

The Solid State

General characteristics of solid state:

- Definite mass, volume and shape
- Short intermolecular distances
- Strong intermolecular forces
- Fixed lattice positions of the constituent particles
- Incompressibility and rigidity

Classification of the solid state:

- Crystalline
- Amorphous (sometimes called pseudo solids or super-cooled liquids)

Differences between the crystalline and amorphous solids

Crystalline	Amorphous
Have definite characteristic geometrical shape	Have irregular shape
Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
When cut with a sharp edged tool, the newly generated pieces are plain and smooth	When cut with a sharp edged tool, the newly generated pieces are with irregular surfaces
Have definite and characteristic heat of fusion	Do not have definite heat of fusion
Are true solids	Are pseudo solids
Anisotropic in nature	Isotropic in nature
Have long-range order	Have only short-range order

Classification of crystalline solids (On the basis of the nature of intermolecular forces)

Molecular solids

- Non-polar molecular solids → These consist either atoms or the molecules formed by non-polar covalent bonds. Example: H_2 , Cl_2 , I_2
- Polar molecular solids → The molecules in these types of solids are held together by strong dipole-dipole interactions. Example: Solid SO_2 , solid NH_3
- Hydrogen-bonded molecular solids → The molecules of such solids contain polar covalent bonds between H and F, O or N atoms. Example: Ice (H_2O)

Ionic solids

Ions are the constituent particles; e.g., NaCl, KNO₃

Metallic solids

Each metal atom is surrounded by electrons; e.g., Fe, Cu

Covalent or network solids

Formed by covalent bonds; e.g., diamond, silicon carbide

Crystal lattice: A regular three-dimensional arrangement of points in space.

- There are 14 Bravais lattices

Unit cells: There are two categories of unit cells –

- **Primitive unit cells:** There are seven types of primitive unit cells –
 - Cubic ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$); e.g., NaCl
 - Tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$); e.g., CaSO₄
 - Orthorhombic ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$); e.g., KNO₃
 - Hexagonal ($a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$); e.g., ZnO
 - Rhombohedral or Trigonal ($a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$); e.g., CaCO₃
 - Monoclinic ($a \neq b \neq c$, $\alpha = \gamma = 90^\circ$, $\beta \neq 120^\circ$)
 - Triclinic ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$); e.g., Na₂SO₄·10H₂O
- **Centred unit cells:** There are three types of centred unit cells –
 - Body-centred unit cells: Contain one constituent particle at its body centre along with the ones present at corners
 - Face-centred unit cells: Contain one constituent particle at the centre of each face along with the ones present at corners
 - End-centred unit cells: Contain one constituent particle at the centre of any two faces along with the ones present at corners

Number of atoms in a unit cell:

- Total number of atoms in one primitive cubic unit cell = 1
- Total number of atoms in one body-centred cubic unit cell = 2
- Total number of atoms in one face-centred cubic unit cell = 4

Close-packed structures:

- **Coordination number:** The number of the nearest neighbours of a particle
- **Packing efficiency:** The percentage of total space filled by the particles

Close-Packing in One dimension

Only one way of arrangement, i.e., the particles are arranged in a row, touching each other

Close-Packing in Two Dimensions

Square close-packing in two dimensions

Close-Packing in Three Dimensions

Three-dimensional close-packing is obtained by stacking two-dimensional layers (square close-packed or hexagonal close-packed) one above the other.

- There are two highly efficient lattices of close-packing –
- Hexagonal close-packed (*hcp*)
- Cubic close-packed (*ccp*) [also called face-centred cubic (*fcc*) lattice]
- In *hcp* and *ccp*, 74% space is filled, i.e., packing efficiency = 74%.
The remaining space is present in the form of voids.

There are two types of voids –

- Octahedral voids
- Tetrahedral voids

The packings other than *hcp* and *ccp* are not close packings as they have less packing efficiency.

- Packing efficiency in bcc = 68%
- Packing efficiency in simple cubic lattice = 52.4%

Number of octahedral voids = Number of close-packed particles

Number of tetrahedral voids = $2 \times$ Number of close-packed particles

In ionic solids, the bigger ions (usually anions) form the close-packed structure and the smaller ions (usually cations) occupy the voids.

The fraction of the octahedral or tetrahedral voids that are occupied depends on the chemical formula of the compound.

Packing Efficiency

Percentage of total space filled by particles

$$\text{packing efficiency} = \frac{\text{Volume of one particle}}{\text{Volume of cubic unit cell}} \times 100\%$$

Calculations involving dimensions of unit cells:

$$\text{Density of a unit cell} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$\Rightarrow d = \frac{zM}{a^3 N_A}$$

Where,

$d \rightarrow$ Density

$z \rightarrow$ Number of atoms present in one unit cell

$M \rightarrow$ Molar mass

$a \rightarrow$ Edge length

$N_A \rightarrow$ Avogadro's number

Imperfections in solids:

• Line defects Jk Study Materials

-These arise due to irregularities in the arrangement of constituent particles in entire rows of a lattice point

• Point defects

-These arise due to irregularities in the arrangement of constituent particles around a point or an atom

-There are three types of point defects: Stoichiometric, Impurity and Non-stoichiometric

Stoichiometric defects (intrinsic or thermodynamic defects)

• Vacancy defect

-Developed when a substance is heated

-Decreases the density of the substance

• Interstitial defect

-Increases the density of the substance

• In ionic solids, the vacancy and interstitial defects exist as Frenkel and Schottky defects.

- Frenkel defect (also called dislocation defect): It occurs when there is a large difference in the size of ions.
- Schottky defect: It is a vacancy defect and it decreases the density of the substance.

Impurity defects:

These defects arise when foreign atoms are present at the lattice site (in place of the host atoms).

