid derivatives break from RCO⁺.

 $\begin{array}{l} RCOZ \xrightarrow{\text{Dil. HCl}} RCOOH \\ \hline \text{or dil. NaOH} \end{array} RCOOH \\ Z = --NH_2, --X(X = Cl, Br, l), OR', RCOO-- etc. \\ \text{Ease of hydrolysis} : RCOCl > (RCO)_2O > RCOOR' > RCONH_2 \end{array}$

(iv) **From nitriles and amides** Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.



(v) **From Grignard reagents** Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid



Physical Properties of Carboxylic Acids

1. Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids.

2. The lower carboxylic acids are freely miscible with water due to the presence of intermolecular hydrogen bonding with H_2O molecules. However, the solubility in water decreases gradually due to increase in the size of alkyl group.

3. Monocarboxylic acids have higher boiling points as compared to the alcohols of comparable molecular masses due to the presence of stronger intermolecular hydrogen bonding as shown below.

hydrogen bonding in carboxylic acids hydrogen bonding in alcohols

4. Melting points of aliphatic monocarboxylic acids shows alternation or oscillation effect, i.e., the m.p. of an acid with even number of carbon atoms is higher than the next lower and next higher homologue containing odd number of carbon atoms. This is because, in case of acids with even number of carbon atoms, the terminal $-CH_3$ and -COOH groups lie on the opposite sides of the zig-zag chain. As a result, they get closely packed in the crystal lattice.

5. Glacial acetic acid is completely pure acetic acid and represents the solid state of acetic acid. Below 16.6°C temperature pure acetic acid is converted into ice like solid hence it is called glacial acetic acid.

Chemical Properties of Carboxylic Acids

Carboxylic acids do not give reactions of carbonyl groups as it enters into resonance with lone pair of O of -OH group.

(i) Acidity



Above reactions are used to detect the presence of carboxyl group Ul an organic compound.,

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



The strength of the acid is expressed in terms of the dissociation constant (K_a), also called acidity constant. A stronger acid has higher K_a but lesser p K_a value ($pK_a == -\log K_a$).

The electron releasing substituents (+1 effect) decrease the acidic strength of the carboxylic acids by destabilising the carboxylate ion.

Order of + I effect : $-H \le -CH_3 \le -C_2H_5 \le -C_3H_7$

Therefore, the order of acidic strength is

HCOOH > CH₃COOH > C₂H₅COOH > C₃H₇COOH

The electron withdrawing substituents (-1 effect) such as halogen atoms (X), nitro (NO₂) group increase the acidic strength by decreasing the magnitude of the negative charge on the carboxylate anion and thus stabilising it. The release of H^+ ion becomes easy.

Acidic strength order



This is because -1 effect decreases in the order : F > C1 > Br > I.



This is because – I effect decreases with distance.

Per acetic acid (CH₃COOO-H) is a weaker acid than acetic acid as acetate ion is stabilised by resonance.

Acidic strength of aromatic acids The parent member of the family benzoic acid which is a weaker acid ($K_a = 6.3 \times 10^{-5}$) than acid ($K_a = 17.7 \times 10^{-5}$) but stronger than acetic acid.

Some order of acidity are



(b) Similarly, K_a values of methyl substituted (toluic acids) at 298 K are as follows:



From the K_a values, it is evident that with the exception of o-isomer, both p and m-toluic acids are weaker acids than benzoic acid whereas the three isomeric nitro benzoic acids are stronger acids than benzoic acid.

(ii) Reactions involving cleavage of C-O-H bond

(a) Formation of anhydride



(b) Esterification

RCOOH + R'OH $\rightleftharpoons^{H^+} R$ COOR' + H₂O

Mechanism



(iii) Chemical reactions involving – COOH group

(a) Reduction

 $\begin{array}{c} RCOOH \xrightarrow{\text{(i) LiAlH}_4/\text{ether}} & R \longrightarrow CH_2 \longrightarrow OH \\ \hline \text{or } B_2H_6(\text{ii) } H_3O^+ & R \longrightarrow CH_2 \longrightarrow OH \\ \hline \text{(b) Decarboxylation} \\ RCOONa \xrightarrow{\text{NaOH, } C_{BO} (\text{Ratio } 3:1)} & R \longrightarrow H + \text{Na}_2CO_3 \end{array}$

(iv) Substitution reactions in the hydrocarbon part α -hydrogen atoms in carboxylic acids are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction

 $R - CH_2 - COOH \xrightarrow{(i) X_2/\text{Red phosphorus}} R - CH - COOH$

The reaction is known as Hell-Volhard-Zelinsky reaction.

(v) **Arndt-Eistert reaction** It is method of converting lower carboxylic acids to their higher homologues



(vi) **Reducing property** Among carboxylic acids, formic acid is the only acid that acts as reducing agent. It reduces, acidified KMnO₄ to MnSO₄, HgCl₂ to Hg, Tollen's reagent to silver mirror and Fehling's solution to red ppt. and itself gets oxidised to CO_2 and H_2O .

 $HCOOH + HgCl_2 \rightarrow Hg + 2HCI + CO_2$

(vii) **Electrophilic substitution reactions of aromatic acids** -COOH group shows -R effect, therefore, acts as a deactivating and meta-directing group. Carboxylic acids do not undergo Friedel-Craft's reaction because the carboxylic group IS deactivating and the catalyst AlCl₃ (anhy.) gets bonded to the carboxyl group.



Uses

- 1. Formic acid is used in leather tanning, textile dyeing and finishing.
- 2. Acetic acid is used in the manufacture of rayon and in plastics, in in rubber and silk industries in explain and in vineser (a = 10% solution of eastic acid)
- industries, in cooking and in vinegar (a 8-10% solution of acetic acid).
- 3. Benzoic acid and its salts are used as urinary antiseptics.
- 4. Formic acid can act as a reducing agent.

Derivatives of Carboxylic acids

These are obtained when -OH group of carboxylic acids is replaced by Cl, NH₂, OR' and OCOR and are called respectively acid chloride, acid amide, ester and acid anhydride.



Properties of Acid Derivatives

1. Chemical reactions of acid halides



2. Chemical reactions of acid amides



3. Chemical reactions of ester

$$\begin{array}{ccc} & \overset{\text{NaOH}}{\longrightarrow} & R\text{COONa} + R'\text{OH} \text{ (saponification)} \\ & & \overset{\text{NH}_3}{\longrightarrow} & R\text{CONH}_2 + R'\text{OH} \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & &$$

4. Chemical reactions of anhydrides

$$(RCO)_{2}O \xrightarrow{R'OH} RCOOR' + RCOOH$$

$$C_{6}H_{6}/AlCl_{3} \xrightarrow{C_{6}H_{5}COR + RCOOH}$$

$$C_{2}H_{6}NH_{2} \xrightarrow{KCONC_{2}H_{5} + RCOOH}$$

Chemistry Notes for class 12 Chapter 13 Amines

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of NH 3 molecule by alkyl/aryl group(s).



In the IUPAC system, the amines are regarded as alkanamines, e.g.,



Structure

The nitrogen atom in amine is spa-hybridised. The three hybrid orbitals are involved in bond formation and one hybrid atomic orbital contains the lone pair of electrons, giving the pyramidal geometry of amines.



Methods of Preparation of Amines

(i) Reduction of nitro compounds

$$R \longrightarrow R_2 \longrightarrow R \longrightarrow R_2 + 2H_2O$$

Reduction can takes place by Sn/HCl, Ni/H₂, Zn/NaOH, Pd/H₂.



The reduction of nitroalkane or nitrobenzene in neutral medium gives hydroxyl amines.

(ii) Ammonolysis of alkyl halides



Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

However, primary amine is obtained as a major product by taking large excess of NH₃.

Order of reactivity of halides 'with amines is RI > RBr > RCI.

Aromatic amines could not be prepared since aryl halides are much less reactive towards nucleophilic substitution reactions.

(iii) Reduction of nitriles or cyanides

$$R - C = N \xrightarrow{\text{Ni/H}_2} R - CH_2 NH_2$$

(iv) Schmidt reaction

 $\begin{array}{ccc} R\text{COOH} + & \text{N}_3\text{H} & \xrightarrow{\text{Conc H}_2\text{SO}_4} & R - \text{NH}_2 + \text{N}_2 + \text{CO}_2 \\ & \text{alkylamine} \end{array}$

It is a modification of Curtius degradation.

(v) Reduction of amides



(vi) Gabriel's phthalimide reaction



It only produces 1 0 amines. This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

(viii) Hofmann bromamide degradation reaction



In Hofmann degradation reaction, the amine formed has one carbon less than the parent amide. To obtain primary amine with same number of carbon atoms from primary amide, reduction is done with LiAlH₄/ether.

Physical Properties of Amines

- 1. The lower aliphatic amines are gases with fishy smell.
- 2. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
- 3. Lower aliphatic amines are water suluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase in hydrophobic alkyl group.
- 4. Boiling points order primary > secondary > tertiary
5. Tertiary amines does not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

Basic Strength of Amines

Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom.

More the K_b (dissociation constant of base), higher is the basicity of amines.

Lesser the pK_b higher is the basicity of amines.

Aliphatic amines (CH₃NH₂) are stronger bases than NH₃ due to the electron releasing +/ effect of the alkyl group.

Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows

 $(C_2H_5NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

 $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Aromatic amines are weaker bases than aliphatic amlnes and NH_3 , due to the fact that the electron pair on the nitrogen atom is involved in resonance with the π -electron pairs of the ring.

Electron releasing groups (e.g., $-CH_3$, $-OCH_3$, $-NH_2$ etc.) increase the basic strength of aromatic amines while electron withdrawing groups (like $-NO_2$, -X, -CN etc.) tend to decrease the same.

o-substituted aromaticamines are usually weaker bases than aniline irrespective of the nature of substituent whether electron releasing or electron withdrawing. This is called ortho effect and is probably due to sterk and electronic factors.

chemical Properties of Amines

(i) Alkylation All the three types of amines react with alkyl halides to form quaternary ammonium salt as the final product provided alkyl halide is present in excess.

$$\begin{array}{cccc} C_2H_5NH_2 &+ C_2H_5Br & \xrightarrow{-HBr} & (C_2H_5)_2NH & \xrightarrow{C_2H_5Br} & (C_2H_5)_3N \\ & & \downarrow C_2H_5Br \\ & & \downarrow C_2H_5Br \\ & & (C_2H_5)_4NBr \end{array}$$

Aromatic amines also undergo alkylation as given below.