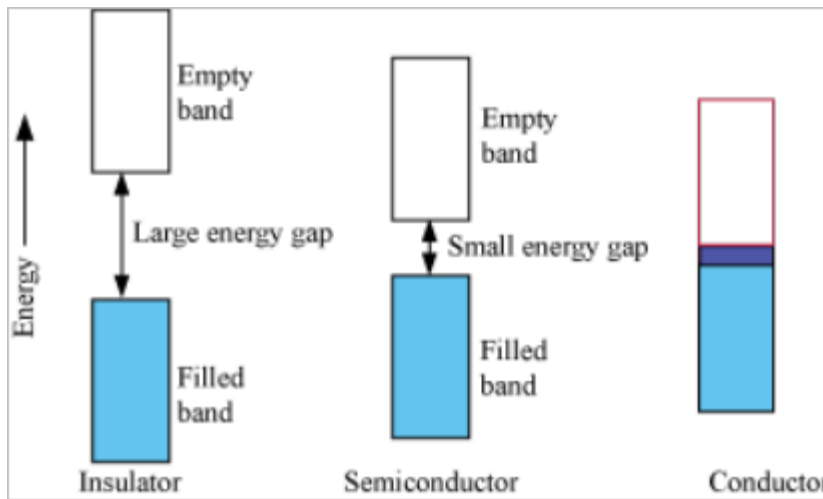
Non-stoichiometric defects:

- Metal excess defect
 - Metal excess defect due to anionic vacancies
 - Metal excess defect due to the presence of extra cations
- Metal deficiency defect: Occurs when the metals show variable valency, i.e., the transition metals

Classification of solids on the bases of conductivities:

- Conductors
- Insulators
- Semiconductors

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Doping: Adding an appropriate amount of suitable impurity to increase conductivity

- ***n*-type semiconductor**
 - Doped with electron-rich impurities
- ***p*-type semiconductor**

-Doped with electron-deficient impurities

- Semiconductors are widely used in electronic industries.

Magnetic properties:

Magnetic properties of substances originate because each electron in an atom behaves like a tiny magnet.

-Classification of substances on the basis of magnetic properties:

- Paramagnetic: e.g., O_2
- Diamagnetic: e.g., H_2O
- Ferromagnetic: e.g., CrO_2
- Anti-ferromagnetic: e.g., MnO
- Ferrimagnetic: e.g., Fe_3O_4

Ferromagnetic substances can be made permanent magnets.

These magnetic properties are used in audio, video and other recording devices.

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Solutions

- **Mixture**

1. Mixtures refer to those substances which consist of two or more elements or compounds, mixed together in any ratio and do not give rise to new compound. For example: sea water, air, chocolate milk etc.
 2. Mixture is composed of two or more substances mixed together in any ratio i.e. the composition is variable and do not possess properties like fixed melting or boiling point.
 3. Mixture shows the properties similar to that of its constituents and they can be separated by using physical and chemical methods.
 4. There are two types of mixtures:
 - i. **Homogeneous mixtures:** Such mixtures have only one phase. They have the same composition throughout and there is no visible separation of line between the constituents. For example: sugar solution, vinegar etc.
 - ii. **Heterogeneous mixture:** Mixtures which has more than one phase is known as heterogeneous mixture. There is a visible boundary of separation between the components and they do not have the same composition throughout.
 5. Homogeneous mixtures are of three types: (i) Solid homogeneous mixture (alloys), (ii) Liquid homogeneous mixture (solution of alcohol in water) and (iii) Gaseous homogeneous mixture (air).
 6. Heterogeneous mixtures are of three types: (i) Solid heterogeneous mixture (mixture of sand and sugar), (ii) Solid-liquid heterogeneous mixture (solution of chalk in water) and (iii) Gaseous heterogeneous mixture (smoke in air).
- **Substance** – Cannot be separated into its constituent particles by any physical process
 - **Solution** – Homogeneous mixture of two or more substances
 - **Alloys** – Homogeneous mixture of metals

- **Solution:**

- The component of the solution that dissolves the other component in it is called solvent (present in larger amount).
- The component of the solution that is dissolved in the solvent is called solute (present in lesser quantity).

- **Properties of solution:**

- Homogeneous mixture
- Particles are extremely small, not visible to the naked eye
- Light path not visible
- Solute particles cannot be separated by filtration

Solubility: Solubility of a substance is the maximum amount of the substance that can be dissolved in a specified amount of a solvent at a specified temperature.

- **Solubility of a solid in a liquid:**

-Effect of temperature (Le Chatelier's principle) –

When the dissolution process is endothermic, the solubility will increase with increase in temperature.

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When the dissolution process is exothermic, the solubility will decrease with increase in temperature.

-Effect of pressure: Pressure does not affect solubility.

- **Solubility of a gas in a liquid:**

Henry's law → The solubility of a gas in a liquid is directly proportional to the pressure of the gas.

Or

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

$$p = K_H x$$

Where, K_H → Henry's law constant

- Some applications of Henry's law –

- The solubility of CO_2 in soft drinks and soda water is increased by sealing the bottles under high pressure.
- At high pressure underwater, scuba divers have to cope with high concentrations of dissolved gases while breathing air.
- At high altitudes, climbers become weak and are unable to think clearly, which are symptoms of a condition called anoxia

Effect of temperature –

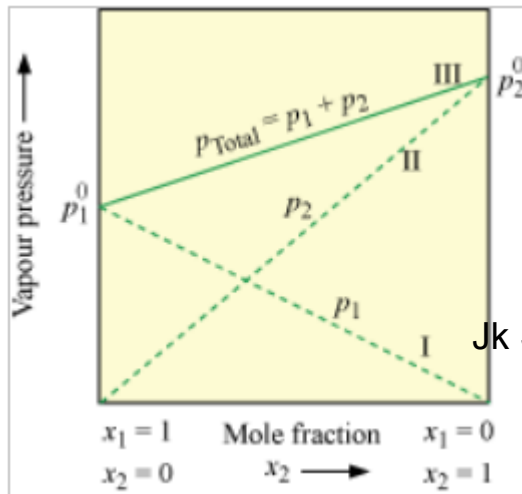
With increase in temperature, the solubility of gases in liquids decreases.