(iii) Benzoylation

$$CH_3NH_2 + C_6H_5COCI \longrightarrow CH_3NHCOC_6H_5 + HC1$$

Benzoylation of aniline is known as Schotten Baumann reaction.

(ivii) Carbylamine reaction [only by 1° amines]

$$\begin{array}{ccc} R & \longrightarrow & \text{Heat} \\ R & \longrightarrow & \text{Heat} \\ \text{isocyanide} \\ \text{(a bad smelling compound)} \end{array} \xrightarrow{\text{Heat}} R & \longrightarrow & \text{Heat} \\ & \text{Heat} \\ \text{isocyanide} \\ \text{(a bad smelling compound)} \end{array}$$

**

MIC or methyl isocyanate gas ($CH_3 - N = C = O$) was responsible for Bhopal gas tragedy in December 1984.

(v) Reaction with nitrous acid

 $RNH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [RN_2^+Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

C₆H₅-NH₂ $\xrightarrow{\text{NaNO}_2 + 2\text{HCl}}_{273-278 \text{ K}}$ C₆H₅N⁺₂Cl⁻ + NaCl + 2H₂O benzene diazonium chloride But secondary and _tertiary amines react with nitrous acid in different manner.

Methyl amine give dimethyl ether with HNO₂.

(vi) Reaction with aryl sulphonyl chloride [Hinsberg reagent] The reaction of benzenesulphonyl chloride with primary amine yield N-ethyl benzenesulphonyl amide.



Tertiary amines does not react with benzenesulphonyl chloride.

(vii) Reaction with aldehydes Schiff base is obtained.

 $C_{6}H_{5}NH_{2} + \underbrace{OHCC_{6}H_{5}}_{\text{benzaldehyde}} \xrightarrow{\begin{array}{c} ZnCl_{2} \\ \Delta \\ -H_{2}O \end{array}} C_{6}H_{5}N = CHC_{6}H_{5}$ $\underbrace{C_{6}H_{5}N = CHC_{6}H_{5}}_{\text{benzylidene aniline}}$ (Schiff base)

(viii) Electrophilic substitution reactions Aniline is ortho and para directing towards electrophilic substitution reaction due to high electron density at ortho and para-positions.



To prepare monosubstituted derivative, activating effect of $-NH_2$ group must be controlled. It can be done by protecting the $-NH_2$ group by acetylation with acetic anhydride.



(b) Nitration Direct nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by acetylation.



In strongly acidic medium, aniline is protonated as anilinium ion which is meta directing so it gives meta product also.



(d) Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence. behave like a strong deactivating group for further chemical reaction.

(ix) Oxidation Use of diffrent oxidising agents gives difTerent products.

e.g.,

Oxidising agent	Product	
Accidified KMnO ₄ (or Na ₂ Cr ₂ O ₇ + CuSO ₄ + dil acid)	Aniline black (a dye)	
Chromic acid (Na2Cr207 + Conc H2SO4)	p-benzoquinone	
Caro's acid (H ₂ SO ₅) nitrobenzene and nitrosobenzene		
Conc. nitric acid	decomposes	

Separation of Mixture of Amines (1°, 2° and 3°)

(a) Fractional distillation This method Is based on the boiling points of amines and is used satIsfactorily in Industry.

(b) Hofmann's methoOd Diethyloxalate is called Hofmann's reagent with which mixture of amines is treated.

- 1° amine forms solid dialkyl oxamide (CONHR)₂
- 2° amine forms liquid dialkyl oxamlc ester(CONR₂-COOC₂H₅)
- 3° amlnes do not react

(c) Hlnsberg's method see.chemkal reactions.

Benzene Diazonium Chloride (C₆H₅N₂⁺;Cl⁻)

Preparation (Diazotisation reaction)

$\begin{array}{c} C_{\theta}H_{5}NH_{2} + NaNO_{2} + 2HCl \xrightarrow{273 \cdot 278 \text{ K}} C_{\theta}H_{5}N \Longrightarrow N \longrightarrow Cl \\ + NaCl + 2H_{2}O \end{array}$

The excess acid in diazotisation reaction is necessary to maintain proper acidic medium for the reaction and to prevent combination of diazonium salt formed with the undiazotised amine.

Diazonium salts are prepared and used in aqueous solutions because in solid state, they explode.

Properties

It is a colourless crystalline solid, soluble in water. It has tendency to explode when dry.

Stability of Arenediazonium salts

It is relatively more stable than the alkyldiazonium salt. The arenediazonium ion is resonance stabilised as is indicated by the following resonating structures:



Various resonating structures of arenediazonium ion

Chemical Reactions





Alkyl Cyanides'

These compound have formula RCN. These are the derivatives of RCN.

According to IUPAC system, cyanides are named as 'alkane nitrile', e.g.,

C₃H₇CN , C₆H₅CN butanenitrile benzenenitrile **Methods of Preparation**

(i) From alkyl halides $RX + KCN(alc) \xrightarrow{100^{\circ}C} RCN + RNC$ (major) (ii) From acid amides $RCONH_2 \xrightarrow{P_2O_5, \Delta} RC \equiv N$

Physical properties

- 1. These are neutral compound with pleasent odour, similar to bitter almonds.
- 2. These are soluble in water as well as organic solvents.
- 3. These are poisonous but less than HCN.

Chemical Properties



Alkyl iscoyanides (RNC)

Accordinlg to IUPAC system, these are named as 'alkane isonitrile'

e.g., CH₃NC methyl isonitrile

C₆H₅NC benzene isonitrile

Methods of Preparation

(a) From alkyl halides

$$R \longrightarrow X + \text{AgCN} \xrightarrow{C_2H_5OH} RNC + RCN$$

(b) Carbylamine reaction

$$RNH_2 + CHCl_3 + 3KOH(alc) \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$$

(c) From N-alkyl formamide

$$R - NH - C - H \xrightarrow{POCl_3} R - N \stackrel{POCl_3}{\longrightarrow} C + H_2O$$

Physical Properties

- 1. These are colourless unpleasent smelling liquids.
- 2. These are soluble in organic solvents but insoluble in water.

Chemical Properties

(i) Hydrolysis

$$R \longrightarrow R + 2H_2O \xrightarrow{H^+} RNH_2 + HOOOH$$

(ii) Reduction

$$RN \stackrel{i}{=} C + 4[H] \xrightarrow[]{Na/C_2H_5OH}_{or Ni or Pt} \stackrel{RNHCH_3}{\xrightarrow[]{2^{\circ} amine}}$$

(iii) Addition reaction Due to the presence of unshared pair of electrons on C atom, alkyl isocyanides give addition reaction.

$$RNC + S \longrightarrow RNCS$$
$$RNC + HgO \longrightarrow RNCO + Hg$$
$$RNC + O_3 \longrightarrow RNCO$$

(iv) Isomerisation At 250°C, it isomerises to nitrile.

$$RNC \xrightarrow{\Delta} RCN$$

Nitro Compounds

These are obtained by replacing one H of hydrocarbon by -NO₂ group.

These are named according to IUPAC system as 'nitro alkane'.

Methods of Preparation

(i) From alkyl halides

$$RX + AgNO_2 \xrightarrow{\Delta} RNO_2 + AgX$$

(ii) Nitration Nitrating mixture is conc HNO₃ + conc H₂SO₄.



Physical Properties

- 1. These are colourless pleasent smelling liquids.
- 2. Their boiling point are much higher than isomeric alkyl nitriles.
- 3. These are less soluble in water but readily soluble in organic solvents.

Chemical Properties

(i) Reduction With Sn/HCl or catalytic hydrogenation, nitroalkanes are reduced to amines.

$$RNO_2 + 6[H] \xrightarrow{Sn/HCl} R - NH_2 + 2H_2O$$

If neutral reducing agent like Zn dust + NH₄Cl is used, hydroxylamines are obtained as major product.

$$RNO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} R - NHOH + H_2O$$

N-alkylhydroxylamine

In the presence of (NH4)2S or Na2S, selective reduction takes place.



Nitrobenzene gives different prociucts with different reagents and in different mediums.

Medium	Reagent	Product	
Acid Neutral	Sn/HCl Zn/NH4Cl	aniline	
	Na ₃ AsÔ ₂ /NaOH	azoxybenzene ($C_6H_5N = NC_6H_5$)	
Alkaline	Zn/NaOH, CH ₃ OH	azobenzene	
Metallic hydride Electrolytic	Zn/NaOH, C ₂ H ₅ OH LiAIH ₄ dil H ₂ SO ₄	hydrazobenzene aniline p-aminophenol	

(ii) Action of HNO2

32; 2

1° nitroalkane gives nitrolic acid which gives red colour with NaOH.

$$RCH_2NH_2 \xrightarrow{HNO_2} RC(NO_2) = NOH$$

nitrolic acid

$$\xrightarrow{\text{NaOH}} RC(NO_2) = NONa$$
(red)

2° nitroalkanes give pseudonitrol with HNO2.

$$\begin{array}{ccc} R_2 \text{CH(NO}_2) & \xrightarrow{\text{HNO}_2} & R_2 \text{C} & \text{NO} & \xrightarrow{\text{NaOH}} & \text{Blue} \\ & & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & &$$

3° nitroalkanes does not react with HNO2

(iii) Nef carbonyl synthesis Na or K salt of 1° or 2° nitroalkanes give carbonyl compounds on acidification with 50% H₂SO₄ at room temperature. This reaction is called Nef carbonyl synthesis.



(iv) Electrophifie substitution On nitration, nitrobenzene gives m-dinitrobenzene (as -NO₂ is a m-directing group and strongly deactivating).



It does not give Friedel-Craft's alkylation.

(v) Nucleophilic substitution reaction $-NO_2$ group activates the ring towards nucleophilic substitution.



Chemistry Notes for class 12 Chapter 14 Biomolecules

Biomolecules are the organic compounds which form the basis of life, i.e., they build up the living system and responsible for their growth and maintenance.

The sequence that relates biomolecules to living organism is

Biomolecules \rightarrow Organelles \rightarrow Cells \rightarrow Tissues \rightarrow Organs \rightarrow Living organism.

Carbohydrates

Optically active polyhydroxy aldehydes (aldcses) or ketones (ketoses) or compounds which on hydrolysis give these units are known as carbohydrates. They are also called saccharides

(Latin Saccharum = sugar) due to sweet taste of simpler members.

Depending upon their behaviour towards hydrolysis, carbohydrates can be of following three types

Monosaccharides

These cannot be hydrolysed to simpler molecules and further subdivided into tetroses, pentoses or hexoses depending upon the number of carbon atoms. These are also called homopolysaccharides.

- Aldotetroses Erythrose, Threose
- Aldopentoses Xylose, Ribose,
- Aldohexoses Glucose, Galactose,
- Ketohexoses Fructose

All naturally occurring monosaccharides belong to D-series.

killiani synthesis is used to convert an aldose into next higher aldose.

Oligosaccharides

(Greek oligos = few). On hydrolysis, they generally give two to nine monosaccharides (same or different) and are further classified as disaccharides, e.g., sucrose, maltose, lactose, trisaccharides and so on. $C_{12}H_{22}O_{11}$ is a disaccharide because it gives two monosaccharides.

 $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6 H_{12} O_6 + C_6 H_{12} O_6$ fructose sucrose

The bond formed between two monosaccharides is called a glycosidic bond and normally it is (1, 4) bond.

Sucrose is most abundant in plants and known as cane sugar or table sugar or invert sugar as equimolar mixture of glucose and fructose is obtained by hydrolysis of sucrose.



Trisaccharides Raffinose (C₁₈H₃₂O₁₆)

$$(C_{18}H_{32}O_{16}) + 2H_2O \xrightarrow{H^+} Glucose + Fructose + Galactose$$

Polysaccharides

These are polymers of monosaccharides. Examples are starch, cellulose, glycogen, etc.

1. Starch, $(C_6H_{10}O_5)_N$

It is a polymer of a-glucose and a major reserve food in plants. It turns blue with iodine. It is a mixture of two components:

- 1. Amylose (20%), an unbranched water soluble polymer.
- 2. Amylopectin (80%), a branched water insoluble polymer.

Sources of starch are potatoes, wheat, rice, maize, etc.



2. Cellulose, $(C_6H_{10}O_5)_n$

It is the most abundant and structural, polysaccharide of plants. It is important food source of some animals It is a polymer of D (+) β -glucose.

The chief sources of cellulose are wood (Contains 50% cellulose rest being lignin, resins, etc) and cotton (contains 90% cellulose rest being fats and waxes).



Several materials are obtained from cellulose:

- 1. **Mercerised cotton** Cellulose treated with cone. sodium hydroxide solution acquire silky lustre. It is called mercerissd cotton.
- 2. **Gun cotton** It is completely nitrated cellulose (cellulose nitrate), highly explosive in nature and is used in the manufacture of smokeless gun powder, called blasting gelatin.
- 3. Cellulose acetate It is used for making acetate rayon and motion picture films.
- 4. **Cellulosexanthate** It is obtained by treating cellulose with sodium hydroxide and carbon disulphide and is the basic material for VISCOSE rayon.

Oligosaccharides and heteropolysaccharides are also called heteropolysaccharides.

Reducing and Non-reducing sugars

Based upon reducing and non-reducing properties, carbohydrates are classified as reducing and non-reducing sugars. Carbohydrates reducing Fehling reagent or Tollen's reagent are termed as reducing carbohydrates. e.g., All monosaccharides and disaccharides (except sucrose). But carbohydrates which do not reduce such reagents are known as non-reducing carbohydrates. e.g., sucrose and polysaccharides.

Sugars and Non-sugars

On the basis of their, taste, carbohydrates are classified as sugars and non-sugars. The monosaccharides and oligosaccharides having sweet taste are collectively known as sugars. Polysaccharides which are insoluble in water and not sweet in taste, are non-sugars.

Glucose

Dextrose, grape sugar, corn sugar, blood sugar ($C_6H_{12}O_6$).

Manufacture

By hydrolysis of starch with hot dil mineral acids and by hydrolysis of sucrose.

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Extra glucose is stored in liver as glycogen.

α and β glucose

In intermolecular hemiacetal formation (cyclic structure), -CHO is converted into -CHOH which can have two configurations as shown below.



Glucose having (i) configuration about C_1 is the α -glucose and having (ii) configuration about C_1 is β -glucose.

The carbon C_1 is known as anomeric carbon and these compounds are called anomers. Both the forms are optically active. ex-D-glucosehas specific rotation +111.5° and β -D-glucose has specific rotation + 19.5°.

Mutarotation

When either of the two forms of glucose is dissolved in water, there is a spontaneous change in specific rotation till the equilibrium value of $+52.5^{\circ}$. This is known as mutarotation.

 α -D(+) Glucose \rightleftharpoons Equilibrium mixture \rightleftharpoons β -D-(+) Glucose +111.5° + 52.5° + 19.5°

Properties of glucose

Glucose has one aldehyde group, one primary hydroxyl (-CH₂OH) and four secondary hydroxyl (-CHOH) groups and gives the following reactions:

(i) Glucose on acetylation with acetic anhydride gives a pentaacetate confirming the presence of five hydroxyl groups in glucose.



(ii) Glucose reacts with hydroxylamine to give monoxime and adds with a molecule of hydrogen cyanide to give a cyanohydrin.

CH2OH(CHOH)4C	HO HON	\rightarrow CH ₂ OH(CHOH) ₄ CH $<$
glucose	1	glucose cyanohydrin CN
	NH ₂ OH	CH OH(CHOH) CH-NOH
£31	-H ₂ O	glucose oxime

These reactions confirm the presence of a carbonyl group in glucose.

(iii) Glucose reduces ammoniacal silver nitrate solution (Tollen's reagent) to metallic silver and also Fehling'S solution or Benedict solution to reddish brown cuprous oxide (Cu_2O) and itself gets oxidised to gluconic acid. This confirms the presence of an aldehydic group in glucose.

(iv) With mild oxidising agent like bromine water, glucose is oxidised to gluconic acid. Glucose on oxidation with nitric acid gives saccharic acid.



gluconic acid

(v) Glucose on prolonged heating with HI forms n-hexane, suggesting that all the 6 carbon atoms in glucose are linked linearly.

HOCH₂—(CHOH)₄—CHO
$$\xrightarrow{\text{HI}, \Delta}$$

H₃C—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂

However, with Na/Hg and water, glucose is reduced to sorbito HOH₂C(CHOH)₄CH₂OH.

(vi) D-glucose reacts with three molecules of phenyl hydrazine to give osazone (glucosazone).



(vii) Glucose on reaction with methyl alcohol in the presence of dry HCl(g) forms α and β -methyl glycosides. The reaction occurs only at the OH of hemiacetylic carbon.



Cyclic structure of glucose Given by Haworth and Hirst.



Glucose is sometimes illustrated as a chair form :



Fructose Fruit Sugar (C₆H₁₂O₆)

Manufacture

By hydrolysis of inulin.

$$(C_{6}H_{16}O_{5})_{n} + nH_{2}O \xrightarrow{H^{+}} nC_{6}H_{12}O_{6}$$

inulin fructose

Structure

Fructose has furanose structure, *i.e.*, ring structure consisting of four C atoms and one O atom.



α and β-fructose

The two forms have different configuration about C₂.

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Fructose does not reduce Br2 water.

Epimers

Monosaccharides differing in configuration at a carbon other than anomeric carbon are called epimers, e.g., glucose and galactose differ in configuration at C_4 , hence called epimers.

Osazones

Monosaccharides and reducing disaccharides react with excess of phenyl hydrazine to form crystalline substances of the structure



It is known as osazones glucose and fructose give same osazone.

Molisch Test for Carbohydrates

In aqueous solution of compound add solution of α -naphthol in alcohol and then cone. H₂SO₄ along the walls of the test tube. Purple coloured ring is obtained at the junction.

Relati	ve S	weeter	less of Some Sug	ars _
Cane sugar is assur sugars is	ned to l	nave a sweet	teness of 10. The relative sweet	eness of othe
Lactose	:	1.6	Invert sugar : 12.6	
Fructose	:	17.3	Maltose : 3.2	
Saccharin	:	300 (an artificial sweetener)		* 3
Glucose		74		16

Amino Acids

The compounds containing amino group (-NH₂) and carboxylic group (-COOH) are called amino acids.



R = H, alkyl or aryl group. Except glycine (H₂N.CH₂COOH), others are optically active in nature.

Classification of Amino Acids

- (a) α , β , γ -amino acids Depending upon the position of $-NH_2$ wrt -COOH group.
- (b) Neutral Having one ----NH₂ and one ----COOH, e.g., NH₂ · CH₂ · COOH (glycine).
- (c) Acidic Having one -NH2 and two -COOH, e.g., NH2

(d) **Basic** Having two or more $-NH_2$ and one -COOH, e.g., NH_2 | $H_2N(CH_2)_4-CH-COOH$ (lysine).

Essential and Non-essential Amino Acids

Human body can synthesise ten amino acids, called non-essential amino acids. The remaining ten amino acids required for protein synthesis are not synthesised by body and are called essential amino acids. They are

- 1. Phenylalanine
- 2. Histidine
- 3. Tryptophan
- 4. Valine
- 5. Methionine
- 6. Threonine
- 7. Arginine
- 8. Leucine

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9. Isoleucine 10.Lysine

Nomenclature

They are known by their common names and abbreviated by first three letters of their common names e.g., glycine as 'gly' and alanine a as 'ala'.



Naturally occurring α-amino acids are L-amino acids. D-amino acids occur in some antibiotics and bacterial cell walls.



Peptides

Peptides are condensation products of two or more amino acids.



Two molecules of different amino acids can form two dipeptides. Three molecules of different amino acids can give six tripeptides.

Dipeptide has only one peptide bond, tripeptide has two peptide bonds and so on. Thus, a polypeptide made up of n-amino acids has (n - 1) peptide bonds.

Polypeptides

Condensation Products of many amino acids ('In P xiucts of many amino acids (≈ 10000) is known as polypeptide and those polypeptides which have molecular mass above than 10000 are called proteins.

Proteins

They are linear polymers of a-amino acids.

Structure of Proteins

(a) Primary structure

It simply reveals the sequence of amino acids.

(b) Secondary structure α -helix structure maintained by hydrogen bonds or β -pleated sheet structure when R is small group.

(c) **Tertiary structure** The folding and superimposition of polypeptide chains forms a compact globular shape, termed as tertiary structure. It is stabilised by covalent, ionic, hydrogen and disulphide bonds.

The precise arrangement constitutes the quaternary structure.