Vapour pressure of liquid solutions:

- Vapour pressure of liquid–liquid solutions:
- Raoult's law → For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

$$p_1 = p_1^o x_1$$

$$p_{\text{total}} = p_1^o + (p_2^o - p_1^o) x_2$$



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(For an ideal solution at constant temperature)

- Vapour pressure of solutions of solids in liquids:

$$p_1 = x_1 p_1^o$$

Ideal and non-ideal solutions:

- Ideal solutions –
Solutions which obey Raoult's law over the entire range of concentrations

$$\Delta_{\text{mix}} H = 0$$

$$\Delta_{\text{mix}} V = 0$$

-In an ideal solution, the solute–solute and solvent–solvent interactions are nearly equal to the solute–solvent interactions.

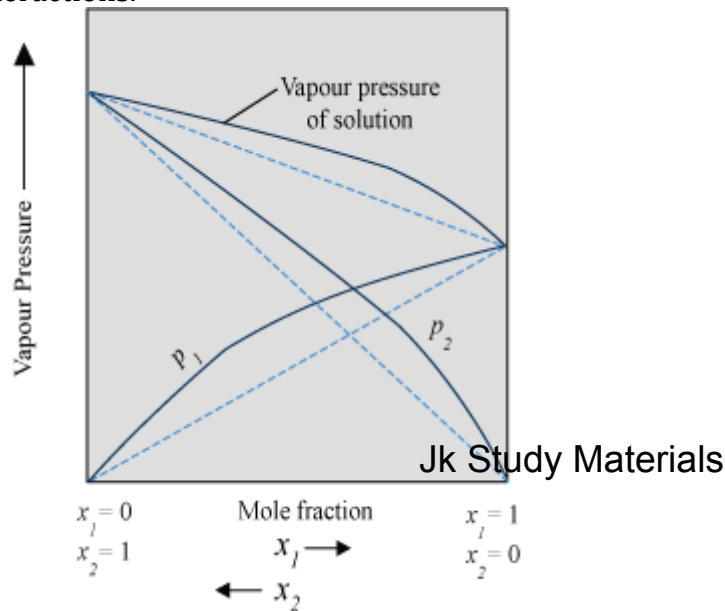
- Non-ideal solutions – Solutions which do not obey Raoult's law over the entire range of concentrations

-Positive deviation from Raoult's law –

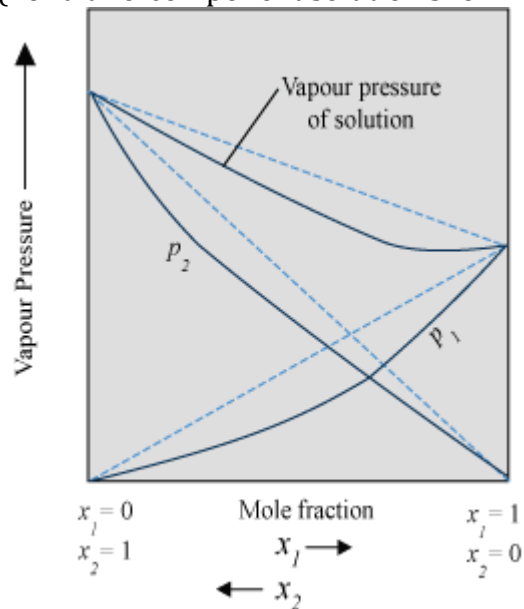
-Vapour pressure of the solution is higher than that predicted by Raoult's law.
-Solute-solvent interactions are weaker than solute-solute and solvent-solvent interactions.

-Negative deviation from Raoult's law –

-Vapour pressure of the solution is lower than that predicted by Raoult's law.
-Solute-solute and solvent-solvent interactions are weaker than solute-solvent interactions.



(For a two-component solution showing positive deviation from Raoult's law)



(For a two-component solution showing negative deviation from Raoult's law)

Colligative properties and determination of molar mass:

- Relative lowering of vapour pressure:**

- Relative lowering of vapour pressure is equal to the mole fraction of the solute.

$$\frac{p_1^0 - p_1}{p_1^0} = x_2$$

i.e.,

$$x_2 = \frac{n_2}{n_1 + n_2}$$

However,

Where, n_2 = Number of moles of solute

n_1 = Number of moles of solvent

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

Now,

For dilute solution, $n_1 \gg n_2$

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1}$$

Therefore,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1}}$$

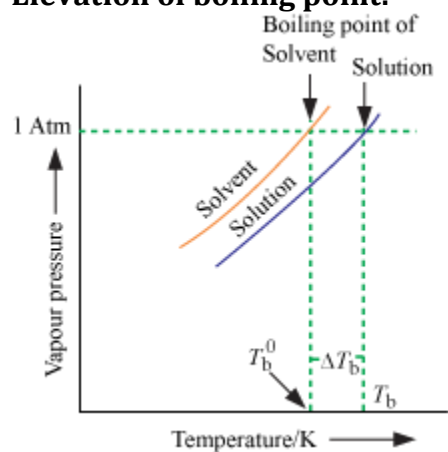
Or,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

Or,

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- Elevation of boiling point:**