Classification on the Basis of Hydrolysis Products

(i) Simple These yield only a-amino acids upon hydrolysis.

e.g., albumin.

(ii) Conjugated proteins These yield α -amino acids and non-protein part, called prosthetic group.

ProteinProsthetic groupNucleoproteinsNucleic acidPhospho proteinsPhosphoric acidGlycoproteinsCarbohydratesMetalioproteinsMetals

Lipoproteins Lipids

(iii) **Derived proteins** These are obtained by partial hydrolysis of simple or conjugated proteins.

 $Proteins \rightarrow Proteoses \rightarrow Peptones \rightarrow Polypeptides$

Classification on the Basis Functions

- 1. Structural proteins Fibrous proteins
- 2. Enzymes Serve as biological catalyst e.g., pepsin, trypsin etc.
- 3. Hormones Insulin
- 4. Contractile proteins Found in muscles, e.g., myosin, actin.
- 5. Antibodies Gamma globulins present in blood.
- 6. Blood protein Albumms, haemoglobin and fibrinogen.

Haemoglobin is a globular protein. Its prosthetic group is heme. It Contains 574 amino acid units distributed in four polypeptide chains.

Two chains containing 141 amino acid residues each are called α -chains and the two chains containing 146 amino acid residues are called β -chains.

Sickle cell anaemia is caused by defective haemoglobin obtained by replacing only one amino acid, i.e., glutamic acid by valine.

Denaturation of Proteins

The process that changes the three dimensional structure of native proteins is called denaturation of proteins. It can be caused by Change in pH, addition of electrolyte, heating or addition of solvent like water, alcohol or acetone.

Tests of Proteins

(i) Biuret Test

Protein solution + NaOH + dil. CuSO₄ \rightarrow pink or violet colour.

(ii) Millon's Test

Protein solution + Millon's reagent \rightarrow pink colour

Millon's reagent is solution of mercuric nitrate and nitrite in nitric acid containing traces of nitrous acid.

(iii) Iodine reaction

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Protein solution + iodine in potassium iodide solution \rightarrow yellow colour.

(iv)Xanthoprotic test

Protein solution + conc. $HNO_3 \rightarrow yellow \ colour \xrightarrow{NaOH} orange colour.$

Enzymes

Enzymes constitute a group of complex proteinoid compounds, produced by living organisms which catalyse the chlemical reaction.

Non-proteinous components enhance the activity of certain enzymes and are known as coenzymes. These include metal ions like Mn^{2+} , Mg^{2+} , K^+ , Na^+ , Zn^{2+} , Co^{2+} etc., heterocyclic ring systems (pyrrole, purine, pyridine, etc.), a sugar residue, phosphoric acid residue of vitamins like thiamine, riboflavin etc.

Endoenzyme acts in the same cell in which it is synthesised, while exo-enzyme acts outside the cell in which it is synthesised.

Nomenclature

They are usually named by adding the suffix 'ase' to the root name of the substrate e.g., urease, maltase, diastase, invertase, etc.

Oxidative Enzymes

They catalyse oxidation-reduction reaction and are mostly conjugated proteins.

Some Common Enzyme

Name	Substrate	Products
Urease	Urea	$CO{<\!\!sub\!\!>}2{<\!\!/sub\!\!>}+NH{<\!\!sub\!\!>}3{<\!\!/sub\!\!>}$
Maltase	Maltose	Glucose
Invertase	Sucrose	Glucose + fructose
Amylase	Starch	Maltose
Trypsin	Proteins	Amino acids
Ascorbic acid oxidase	Ascorbic acid	Dehydroascorbic acid

Characteristic Features of Enzymes

- 1. Rate of reaction They increase the rate of reaction up to 10^6 to 10^7 times.
- 2. **Specific nature** Urease catalyse the hydrolysis of urea and not methyl urea, so these are specific in nature.

- 3. **Optimum temperature** It is about 20-30°C.
- 4. **pH of medium** It is about 7 but for pepsin, it is 1.8.2.2 and for trypsin, it is 7.5-8.3.
- 5. Concentration Dilute solutions are more effective.
- 6. Amount of enzyme Very small amount can accelerate the reaction.
- 7. **Enzyme inhibitors** These compounds inhibit the enzyme action. With the help of such compounds, the reaction can be controlled.

Mechanism of Enzyme Action

 $Enzyme + Substrate \rightarrow [Enzyme substrate] \rightarrow Product + Enzyme Activated complex$

Applications of Enzymes

(i) **Treatment of diseases** The congenital disease phenyl ketonurie caused by phenylalanine hyroxylase can be cured by diet of low phenylalanine content. Enzyme streptokinase is used for blood clotting to prevent heart disease.

(ii) In industry Tanning of leather, fermentation process etc.

Nucleic Acids

Important Terms of Nucleic Acids

1. Nucleotldes

Nucleotides consist of 5-carbon sugar + nitrogenous base + 1, 3-phosphate groups.

2. Pentose sugar

It is either ribose or deoxy ribose (not having oxygen at C_2).

3. Nitrogenous base

Derived from purines having two rings in their structure e.g., Adenine (A) and Guanine (G) and derived from pyrimidines having one ring in their structure e.g.,

Thymine (T), Uracil (U) and Cytosine (C).

Two H-bonds are present between A and T (A = T) while three H-bonds are present between C and G (C \equiv G).

4. Ribonucleotide

Phosphate unit + Ribose + one base unit from A, G, C, or U.

5. Deoxyrlbo nucleotide

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Phosphate unit + Deoxyribose + one base from A, G, C or T.

6. Nucleoside

Ribose-/deoxyribose + one base unit from A, G, C, Tor U.

DNA and RNA

Nucleic acid is polynucleotide, present in the living cells or bacterial cells having no nucleus and in viruses having no cells.

(i) DNA Deoxy ribonucleic acid.

 $DNA + H_{2O \rightarrow Phosphoric acid + deoxyribose + A, G, C, T$

(ii) **RNA** Ribonucleic acid

 $RNA + H_{2O \rightarrow Phosphoric acid + Ribose + A, G, C, U}$

Structure of DNA

It consists of two polynucleotide chains, each chain form a right handed helical spiral with ten bases in one turn of the spiral. The two chains coil to double helix and run in opposite direction. These are held together by hydrogen bonding.

Structure of RNA

It is usually a single strand of ribonucleotides and take up right handed helical conformation. Up to 12000 nucleotides constitute an RNA.

It can base pair with complementary strands of DNA or RNA according to standard base pairing rules-G pairs with C, A pairs with U or T. The paired strands in RNA-RNA or RNA-DNA are anti parallel as in DNA.

In both DNA and RNA, heterocyclic base and phosphate ester linkages are at C_1 and C_5 ' respectively of the sugar molecule.



Types of RNA

- 1. Messanger RNA (m-RNA) It is produced in the nucleus and carries information for the synthesis of proteins.
- 2. Transfer RNA (Soluble or Adoptive RNA) (s-RNA, t-RNA) It is found in cytoplasm. Its function-is to collect amino acids from cytoplasm for protein synthesis.

Functions of Nucleic Acids

- 1. Direct the synthesis of proteins.
- 2. Transfer the genetic information (hereditary characters).

Replication

It is a process in which a molecule of DNA can duplicate.

Template It means pattern. In the process of replication of DNA, the parent strand serves as template.

Gene The portion of DNA carrying information about a specific protein is Called gene.

Genetic code The relation between the amino acid and the nucleotide triplet is called genetic code.

Codons The nucleotide bases in RNA function in groups of three (triplet) in coding amino acids. These base triplets are called codons.

The world code is used with reference to DNA, codon with reference to m-RNA and anticodon with reference to t-RNA.

Lipids

The constituents of animals and plants soluble in organic solvents (ether, chloroform. carbon tetrachloride), but insoluble in water are called lipids. (Greek lipose = fat)

Types of Lipids

(i) Simple lipids

(a) Fats and oils on hydrolysis give long chain fatty acids + glycerol.

(b) Waxes Long chain fatty acids + long chain alcohols.

Vegetable and animal oils and fats have similar chemical structure and are triesters of glycerol, called glycerol.

Simple glycerides contain one type of fatty acids. Mixed glycerides contain two or three types of fatty acids.

Common saturated fatty acids CH₃-(CH₂)_nCOOH.

When n = 4 caproic acid; n = 6 caprylic acid; n = 8 capric acid, n = 10 lauric acid n = 12 myristic acid; n = 14 palmitic acid, n = 16 stearic acid.

Common unsaturated acids

C₁₇H₃₃COOH oleic acid; C₁₇H₃₃COOH linoleic acid.

Difference between oils and fats Oils are liquids at ordinary temprature (below 20° and contain lower fatty acids or unsaturated fatty acids.

Fats are solids or semisolids above 20°C and contain higher saturated fatty acids. Oils and fats act as "energy reservoirs" for the cells.

(ii) **Phospholipids** Phosphate + glycerol + fatty acids + a nitrogen containing base.

Function of phospholipids are

1. As emulsifying agents since they carry hydrophilic polar groups and hydrophobic non-polar groups.

2. They absorb fatty acids from the intestine and transport to blood cells.

(iii) Glycolipids They contain one or more simple sugars and are important components of cell membranes and chlorplast membranes.

(iv) Steroids and Terpenes Menthol, camphor are common plant terpenes. Carotenoids and pigments are also terpenes.

(a) Essential oils The volatile, sweet smelling liquids obtained from flowers, leaves, stems, etc. Example of terpenes are esters of lower fatty acid, e.g., clove oil, rose oil, lemon oil.

(b) Drying oils The oils which are converted into tough, transparent mass when exposed to air by oxidation polymerisation process are called drying oils. e.g., Linseed oil, perilla, poppy seed oils.

Cotton seed oil and til oil are semidrying oils.

Acid Value

It is the number of milligrams of KOH required to neutralise the free acid present in 1 g of oil or fat.

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Saponification Value

It is the number of milligrams of KOH required to saponify 1g of oil or fat or the number of milligrams of KOH required to neutralise the free acidresulting from the hydrolysis of 1 g of an oil or fat.

Iodine Value

It is the number of grams of iodine absorbed by 100 g of oil or fat.

Relchert-Meissel Value (R/M Value)

It is the number of cc of N/10 KOH required to neutralise the distillate of 5 g of hydrolysed fat.

Blood

An average person has about 6.8 L of blood which is about 6-10% of the body weight. pH of blood is about 7.4.

Haemoglobin is globular protein. It is made up of four polypeptide chains which are arranged in tetrahedral manner. Each chain is associated with a non-protein part, called haem.

Haemoglobin

These axe the chemical substances which are produced by ductless glands in the body. Hormones acts as chemical messengers.

Some examples of ductless '(endocrine) glands are thyroid, pitutary, adrenal, pancreas, testes and ovaries.

Hormones are divided into three types:

- 1. steroids
- 2. proteins or polypeptides
- 3. amines.

	Hormone	Source	Chemical name	Function	
1.	Thyroxin	Thyroid	Amino acid	Stimulates metabolism.	
2.	Adrenaline	Adrenal	Amine	Increases pulse rate and bloom pressure, release glucose from glycogen and fatty acids from fats.	
3.	Insulin	Pancreas	Peptide	Decreases blood glucose.	
4.	Glucogon	Pancreas	Peptide	Increases blood glucose.	
5.	Testosterone	Testes	Steroid	Controls normal functioning of male sex organs.	
6.	Estrone and Estradiol	Ovary	Steroid	Controls normal functioning di female sex organs.	
7.	Progesterone	Ovary	Steroid	Prepare uterus for pregnancy, controls menstrual cycle;	
8.	Cortisone	Adrenal cortex	Steroid	Metabolism of water, mineral salts, fats, proteins and carbohydrates.	

Insulin is a protein hormone which is secreted by β -cells of the pancreas. Insulin was the first polypeptide in which the amino acid sequence was experimentally determined. Its deficiency leads to diabetes mellitus.

Vitamins

The organic compounds other than carbohydrates, proteins and facts which are required by body to maintain normal health, growth and nutrition are called vitamins.

The vitamins are complex organic molecules. They are represented by letters such as A, B, C, D, E, K.

Vitamins are broadly classified into two types,

- 1. Water soluble vitamins and
- 2. oil soluble vitamins.

Vitamins A, D, E and K are oil soluble whereas vitamins B and C are water soluble. Vitamin H is neither fat soluble nor water soluble.

Vitamin	Chemical nature	Deficiency diseases	
Vitamin: A (Carotenoids or Axerophytol or ratinol)	Soluble in oils and fats, but insoluble in water.	Night blindness, Xerophthalmia (cornea becomes opaque), drying of skin.	
Vitamin B1 (Thiamine) Soluble in water, destroyed by heat.		Beriberi, loss of appetite.	
Vitamin 82 (Ribollavin)	Soluble in water, stable to heat, destroyed by light.	Cracked lips, sore tongue and skin disorders.	
Vitamin B ₆ (Pyridoxine)		Nervous disturbances and convulsions (pernious anaemia).	
Vitamin B ₁₂ (Cyano cobalamin)	Soluble in water and contains cobalt, red crystalline.	A serious type of anaemia.	
Vitamin C (Ascorbic, Acid, CeHgOs)	Soluble in water, destroyed by cooking and exposure to air.	Scurvy, dental caries, pyorrhea, anaemia,	
Vitamin D (Calciferol)	Mixture of four complex compounds containing C,H and O. Soluble in fats and oils but insoluble in water. Stable towards heat and oxidation. This vitamin regulates the absorption of calcium and phosphate in intestine.	Infantile rickets deformation of bone and teeth.	
Vitamin E (Tocopherol)	Mixture of 3 complex substances containing C, H and O. Soluble in fats and oils but insoluble in water. Stable to heat and oxidation.	Loss of sexual power and degeneration of muscle fibres in animals.	
Vitamin K	Tendency to haemorrhage and impaired clotting of blood.		

Chemistry Notes for class 12 Chapter 15 Polymers

The word polymer has a Greek origin. which means many units (parts). Polymer is defined as a chemical substance of a high molecular mass formed by the combination of a large number of simple molecules, called monomers. e.g.,

$$\begin{array}{c} n(CH_2 = CH_2) \longrightarrow [-CH_2 - CH_2 -]_n \\ ethylene & polyethylene \end{array}$$

Polymerisation

The process by which the monomers get combined and transformed into polymers. is known as polymerisation.

n [Monomer] \rightarrow Polymer

Difference between Polymers and Macromolecules

Polymers are also called macromolecules due to their large size but converse is not always true. A macromolecule mayor may not contain monomer units, e.g., chlorophyll ($C_{55}H_{72}O_5N_4Mg$) is a macromolecule but not a polymer since there are no monomer units present so we can conclude that all polymers are macromolecules while all macromolecules may not be polymers in nature.

Classification of Polymers Based on Source of Origin

(i) Natural polymers Those polymers which occur in nature. i.e., in plants or animals. are called natural polymers.

S.N.	Natural polymer	Occurrence
1.	Starch	Main reserve food of plants
2.	Cellulose	Main structural material of plants
3.	Proteins	Act as building blocks in animals.
4.	Natural rubber	Occurs as latex (a colloidal dispersion of rubber in water) in the bark of many tropical trees, particularly from Heva Brasiliensis.

(ii) **Synthetic polymers** The polymers which are prepared in the laboratory are known as synthetic polymers or man-made polymers, e.g., polythene, synthetic rubber, PVC, nylon-66, teflon, orlon etc.

(iii) **Semisynthetic polymers** Polymers obtained by making some modification in natural polymers by artificial means, are known as semi synthetic polymers, e.g., cellulose acetate (rayon), vulcanised rubber etc.

Classification of Polymers Based on Structure



Linear chain polymer

(i) **Linear polymers** These are the polymers in which the monomer units are linked to one another to form long linear chains. These linear chains are closely packed in space. The close packing results in high densities, tensile strength and high melting and boiling points. e.g., high density polyethene, nylon and polyesters are linear polymers.

Branched chain polymer

(ii) **Branched chain polymers** In such polymers, the monomer units are linked to form long chains with some branched chains of different lengths with source. As a result of branching, these polymers are not closely packed in space. Thus, they have low densities, low tensile strength as well as low melting and boiling points. Some common examples of such polymers are low density polyethene, starch, glycogen etc.



(iii) **Cross-linked polymers or network polymers** In such polymers, the monomer units are linked together to form three dimensional network. These are expected to be quite hard, rigid and brittle. Examples of cross linked polymers are bakelite, glyptal, melamine-formaldehyde polymer etc.

Classification of Polymers Based on Mode of Polymerisation

(i) **Addition polymers** The polymers formed by the polymerisation of monomers containing double or triple bonds (unsaturated compounds) are called addition polymers. Addition polymers have the same empirical formula as their monomers.

Addition polymers can further be classified on the basis of the types of monomers into the following two classes:
Homopolymers The polymers which are obtained by the polymerisation of a single type of monomer are called homopolymers.

 $\begin{array}{ccc} n(\mathrm{CH}_2 = \mathrm{CH}_2) & \longrightarrow & (\mathrm{CH}_2 - \mathrm{CH}_2)_n \\ \downarrow & \text{ethene} & & \text{Polythene} \end{array}$

Copolymers The polymers which are obtained by the polymerisation of two or more monomers are called copolymers



(ii) **Condensation polymers** The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers, e.g., nylon 6,6 is formed by the condensation of hexamethylene diamine with adipic acid.

$nH_2N(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \longrightarrow$ - $(-NH(CH_2)_6NHCO(CH_2)_4CO + nH_2O)_{nylon 6,6}$

Classification of Polymers Based on Molecular Forces

- 1. **Elastomers** These are rubber like solid polymers in which the polymer chains are held together by weakest intermolecular forces, e.g., natural rubber, buna-S, buna-N etc. The weak binding forces permit the polymers to be stretched. A few 'cross links' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber.
- 2. **Fibres** Fibres belong to a class of polymers which are thread-like and can be woven into fabrics. These are widely used for making clothes, nets, ropes, gauzes, etc. Fibres possess high tensile strength because the chains possess strong intermolecular forces such as hydrogen bonding. The fibres are crystalline in nature and have sharp melting points. A few examples of this class are nylon-66, terylene and polyacrylonitrile.

3. **Thermoplastics** These are linear polymers and have weak van der Waals' forces acting in the various chains. These forces are intermediate of the forces present in the elastomers and in the fibres. When heated, they melt and form a fluid which sets into a hard mass on cooling. Thus, they can be cast into different shapes by using suitable moulds, e.g., polyethene and polystyrene.

(Plasticizers are high boiling esters or haloalkanes. These are added to I plastics to make them soft rubber like. ...J

4. **Thermosetting plastics** These are normally semifluid substances with low molecular masses. When heated, they become hard and infusible due to the cross-linking between the polymer chains. As a result, they also become three dimensional in nature. A few common thermosetting polymers are bakelite, melamine-formaldehyde resin and urea formaldehyde resin.

Types of Polymerisation

1. Chain Growth Polymerisation or Addition Polymerisation

It involves formation of reactive intermediate such as free radical, a carbocation or a carbanion. For this polymerisation monomers used are unsaturated compounds like alkenes; alkadienes and their derivatives. Depending upon the nature of the reactive species involved. chain growth polymerisation occurs by the following mechanisms:

- Free radical addition polymerisation
- Cationic polymerisation
- Anionic polymerisation

(i) **Free radical addition polymerisation** The monomers used are generally monosubstituted alkenes. The most commonly used catalysts are benzoyl peroxide, hydrogen peroxide or t-butyl peroxide etc.

Mechanism The reaction involves the following steps

Step I Chain initiation step In this step, peroxide undergoes homolytic fission, e.g., benzoyl peroxide on heating produces phenyl initiator free radical.



Step II Chain propagation step The new free radical adds to another molecules of monomer to form a larger free radical.



Step III Chain termination step There are three ways of chain termination: Coupling reaction, disproportionation reaction, chain transfer reaction. One mode of termination of chain is shown as under:

$$C_{\theta}H_{6}(CH_{2}-CH_{2})_{n}CH_{2}\dot{C}H_{2}$$

 $C_{\theta}H_{6}(CH_{2}-\dot{C}H_{2})_{n}CH_{2}\dot{C}H_{2}$
 $C_{\theta}H_{6}(CH_{2}-\dot{C}H_{2})_{n}CH_{2}\dot{C}H_{2}$
 $C_{\theta}H_{6}-(CH_{2}CH_{2})_{n}CH_{2}CH_{2}CH_{2}CH_{2}(CH_{2}-CH_{2})_{n}C_{\theta}H_{5}$
polymer

(ii) **Cationic polymerisation** It involves formation of carbocation which are generated by Lewis acids (like BF₃, AICI₃, SnCI₄, etc.) and protonic acids such as H₂SO₄, HF, etc.