- Here, $\Delta T_b = T_b - T_b^0$ = Elevation of boiling point

Where,

T_b = Boiling of solution

T_b^0 = Boiling point of solvent

- $\Delta T_b \propto m$ (for dilute solution)

$$\Rightarrow \Delta T_b = K_b m$$

Where,

m = Molality

K_b = Proportionality constant known as Boiling Point Elevation Constant or Molal Elevation Constant or Ebullioscopic constant (Unit = K kg mol⁻¹)

$$m = \frac{\frac{w_2}{M_2}}{\frac{w_1}{1000}} = \frac{1000 \times w_2}{M_2 \times w_1}$$

However,

Where,

w_2 = Mass of solute

M_2 = Molar mass of solute

w_1 = Mass of solvent

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

Now,

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1}$$

Or,

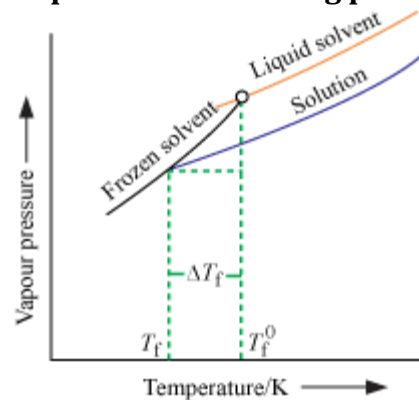
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Where, K_b = Boiling-point elevation constant

Or, Molal elevation constant

Or, Ebullioscopic constant

- **Depression of freezing point:**



- Here, $\Delta T_f = T_f^0 - T_f$ = Depression of freezing point

Where,

T_f^0 = Freezing point of solvent

T_f = Freezing point of solution

- For dilute solution (ideal solution),

$$\Delta T_f \propto m$$

$$\Rightarrow \Delta T_f = K_f m$$

Where,

m = Molality

K_f = Proportionality constant known as Freezing Point Constant or Molal Depression Constant or Cryoscopic constant (Unit = K kg mol⁻¹)

$$m = \frac{\frac{w_2}{M_2}}{\frac{w_1}{1000}} = \frac{1000 \times w_2}{M_2 \times w_1}$$

However,

Where,

w_2 = Mass of solute

M_2 = Molar mass of solute

w_1 = Mass of solvent

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

Now,

$$M_2 = \frac{1000 \times w_2 \times K_f}{\Delta T_f \times w_1}$$

Or,

- The value of K_b and K_f can be determined by the following relations:

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{\text{vap}} H}$$

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{\text{fus}} H}$$

Where,

M_1 = Molar mass of the solvent

R = Gas constant

$\Delta_{\text{vap}} H$ = Enthalpy of vaporisation

$\Delta_{\text{fus}} H$ = Enthalpy of fusion

- Osmosis and osmotic pressure:**

$$\pi = CRT$$

$$\text{Or, } \pi = \left(\frac{n_2}{V} \right) RT$$

$$\text{Or, } M_2 = \frac{w_2 RT}{\pi V} \quad \left[n_2 = \frac{w_2}{M_2} \right]$$

- If two solutions have the same osmotic pressure at a given temperature, then the solutions are called isotonic solutions.
- **Abnormal molar masses:** Molar mass lower or higher than expected or normal value
- **Van't Hoff factor, i :** Expresses the quantitative extent to which a solute is dissociated or associated

$$\frac{p_1^\circ - p_1}{p_1^\circ} = i \frac{n_2}{n_1}$$

$$\Delta T_b = iK_b m$$

$$\Delta T_f = iK_f m$$

$$\pi = i \left(\frac{n_2}{V} \right) RT$$

- **Modification of the equations for colligative properties:**

$$\frac{p_1^\circ - p_1}{p_1^\circ} = i \frac{n_2}{n_1}$$

$$\Delta T_b = iK_b m$$

$$\Delta T_f = iK_f m$$

$$\pi = i \left(\frac{n_2}{V} \right) RT$$

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Electrochemistry

Electrochemical cells:

- Two types – Galvanic cell or voltaic cell, and Electrolytic cell

Galvanic cell:

Converts the chemical energy of a spontaneous redox reaction into electrical energy
Daniell cell -

$$\Delta_r G^\ominus = -RT \ln K$$

The standard potential of a cell is given by

$$\Delta_r G^\ominus = -nFE_{\text{cell}}^\ominus$$

The potential of an individual half cell cannot be measured.

Relation between the standard potential of a cell and standard Gibbs energy:

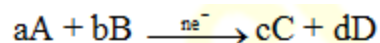
$$\Delta_r G^\ominus = -nFE_{\text{cell}}^\ominus$$

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Relation between standard Gibbs energy and the equilibrium constant:

$$\Delta_r G^\ominus = -RT \ln K$$

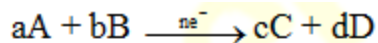
- Nernst equation:
 - Gives the concentration dependence of the potentials of the electrodes and the cells
- For the electrode reaction



Nernst equation is given by

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

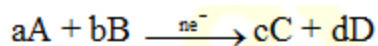
Nernst equation is given by



Nernst equation is given by

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- For a general electrochemical reaction of the type



Nernst equation is given by

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Conductance of electrolytic solutions:

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

Where,

$l \rightarrow$ Length

$A \rightarrow$ Area of cross-section

$\rho \rightarrow$ Resistivity or specific resistance

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

Where, κ Conductivity or specific conductance

The SI unit of conductance is Ω^{-1} (siemens or mho).

The conductivity of an electrolyte depends upon

- nature of the solvent
- nature of the electrolyte added
- concentration of the electrolyte
- temperature

Molar conductivity, $\Lambda_m = \frac{\kappa}{C}$

Variation of conductivity

- For both strong and weak electrolytes, conductivity decreases with decrease in concentration.