Higher the stability of carbocation intermediate, more is the reactivity of monomers towards cationic addition polymerisation. It involves the following steps:

Step I. Initiation Step

 $H_{2}SO_{4} \longrightarrow H^{+} + HSO_{4}^{-}$ $BF_{3} + H_{2}O \longrightarrow H^{+} + BF_{3}(OH^{-})$ $CH_{2} = C(CH_{3})_{2} + H^{+} \longrightarrow (CH_{3})_{3}C^{+}$ carbocation Step II. Propagation $(CH_{8})_{3}C^{+} + CH_{2} = C(CH_{8})_{2} \longrightarrow (CH_{3})_{3} - C - CH_{2}C^{+}(CH_{3})_{2}$ $\xrightarrow{nCH_{2} = C(CH_{3})_{2}} (CH_{3})_{3}C - [CH_{2} - C(CH_{3})_{2}]_{n} - CH_{2} \cdot C^{+}(CH_{3})_{2}$ $\xrightarrow{step \text{ III. Termination}} (CH_{3})_{3}C[CH_{2} \cdot C(CH_{3})_{2}]_{n} CH_{2}C^{+}(CH_{3})_{2}]$ $\xrightarrow{-H^{+}} (CH_{3})_{3}C[CH_{2} \cdot C(CH_{3})_{2}]_{n} CH_{2} = C(CH_{3})_{2}$

(iii) **Anionic polymerisation** It involves formation of a carbanion, Steps involved in this process are

Step I Initiation Strong bases act as initiator.



Step Growth Polymerisation

Condensation polymerisation which occurs in a stepwise manner with elimination of some smaller molecules like H₂O, NH₃, HCI, ROH, etc., is concerned with step growth polymerisation, e.g., adipic acid and hexamethylenediamine phenol and formaldehyde etc., undergo step Growth Polymerisation.

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S.No.	Chain growth polymerisation	Step growth polymerisation		
1.	It proceeds by a chain mechanism characterised by initiation, chain propagation and chain termination.	It proceeds by an equilibrium step mechanism. The step growth process is usually much slower than chain growth polymerisation.		
2.	Only one repeating unit is added at a time.	Any two species present can react with elimination of some by product.		
3.	Reaction mixture contain only monomers, polymers and the growing chain.	All the molecular species are present at every stage of polymerisation.		

Molecular Mass of Polymers

The growth of the polymer chain depends upon the availability of the monomers in the reaction. Thus, the polymer sample contains chain of varying lengths and hence, its molecular mass is always expressed as an average molecular mass.

Number-Average Molecular Mass M_n

If N_1 molecules have molecular mass M_1 each, N_2 molecules have molecular mass M_2 each, N_3 molecules have molecular mass M_3 each and so on,

then, $M_n = \Sigma N_i M_i / \Sigma N_i$

It is determined by osmotic pressure method.

Mass-Average Molecular Mass (\overline{M}_w)

1

Supposing, as before that N_1, N_2, N_3 etc., molecules have molecular mass M_1, M_2, M_3 etc., respectively,

then,

$$\overline{M}_{w} = \frac{\Sigma N_{i} M_{i}^{2}}{\Sigma N_{i} M_{i}}$$

It is determined by light scattering and ultracentrifugation method.

PoLydispersity Index

It is the ratio of the mass average molecular mass to the number average molecular mass

 $PDI = M_w / M_n$

For natural polymers, PDI is usually equal to one which means that they are monodisperse. In other words, such polymers are more homogeneous. On the contrary, synthetic polymers generally have PDI > 1 which means that they are less homogeneous.

Polyolefins

These are obtained by the addition polymerisation of ethylene and its derivatives

1. Polythene

Polymer of ethylene or ethene.

(i) Low density polythene (LDP)

 $n(CH_2 = CH_2) \xrightarrow[(Traces of oxygen]{1000 to 2000 atm} (Traces of oxygen or a peroxide initiator)} -[CH_2 - CH_2]_{LDP}$

It is tough, flexible, transparent, chemically inert as well as poor conductor pf electricity. It has moderate tensile strength but good tearing strength.

It is used in the insulation of electricity carrying wires and manufacture of queeze bottles, toyes and flexible pipes.

(ii) High density polyethylene (HOP)

$$n(CH_2 = CH_2) \xrightarrow[6-7]{6-7 \text{ atm}} (CH_2 = CH_2) \xrightarrow[6-7]{6-7 \text{ atm}} (CH_2 = CH_2) \xrightarrow[6-7]{n}$$

It has high density due to close packing. It is also chemically inert and more tougher and harder.

It is used for making containers, house wares, bottles, toyes, electric insulation etc.

2. Polystyrene (Styrone)

The monomers are styrene molecules. It is thermoplastic. It is used for making toys, radio and TV cabinets

$$n \begin{bmatrix} CH = CH_2 \\ C_6H_5 \\ styrene \end{bmatrix} \xrightarrow{(C_2H_5COO)_2} \begin{bmatrix} -CH - CH_2 \\ C_6H_5 \\ C_6H_5 \end{bmatrix}_n$$

3. Polyvinylchloride (PVC)



It is used for making rain coats, toys, electrical insulation. It is hard and resistant to heat and chemicals.

4. Polypropylene (PP)

It is obtained by polymerising propylene in the presence of Ziegler-Natta catalyst.



5. Polytetrafluoroethene (Teflon)

 $\begin{array}{c} n(\mathrm{CF}_2 = \mathrm{CF}_2) & \xrightarrow{\mathrm{Catalyst}} & -\mathrm{FCF}_2 - \mathrm{CF}_2 \ \frac{1}{2n} \\ \text{tetrafluoroethene} & \operatorname{High \ pressure} & \operatorname{teflon} \end{array}$

It is chemically inert and resistant to attack by corrosive reagent. It is used in making oil seals, gaskets and also for non-stick surface coated utensils.

6. Polyacrylonitrile



It is used as a substitute for wool in making commercial fibres as orIon or acrilan.

Polyamides

The polymers which contain an amide linkage in chain are known as pOlyamide, e.g., nylon-6, 6.

1. Nylon-66

It is obtained by the condensation of adipic acid and hexamethylenediamine with the elimination of water molecule



The polyamides are identified by numbers. These numbers refer to the number of carbon atoms in diamine and in the dibasic acid. As in the above case, the carbon atoms are 6 in each case, therefore the product is described as _nylon-66.

Properties and uses

Nylon-66 is a linear polymer and has very high tensile strength. It shows good resistance to abrasion. Nylon-66 is usually fabricated into sheets. It is used in bristles for brushes and in textile

2. Nylon-6

Nylon-6 is obtained by heating caprolactam with water at a high temperature.



Resins

1. Phenol-Formaldehyde Polymer

(Bakelite and Related Polymers)

These polymers are obtained by the condensation reaction of phenol with formaldehyde in the presence of either acid or a base catalyst. The reaction involves the formation of methylene bridge at ortho, para or both ortho and para positions. A linear or cross linked material is obtained depending upon the condition of reaction.



cross linked polymer (bakelite)

Uses

Bakelite is used for making combs, photograph records, electrical switches etc. Soft bakelites with low degree of polymerisation are used as binding glue for laminated wooden plants, in varnishes and lacquers.

2. Melamine-formaldehyde Resin

It is a copolymer formed by the polymerisation of melamine (which is a heterocyclic triamine) and formaldehyde as follows :



Properties and Uses

It is very hard and tough. It has assumed great importance these days particularly in making crockery. They do not break even when droped from a height.

3. Urea-formaldehyde Resin



4. Natural Rubber

Natural.rubber is a coiled linear 1, 4-polymer of isoprene.

In the polymer chain of natural rubber, the residual double bonds are located between C_2 and C_3 of the isoprene unit. All these double bonds have cis configuration, and thus natural rubber is cis-l,4-polyisoprene.



In the natural rubber, there is no polar substituent. The only intermolecular forces are van der Waals' type. The cis-configuration gives the polymeric chain of natural rubber a coiled structure. As a result, it can be stretched by the application of a force. When the force is removed, the chain returns back to its original coiled shape.

Natural rubber is soft and sticky. It can be used only in the temperature range 10°C-50°C. At higher temperature, it becomes soft and at low temperature, it becomes brittle. It has higb water absorption capacity. It is attacked by oxidising agents and organic solvents. As such, it cannot be used very extensively for commercial puposes.

Vulcanisation of Rubber

The properties of natural rubber can be modified by introducing -S-S- polysulphide crosslinks in its structure. This process of introducing -S-S- crosslnks in the structure of natural rubber by heating with sulphur at 110°C is called vulcanlsation of rubber.

Vulcanisation is carried out by adding sulphur (3-5%) and zinc oxide to the rubber, and then heating the object at about 110°Cfor about 20-30 minutes. Zinc oxide accelerates the rate of vulcanisation. Vulcanisation introduces polysulphide (-S-S-) bonds between the adjacent chains. These crosslinks tend to limit the motion of chains relative to each other.

5. Neoprene

Polymer formed by polymerisation of chloroprene is neoprene or synthetic rubber.



It is used for the manufacturing conveyers belts, gasket and hoses.

6. Buna-N

It is a copolymer of buta-I, 3-diene and acrylonitrile. It is formed as follows



Properties and Uses

It is insulator in nature and is used for making conveyor belts and printing rollers.

Polyesters

The polymers which contain an ester linkage are known as polyester, e.g., dacron.

1. Polymethylmethacrylate (PMMA)

It is prepared by the polymerisation of methylmethacrylate in the presence of suitable organic peroxide.



The polymer is known by several commercial names such as lucite, acrylite, plexiglass and perspex.

Properties and uses

It is a hard and transparent polymer and is quite resistant to the effect of light, heat and ageing. It is used, in the manufacture of unbreakable lights, protective coatings, dentures, and in making windows for aircrafts.

2. Glyptal

It is a polyester having crosslinks. It is a thermosetting plastic. It is obtained by condensation of ethylene glycol and phthalic acid or glycerol and phthalic acid.



When its solution in a suitable solvent is evaporated, it leaves a tough but non-flexible film. It is, therefore, used in the manufacture of paints and lacquers.

3. Terylene (Dacron)

It is a condensation product of ethylene glycol and terephthalic acid.

Polymerisation is carried out at 420 to 460 K in the presence of catalyst mixture of zinc acetate and antimony trioxide.