Variation of molar conductivity

- For both strong and weak electrolytes, molar conductivity increases with decrease in concentration.

Limiting molar conductivity – molar conductivity when concentration approaches zero

Degree of dissociation, $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$

- Kohlrausch law of independent migration of ions:**

According to this law, for an electrolyte, the molar conductivity at infinite dilution is the sum of the contribution of the molar conductivity of the ions in which it dissociates.

Electrolytic cells and electrolysis

$$1F = 96487 \text{ C mol}^{-1}$$

- Faraday's first law of electrolysis:** The amount of chemical reaction occurring at any electrode during the process of electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.
- Second law of electrolysis:** The amounts of different substances liberated when same quantity of electricity is passed through the electrolytic solution are proportional to their chemical equivalent weights.

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Battery is a galvanic cell in which chemical energy of the redox reaction is converted into electrical energy.

Mainly two types:

- Primary batteries
- Secondary batteries
- Primary Batteries**

In primary batteries, reaction occurs only once.

After use over a period of time, these become dead and cannot be reused.

Examples: Dry cell (or Leclanche cell), Mercury cell

Secondary Batteries

- Secondary batteries can be recharged again by passing current through them in the opposite direction.

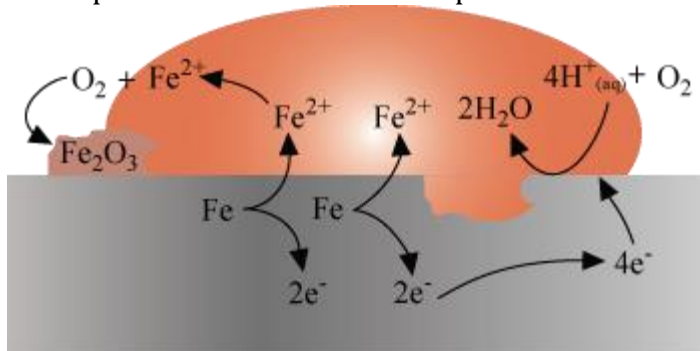
- Examples: Lead storage battery, Nickel-cadmium cell

Corrosion: Oxidation of a metal by loss of electrons to oxygen and formation of oxides

Corrosion of Iron

Known as rusting

The spot where oxidation takes place behaves as anode.



Prevention of Corrosion

- Preventing the surface of the metal from coming in contact with atmosphere
- By covering the surface with paint or chemicals such as bis-phenol
- By covering the surface with other metals such as Sn, Zn, Mg.

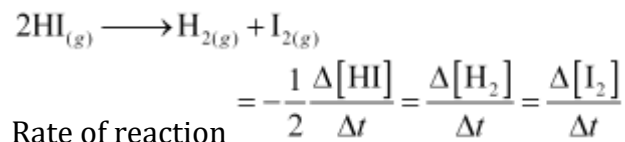
The Hydrogen Economy: Based on electrochemical principles

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Chemical Kinetics

For a reaction $R \rightarrow P$

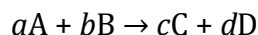
$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$



Factors influencing the rate of a reaction:

Rate of a reaction depends upon the concentration of reactants (pressure in the case of gas), temperature and catalyst.

- Rate expression and rate constant



Rate expression

$$\therefore \text{Rate} \propto [A]^x [B]^y$$

Differential rate equation ®

$$\Rightarrow -\frac{d[R]}{dt} = k[A]^x [B]^y \quad (1)$$

Where, k is called rate constant

- Order of a reaction:

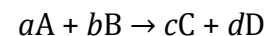
$$\text{Rate} = k[A]^x [B]^y$$

x is Order of the reaction with respect to A

y is Order of the reaction with respect to B

$x + y$ is Overall order of the reaction

1. Order of a reaction can be 0, 1, 2, 3 and even a fraction
2. Units of rate constant



$$\text{Rate} = k[A]^x [B]^y$$

$x + y = n = \text{Order of the reaction}$

$$k = \frac{[\text{Rate}]}{[\text{A}]^x [\text{B}]^y}$$

$$= \frac{\text{Concentration}}{\text{Time}} \times \frac{1}{(\text{Concentration})^n}$$

[[A] = [B] and $x + y = n = \text{Order of the reaction}$]

1. For a zero-order reaction, $n = 0$

$$\text{Unit of } \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1} \text{s}^{-1}$$

1. For a first-order reaction, $n = 1$

$$\text{Unit of } \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$$

1. For a second-order reaction, $n = 2$

$$\text{Unit of } \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{L s}^{-1}$$

- **Molecularity of a reaction:**

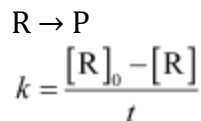
The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction

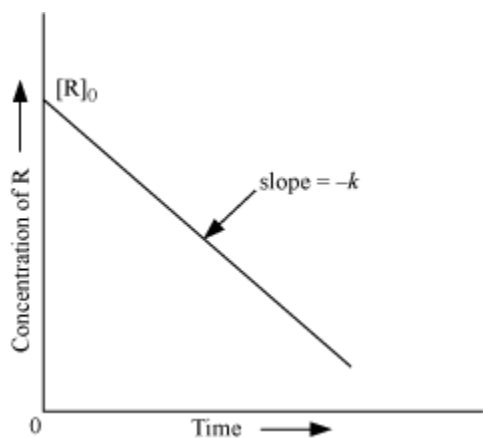
- **Order versus molecularity**

1. Order can be zero and even a fraction. But molecularity cannot be zero or a non-integer.
2. Order is applicable to both elementary and complex reactions whereas molecularity is applicable to elementary reactions only.

Integrated rate equations:

- **Zero-order reactions:**



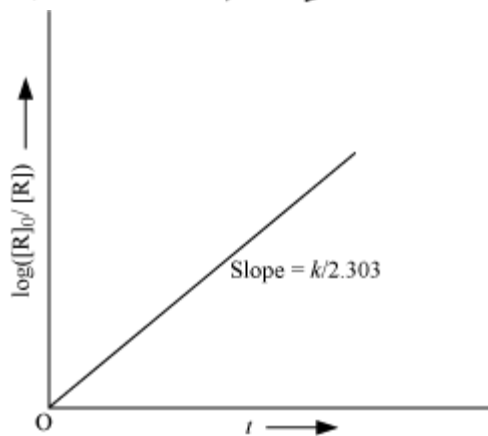
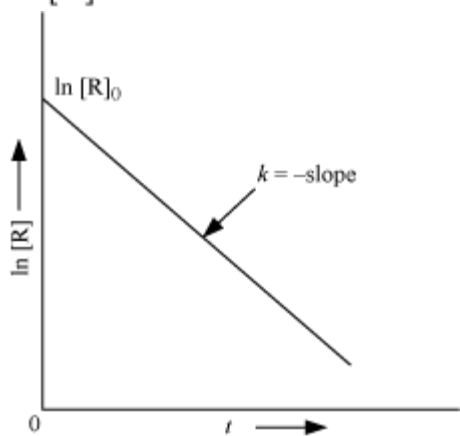


- First-order reactions:**



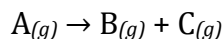
$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\therefore \frac{d[R]}{[R]} = -k dt$$



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- For a typical first-order gas phase reaction:



Here, p_i is initial pressure of A

$P_t = (p_A + p_B + p_C) = \text{Total pressure at time } t$

$$\therefore k = \frac{2.303}{t} \log \frac{p_i}{p_A}$$

$$\Rightarrow k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

- Half-life of a reaction:**

- For a zero-order reaction:

$$t_{1/2} = \frac{[R]_0}{2k}$$

- For a first-order reaction:

$$t_{1/2} = \frac{0.693}{k}$$

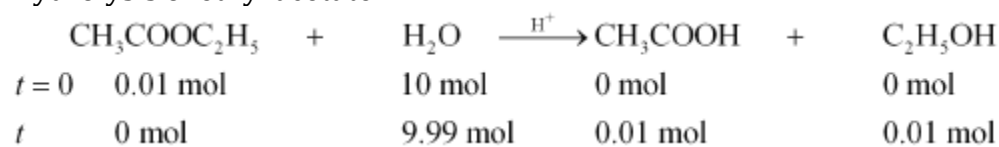
t_1

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That is, $t_{1/2}$ is independent of $[R]_0$

- Pseudo first-order reaction:**

Hydrolysis of ethyl acetate –



$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

Here, $[\text{H}_2\text{O}]$ is constant

So, rate = $k [\text{CH}_3\text{COOC}_2\text{H}_5]$

Where, $k = k' [\text{H}_2\text{O}]$

Temperature dependence of the rate of reaction:

- For a chemical reaction, with a rise in temperature by 10° , the rate constant is nearly doubled.
- Arrhenius equation:**

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

Where,

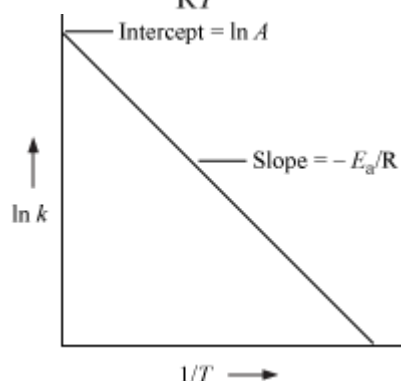
A is Arrhenius factor or frequency factor or pre-exponential factor

R is Gas constant

E_a is Activation energy

On taking natural logarithm on both sides, we have

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



If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, then

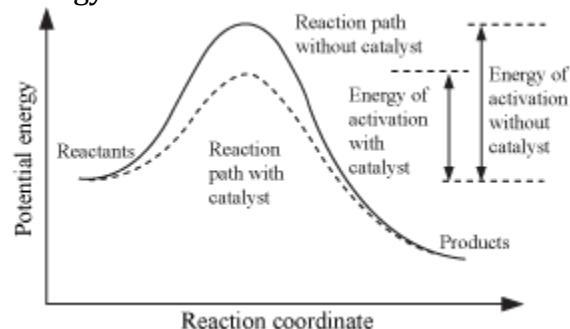
$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\text{or, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

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- Effect of a catalyst:**

A catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy.



- Collision frequency (Z) → The number of collisions per second per unit volume of the reaction mixture

For the reaction $A + B \rightarrow \text{Products}$,

$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$

Where,

Z_{AB} → Collision frequency of reactants A and B

$e^{-E_a/RT}$ → The fraction of molecules with energies equal to or greater than E_a

To account for effective collisions, another factor P (called the probability or steric factor) is introduced.

Then, rate =

$$PZ_{AB} e^{-E_a/RT}$$

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Surface Chemistry

Adsorption: Phenomenon of accumulation of molecules at the surface of a solid, which results in a higher concentration on the surface than in the bulk

- **Adsorbate:** The substance which gets adsorbed onto a surface
- **Adsorbent:** The substance on which adsorption takes place
- **Desorption:** The phenomenon of removing an adsorbate from an adsorbent

- **Types of adsorption –**

1. **Physical adsorption or physisorption**
2. **Chemical adsorption or chemisorption**

	Physisorption		Chemisorption
1.	Arises because of van der Waals forces	1.	Arises because of chemical forces
2.	Not specific in nature	2.	Highly specific in nature
3.	Reversible	3.	Irreversible
4.	Enthalpy of adsorption is low	4.	Enthalpy of adsorption is high
5.	No appreciable activation energy is required	5.	Sometimes, high activation energy is required
6.	Results in multi-molecular layers	6.	Results in uni-molecular layer

- Gas is adsorbed in almost all solids.