Properties and uses

Terylene is highly resistant to the action of chemical and biological agents. Its fibres are quite strong and durable. It can also be blended with wool or cotton to obtain fabrics of desired composition.

Terylene is used in the manufacture of a variety of clothes such as terycot, terywool and terysilk as a result of blending with other yerns. It is also used for preparing magnetic recording tapes, conveyer belts, aprons for industrial workers etc.

Biopolymers and Biodegradable Polymers

Synthetic polymers are mostly non-biodegradable i.e., it is very difficult to dispose off the polymeric waste, e.g., polythene bags.

Nature has provided us a variety of polymers which can be produced by the biological systems in plants and animals. These are called biopolymers, e.g., polysaccharides, proteins, nucleic acids, etc. In the biological system, these polymers decompose or hydrolyse in the Presence of different enzymes. This means that they are biodegradable.

Aliphatic polyesters are the common examples of biodegradable Polymers.

It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



2. Nylon-2-Nylon-6

It is an alternating polyamide copolymer of glycine (H_2N-CH_2-COOH) and amino caproic acid [$H_2N(CH_2)$ ₅COOH] and is biodegradable.

Some More Impotant Polymers

- 1. Saran is a copolymer of vinyl chloride and Isused for wrapping food materials.
- 2. ASS rubber is a copolymer of acrylonitrile, buta-1, 3-diene and styrene.
- 3. Bubble gum contains styrene butadiene rubber.

- 4. Epoxy resins are used In making adhesives such as analdite, etc. These are the copolymer of epichlorohydrin and bisphenol-A.
- 5. Thikol is another variety of synthetic rubber which is a copolymer of ethylene chloride and sodium tetrasulphide (Na_2S_4) .
- 6. Dynells a copolymer of vinyl chloride and acrylonitrile and is used for making human hair wigs.
- 7. Silk Is a thread like natural polymer which is obtained from cocoons of sllk worms. It is a natural polyamide fibre.
- 8. Thermocol Is a foamed plastic obtained by blowing air through molter polystyrene or polyurethane.
- 9. Superglue is a polymer of methyl α -cyanoacrylate and is obtained by anionic polymerisation of monomer.

Chemistry Notes for class 12 Chapter 16 Chemistry in Everyday Life

Medicines or Drugs

Chemicals which may be used for the treatment of diseases and for reducing the suffering from pain are called medicines or drugs.

The branch of science which makes use of chemicals for the treatment of disseases [therapeutic effect] is called chemotherapy. Some important classes of drugs are

Antacid

The chemical substances which neutralize the excess acid in gastric juice and raise the pH to an appropriate level in stomach are raUed antacids.

The most commonly used antacids are weak bases such as sodium bicarbonate [sodium hydrogencarbonate, NaHCO₃), magnesium hydroxide [Mg(OH)₂] and aluminium hydroxide [Al(OH)₃].

Generally liquid antacids are more effective than tablets because .. have more surface area available for interaction and neutralisation acid.

Milk is a weak antacid.

Histamine stimulates the secretion of pepsin and hydrochloric acid. The drug cimetidine [Tegamet] was designed to prevent the interaction of histamine with the receptors present in the stomach Cimetidine binds to the receptors that triggers the release of acid the stomach. This results in release of lesser amount of acid. Now ranitidine (zantac), omeprazole and lansoprazole are used hyperacidity.

Tranquilizers (Psychotherapeutic Drugs)

Chemical substances used for the treatment of stress, anxiety, irritability and mild or even severe mental diseases, are known as tranquilizers. These affect the central nervous system and induce sleep for the patients as well as eliminate the symptoms of emotional distress. They are the common constituents of sleeping pills.

Noradrenaline is one of the neurotransmitter that plays a role in mood change. If the level of noradrenaline is low, the signal sending activity becomes low, and the person suffers from depression. In such situations antidepressant drugs are required. These drugs inhibit the enzymes which catalyse the degradation of noradrenaline. If the enzyme is inhibited, this important neurotransmitter is slowly metabolized and can activate its receptor for longer

periods of time, thus counteracting the effect of depression. Iproniazid and phenelzine are two such drugs.

Barbituric acid and its derivatives viz. veronal, amytal, nembutal, luminal, seconal are known as barbiturates. Barbiturates are hypnotic, i.e., sleep producing agents.



Equanil is used to control depression and hypertension.

Non-hypnotic chlorodiazepoxide and meprobamate are relatively mild tranquilizers suitable for relieving tension.

Analgesics

Medicines used for getting relief from pain are called analgesics. These are of two types :

1. Narcotics

Drugs which produce sleep and unconsciousness are called narcotics. Mhese are habit forming drugs. For example, morphine and codeine. Morphine diacetate is commonly known as heroin.

2. Non-narcotics

These are non-habit forming chemicals which reduce mild to moderate llatn such as headache, toothache, muscle and joint pain, etc. These are also termed as non-addicti,ve. These drugs do not produce sleep unconsciousness. Aspirin (2-acetoxybenzoic acid) is most commonly used analgesic with antipyretic properties. Now these days because its anti-blood clotting action, aspirin is widely used to heart-attacks.



Aspirin is toxic for liver and sometimes also causes bleeding from- stomach. So, naproxen, ibuprofen, paracetamol,dichlorofenac sodium are other widely used analgesics.

Antipyretics

These are the chemical substance which reduce body temperature during high fever. Paracetamol, aspirin, phenacetin (4-hydroxy acetanilide), analgin and novalgin, etc., are common antipyretics. Out of these, paracetamol (4-acetamidophenol) is most common.



Antimicrobials

An antimicrobial tends to kill or prevent development of microbes CII inhibit the pathogenic action of microbes such as bacteria, fungi and virus selectively.

[Sulpha drugs constitute a group of drugs which are derivatives of sulphanilamide and have great antimicrobial capacity, thus, these are widely used against diseases such as dyptheria, dysentry, tubercu losis, etc.]



In structure these drugs are analogues of p-amino benzoic acid Different types of antimicrobial drugs are as follows :

1. Antibiotics

These are the substances (produced wholly or partially by chemical synthesis) which in low concentrations inhibit the growth of microorganisms or destroy them by intervening in their metabolic processes.

Antibiotics are products of microbial growth and thus, antibiotic therapy has been likened to 'setting on.e thief against another'.

Antibiotics are of two types :

- 1. Bactericidal antibiotics have cidal (killing) effect on microbes. For example, penicillin, ofloxacin, amino glycosides, etc.
- 2. Bacteriostatic antibiotics have a static (inhibitory) effect on microbes. For example, erythromycin, tetracycline, chloramphenicol, etc

Penicillin was the first antibiotic discovered (by Alexander Fleming) in 1929. It is a narrow-spectrum antibiotic. Ampicillin and amoxicillin are semi-synthetic Illodifications of penicillin.

Penicillin is not suitable to all persons and some Personsare allergic to it. Consequently, it is essential to test the patients for sensitivity (or allergy) to penicillin, before it is administered.

In India, penicillin is manufactured at Pimpri and Rishikesh (Uttarakhand).

Broad-spectrum antibiotics also called antibiotics, are antibiotics which are effective against different types of harmful microorganisms. e.g., Tetracycline, chloramphenicoltgiven in case of typhoid, dysentery, fever ofloxacin, etc.

2. Antiseptics

These are the chemicals which either kill or prevent the growth microorganisms. Antiseptics are applied to the living tissues such wounds, cuts, ulcers and skin diseases in the form of antiseptic creams like furacin and soframycin. e.g., Some important examples of antiseptics are

(i) **Dettol** is a mixture of chloroxylenol and terpineol.



(ii) **Bithional** is added to soaps to impart antiseptic properties to reduce the odours produced by bacterial organic matter on the skin.



(iii) **Tincture of iodine** is a 2-3% solution of iodine in alcohol, which is a powerful antiseptic for wounds.

(iv) **Iodoform** (CHI₃) is also used as an antiseptic for wounds.

(v) **Boric acid** in dilute aqueous solution is weak anIUS4!pa eyes.

3. Disinfectants

These are the chemical substances which kill microorganisms not safe to be applied to the living tissues. They are generally kill the microorganisms present on inanimate objects such as drainage systems, instruments, etc.

Some common examples of disinfectants are as follows :

(i) 1% phenol solution is disinfectant while in lower concentration 0.2% solution of phenol is antiseptic.

(ii) 0.2-0.4 ppm aqueous solution of chlorine is used for sterilisation of water to make it fit for drinking purpose.

(iii) SO₂ at very low concentrations behaves like disinfectant.

(iv) Formaldehyde (HCHO) in the disinfecting rooms and operation gaseous theatres forms is used in hospitals. for

Antifertility Drugs

These are the chemical substances used to control the pregnancy. These are also called oral contraceptives. They belong to the class of natural products, known as steroids.

Birth control pills essentially contain a mixture of synthetic estrogen and progesterone derivatives. Norethindrone is widely used as antifertility drug.

Chemicals in Food

1. Artificial Sweetening Agents

Sucrose (table sugar) and fructose are the most widely used natural sweeteners. But they add to our calorie intake and promote tooth decay. To avoid these problems many people take artificial sweeteners.

Organic substances which have been synthesized in lab are known to be many times sweeter than cane sugar. Such compounds are known as artificial sweetening agents or artificial sweeteners.

Some important artificial sweeteners are given below :

(i) Saccharin (o-sulphobenzimide)

Discoveredby Johns- Hopkins in 1879 (University of USA).



It is the most popular artificial sweetener. It is 550 times as sweet as cane Sugar, since it is insoluble in water, so it is sold in the market as its soluble or calcium salt.

It is non-biodegradable so excreted from the body in urine (unchanged). Its use is of great value for diabetic persons and people who need to control intake of calories.

(ii) Aspartame

It is the methyl ester of the dipeptide derived from phenylalanine aspartic acid. It is also known as 'Nutra sweet'.

It decomposes at baking or cooking temperatures and hence, can used only in cold food and soft drinks.

Aspartame has the same amount of calories as sugar (4 cal per gram).

Aspartame should not be used by people suffering from the genetic disease known as PKU (phenyl ketone urea). Because in such people decomposition of aspartame gives phenylpyruvic acid. Accumulation ~ phenylpyruvic acid is harmful especially to infants due to brain damage and mental retardation.