- **Factors on which the extent of adsorption of a gas on a solid depends upon:**

- Nature of the gas
- Nature of the solid
- Surface area of the solid
- Pressure of the gas
- Temperature of the gas

- **Adsorption isotherm:**

The relation between the extent of adsorption (x/m) and the pressure of a gas at constant temperature

1. **Freundlich adsorption isotherm –**

$$\frac{x}{m} \propto P^{\frac{1}{n}}$$

$$\frac{x}{m} = kP^{\frac{1}{n}} \quad n > 1$$

Now, taking log,

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

- **Applications of Adsorption**

- Production of high vacuum.
- Gas mask.
- Silica and aluminium gels are used as adsorbents for controlling humidity.
- A number of drugs are used for killing germs; the drugs get adsorbed on the germs.
- Used in heterogeneous catalysis
- Used in chromatographic analysis.
- The substance which alters the rate of a reaction, but itself remains chemically and quantitatively unaltered after the reaction is called a catalyst.

- The phenomenon of using a catalyst is called catalysis.

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- The substances which enhance the activity of a catalyst are called promoters.
- The substances which decrease the activity of a catalyst are called poisons.
- Broadly divided into two groups:
 - Homogeneous catalysis – The reactants and the catalyst are in the same phase
 - Heterogeneous catalysis – The reactants and the catalyst are in different phases

- **Shape selective catalysis:**

Catalysis that depends upon the pore structure of the catalyst, and the size of the reactant and the product

- **Enzyme catalysis or biochemical catalysis:** An enzyme acts as the catalyst
- Highly specific in nature
- Highly active under optimum temperature and pH
- Influenced by inhibitors and poisons

- **Industrial catalytic processes:**

- Haber's process
- Ostwald's process
- Contact process

Colloids:

- Heterogeneous system
- Intermediate between true solutions and suspensions
- Consist of two phases – Dispersed phase and dispersion medium
- Classification of colloids: Colloids are classified depending upon the following three criteria.

Physical state of the dispersed phase and the dispersion medium

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Gem stones, some coloured glasses
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud
Gas	Solid	Solid sol	Stone, foam rubber
Gas	Liquid	Foam	Froth, soap lather

Nature of interaction between the dispersed phase and the dispersion medium

- **Lyophilic colloids (solvent attracting):**

- Also called reversible sols
- Quite stable and cannot be easily coagulated

- **Lyophobic colloids (solvent repelling):**

- Also called irreversible sols
- Can be easily coagulated

- **Type of particles of the dispersed phase**

- Multi-molecular colloids
- Macromolecular colloids
- Associated colloids (Micelles)

- The temperature above which the formation of micelles takes place is called Kraft temperature (T_k).
- The concentration above which the formation of micelles takes place is called critical micelle concentration (CMC).

- **Preparation of colloids:**

- Chemical method
- Electrical disintegration or Bredig's Arc method
- Peptisation – Process of converting a precipitate into colloidal sol by shaking it with the dispersion medium in the presence of a small amount of electrolyte

- **Purification of colloidal solutions:**

Reduction of the amount of impurities to a requisite minimum

- Dialysis – Process of removing a dissolved substance by diffusion through a suitable membrane
- Electro dialysis
- Ultra-filtration

- **Properties of colloidal solutions:**

- Colligative properties
- Tyndall effect
- Colour
- Brownian movement
- Charge on colloidal particles
- **Electrophoresis**– Movement of colloidal particles under applied electric potential.
- **Electro osmosis** – Movement of dispersion medium through membrane in an applied electric field.
- **Coagulation or precipitation** – Process of settling of colloidal particles.
- Ways to carry out coagulation of sol are:
 1. By electrophoresis
 2. By mixing two oppositely charged sols
 3. By boiling
 4. By persistent dialysis
 5. By addition of electrolytes
 6. Hardy-Schulze rule: The greater the valence of the flocculating ion added, the greater is its power to cause precipitation.

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Emulsions

- A colloidal system.
- both the dispersed phase and the dispersion medium are liquids
- There are two types –
 - Oil dispersed in water (O/W type)
 - Water dispersed in oil (W/O type)
 - Emulsifying agent: The third component used for stabilising an emulsion
 - Emulsification: Process of making an emulsion

Colloids around Us

- Dust particles in sky, milk, butter, fruit juices, fog, smoke, mist, rain, blood, river water etc..

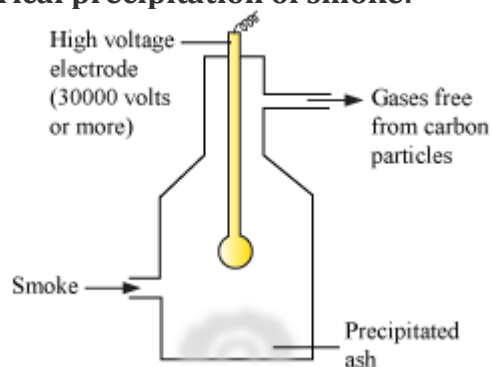
Applications of Colloids

- Purification of drinking water.
- Colloidal Medicines
- Example: Milk of magnesia (an emulsion)

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- Cleansing action of soaps and detergents
- Photographic plates or films
- Paints, inks, rubber, graphite lubricants, etc.,.
- Rubber industry.