(iii) Alitame

It is quite similar to aspartame but more stable than aspartame. It is 2000 times as sweet as sucrose. The main problem for such sweetenerf

is the control of sweeteness of the substance to which it is added because it is high potency sweetener.

(iv) Sucralose

It is a trichloro derivative of sucrose. It's appearance and taste are like sugar. It is stable at cooking temperature. It is almost 600 times 88 sweet as sucrose. However, it neither provides calories nor causes toot.1i decay.

(v) Cyclamate

It is N-cyclohexylsulphamate. It is only 20 times sweeter than cane sugar.



2. Food Preservatives

These are the chemical substances added to food to prevent their spoilage due to microbial growth (bacteria, yeasts and moulds) and to retain their nutritive value for longer periods .

The most commonly used preservatives include table salt, supgar, vegetable oil, vinegar, citric acid. spices and sodium benzonate (C_6H_5COONA). Salts of sorbic acid and propanoic acid are also used" preservatives for cheese, baked food, pickles, meat and fish products.

1. Sodium benzoate is metabolised by conversion into hioppuric acid ($C_6H_5CONHCH_2COOH$), which is ultimately urine. It is used in soft drinks and acidic foods.

2. Antioxidants like BHT(butylated hydroxytoluene) and BRA butylated hydroxyanisole) retard the action of oxygen on the food and help in the preservation of food materials.



Cleansing Agents

The word detergent means cleansing agent. Actually detergent word is derived from Latin word 'detergere' means "to wipe off", Cleansing agents are the substance which remove dirt and have cleansing action in water. These are also called surfactants.

Detergents can be classified into two types.

- 1. Soapy detergents or soaps, and
- 2. Non-soapy detergents or soapless soap.

1. Soaps

Soaps are sodium or potassium salts of higher fatty acids (containing 15-18 carbon atoms) e.g., stearic acid, oleic acid and palmitic acid. Sodium salts of fatty acids are known as hard soaps while the potassium salts of fatty acids are known as soft soaps.

Hard soaps are prepared by cheaper oil and NaOH while soft soaps are Jlrepared by oil of good quality and KOH. The soft soaps do not contain freealkali, produce more lather and are used as toilet soaps, shaving SOapsand shampoos.

Preparation of soaps

Soaps containing 'Sodium salts are formed by heating fat (glyceryl ester ~fatty acid) with aqueous sodium hydroxide solution. This reaction is known as saponification.



The solution left after removing the soap contains glycerol, which can be recovered by fractional distillation. To improve the quality of soaps desired colours, perfumes and medicinal chemical substances, added.

Types of Soaps

Different kind of soaps are made by using different raw materials.

- 1. **Toilet soaps** These are prepared by using better grade of fat or oil and care is taken to remove excess alkali. Colour and perfumes are added to make these more attractive.
- 2. **Floating soaps** These can be prepared by beating tiny bubbles into the product before it hardens.
- 3. **Transparent soaps** These are made by dissolving the in ethanol and then evaporating the excess solvent.
- 4. **Medicated soaps** Medicated soaps are prepared by some antiseptics like dettol or bithional.
- 5. **Shaving soaps** These contain glycerol to prevent drying. A gum called rosin is added while making them. It forms sodium rosinate which lather well.

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- 6. **Laundry soaps** These sodium silicate, borax and contain sodium fillers like carbonate. sodium rosins
- 7. **Soap Chips** These are made by running a thin sheet of melted soap on a cool cylinder and scraping off the soaps in small broken pieces.
- 8. Soap grannules These are dried miniature soap bubbles.
- 9. **Soap powder and scouring soaps** These contain a scouring agent (abrasive) such as powdered pumice or finely divided sand and builders like sodium carbonate and trisodium phosphate. Builders make the soaps act more quickly.

Disadvantages of Soaps

Soap is good cleansing agent and is 100% biodegradable microorganisms present in sewage water can completely oxidise soap to CO_2 , As a result, it does not create any pollution problem. However soaps have two disadvantages:

(i) Soaps cannot be used in hard water since calcium magnesium ions present in hard water produce curdy precipitates of calcium and magnesium soaps.

These insoluble soaps separate as scum in water and causes hinderance to washing because the precipitate adheres onto the fibre of the cloth as gummy mass. Thus, a lot of soap is wasted if water. is hard.

(ii) Soaps cannot be used in acidic solutions since acids precipitate the insoluble free fatty acids which adhere to the fabrics and thus, reduce the ability of soaps to remove oil and grease from fabrics.

 $\begin{array}{ccc} RCOONa + H^+ & \longrightarrow & RCOOH & + Na^+ \\ & & \text{free fatty acid} \\ & & \text{precipitate out} \end{array}$

Soapless Soap/Synthetic Detergents

Synthetic detergents have all the properties of soaps but actually does not contain any soap, so they are known as 'soapless soaps'.

Straight chain alkyl group containing detergents are biodegradable whereas branched chain alkyl group containing detergents are non-biodegradable.

Unlike soaps, synthetic detergents can be used in both soft and hard water. This is due to the reason that calcium and magnesium salts of detergents like their sodium salts are also soluble in water. Synthetic

detergents are mainly classified into three categories:

1. Anionic Detergents

These are sodium salts of sulphonated long chain alcohols or hydrocarbons.

(i) Alkyl hydrogen sulphates formed by treating long chain alcohols with concentrated sulphuric acids are neutralised with alkali to form anionic detergents.



(ii) Alkyl benzene sulphonates are obtained by neutralising alkyl benzene sulphonic acids with alkali.



In such detergents, the anionic part of the molecule is involved in the cleansing action.

They are mostly used for household work and in tooth paste

2. Cationic Detergents

These are quaternary ammonium salts of arnines with acetates, chlorides or bromides as anion. For example,



Cationic detergents are used in hair conditioner. They have germicidal properties but are expensive therefore, these are of limited use.

3. Non-ionic Detergents

Such detergents does not contain any ion in their constitution. One such detergent can be obtained by reaction of stearic acid and polyethylene glycol.



Liquid dish washing detergents are non-ionic type, Mechanism of cleansing action of this type of detergents is the same as that of soaps.

Advantages of syntbeti.c detergents over soaps

Synthetic detergents can be used even in case of hard water whereas soaps fail to do so.
 Synthetic detergents can be used in the acidic medium while soaps cannot because of their hydrolysis to free acids.

3. Synthetic detergents are more soluble in water and hence, form better lather than soaps.

4. Synthetic detergents have a stronger cleansing action than soaps.

Chemistry in Colouring Matter

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The natural or synthetic colouring matter which are used in solution to stain materials especially fabrics are called dyes.

All colouring substances are not dyes, e.g., azobenzene, a coloured substance does 'not act as dye.

A dye have following characteristics :.

- 1. It must have a suitable colour.
- 2. It can be fixed on the fabric either directly or with the help of mordant.
- 3. It must be resistant to the action of water, acid and alkalies. The groups, responsible for colour, are called chromophore, e.g.,

The substance wheih do not given colour itself but intensify the colour of chromophore, are called **auxochrome**.

 $e.g., -OH, -SO_3H, -COOH, -NH_2, -NHR-, -NR_2.$

Classification of Dyes on the Basis of Constitution

(i) Nitro or nitroso dye Chromophore NO_2 or NO group, Auxochrome = -OH group, e.g., picric acid, martius yellow, Gambine, naphthol yellow-S.

(ii) Azo dye, e.g., bismark brown, methyl orange, methyl red, congo red, etc.

(iii) Anthraquinone dye e.g., alizarin

(iv) Indigo is the oldest known dye. Other examples are tyrian purple, indigosol.

(v) Phthalein dye e.g., phenolphthalein, fluorescein, eosin, mercurochrome.

(vi) Triarybnethane dye, e.g., malachite green, rosaniline.

Classification of Dyes on the Basis of Application

(i) Direct dyes These dyes applied directly to fibre and are more useful to the fabrics containing H-bonding like cotton, rayon, wool, silk and nylon, e.g., martius yellow, congo reu/etc.

(ii) Acid dyes These are water soluble and contain porar/acidic groups which interact with the basic group of e.g., Orange-I, congo red, methyl orange, etc. These dyes does not have affinity for cotton but are used for silk, wool, etc.

(iii) Basic dyes These dyes contain basic group (like NHz group) and react with anionic sites present on the fabric. These are used to dye nylons and polyester, e.g., butter yellow, magenta (rosaniline), aniline yellow, etc.

(iv) Vat dyes Being water insoluble, these cannot be applied directly. These are first reduced to a colourless soluble form by a reducing agent in large vats and then, applied to fabrics. After applying, these are oxidised to insoluble coloured form by exposure. to air or some oxidising agents, e.g., Indigo, tyrian purple, etc.

(v) Mordant dyes These are applied with the help of a binding material (e.g., metal ion, tannic acid or metal hydroxide) called mordant. Depending upon the metal ion used, the same dye can give different colours. Alizarin is an important example of such dyes.

(vi) Ingrain dye These dyes are synthesised directly on the fabric. These are water insoluble and particularly suitable for cotton fibres. Azo dyes belong to this group of dye.

Chemistry in Cosmetics

Cosmetics are used for decorating, beautifying or improving complexion of skin. Some of the cosmetics of daily use are as

1. Creams

These are stable emulsions of oils or fats in water and contain emmollients (to prevent water loss) and humectants (to attract water) as two fundamental components.

2. Perfumes

These solutions have pleasent odour and invariably consist of three ingredients: a vehicle (ethanol + H20), fixative e.g., sandalwood oil, benzoin, glyceryl diacetate etc.) and odour producing substance (e.g., terpenoids like linalool, anisaldehyde (p-methoxy-benzaldehyde etc.)

3. Talcum Powder

It is used to reduce irritation of skin. Talc $(Mg_3(OH)_2Si_4O_{10})$, chalk, Zno, zinc sterate and a suitable perfume are the constituents of talcum powder.

4. Deodorants

These are applied to mask the body odour. These possess antibacterial properties. Aluminium salts, ZnO, ZnO₂, $(C_{17}H_{35}COO)_2$ Zn can be used in deodorant preparation.

Rocket Propellants

Substances used for launching rockets are called rocket propellants. These are the combination of an oxidiser and a fuel.

Depending upon the physical states of oxidiser and fuels, rocket propellants are classified as

1. Solid Propellants

These are further divided into two classes

(i) Composite propellants In these propellants, fuel is polymeric binder such as polyurethane or polybutadiene and oxidiser is ammonium per chlorate or potassium perchlorate.