Electrical precipitation of smoke:



General Principles and Processes of Isolation of Elements

Occurrence of metals:

Metal	Ores	Composition
Aluminium	Bauxite	$\text{AlO}_x(\text{OH})_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[\text{Al}_2 (\text{OH})_4 \text{Si}_2\text{O}_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	FeCO_3
	Iron pyrites	FeS_2
Copper	Copper pyrites	CuFeS_2
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	ZnCO_3
	Zincite	ZnO

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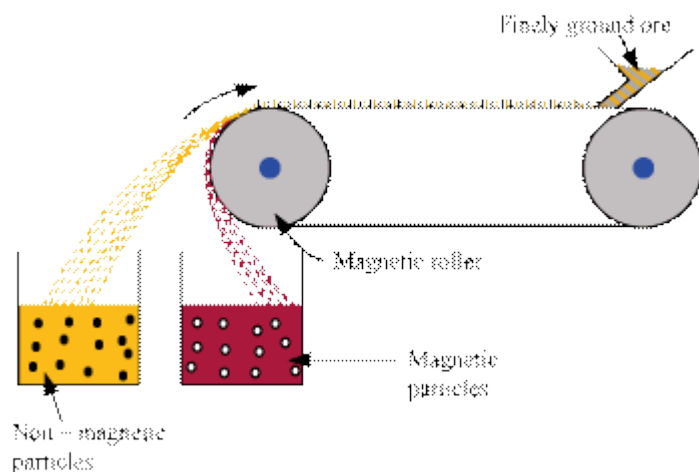
- **Metallurgy:** Process of extracting pure metal from their ore
- **Minerals:** Mixture of metal compounds, soil, sand, limestone and rock
- **Gangue:** Impurities present in ore like mud, silica etc.
- **Ores:** Minerals from which metals can be extracted economically at low cost and with minimum cost
- **Flux:** Substance added in furnace to remove gangue
- **Slag:** The fusible mass formed when flux combined with gangue
- **Smelting:** Process of extracting metal from their oxide ores by reducing the roasted oxides

The major steps involved in the extraction and isolation of metals from ores are:

1. Crushing and grinding ore
2. Concentration of the ore
3. Roasting and Calcination of the ore
4. Reduction of the metal oxide
5. Refining of the pure metal

Concentration of ores:

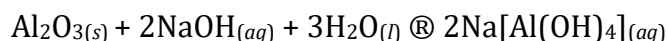
- Hydraulic washing: It is the washing away of lighter gangue particles from the heavier ore. It is based on the gravity difference between the ore and the gangue particles.
- Magnetic separation: This separation is carried out if either the ore or the gangue is attracted by a magnetic field.



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- Froth floatation method: This method is used for removing gangue from sulphide ores. 'Depressants' are used for separating two sulphide ores. E.g., for separating ZnS and PbS, NaCN is used as the depressant.
- Leaching: If the ore is soluble in some suitable solvent, then this process is used. For example, ores of aluminium (bauxite), silver and gold

1. Leaching of alumina



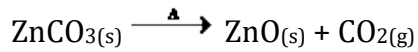
Isolation of crude metal from concentrated ore: It involves two steps –

(i) Conversion into oxide and (ii) Reduction of the oxide to metal

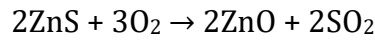
- Conversion into oxide:

1. Calcination → Involves heating

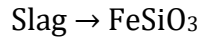
Generally, carbonate ores are converted into oxides by this process.



1. Roasting → Involves heating in a regular supply of air, at a temperature below the melting point of the metal.



Generally, sulphide ores are converted into oxides by this process.



- Reduction of the oxide to metal:

Involves heating with some reducing agents such as C, CO or another metal.

Thermodynamic principles of metallurgy: For any process, the change in Gibbs energy at a temperature is given by

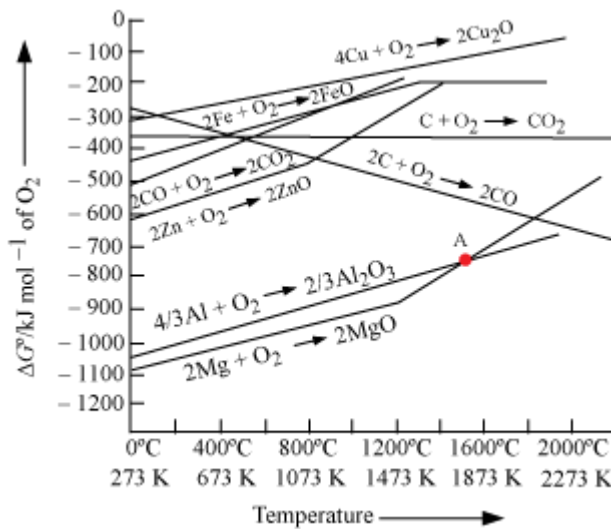
$$\Delta G = \Delta H - T\Delta S$$

$$\text{and } \Delta G^\theta = -RT \ln K$$

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A reaction will proceed when the value of ΔG is negative.

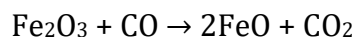
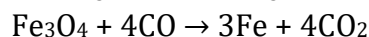
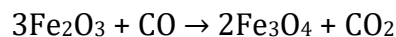
- Applications:



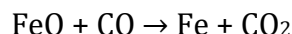
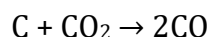
If $\Delta G_{(X, \text{XO})}$ is lower than $\Delta G_{(Y, \text{YO})}$, then X can reduce YO.

Extraction of iron from its oxides:

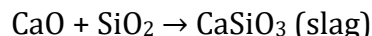
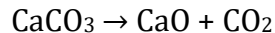
1. Reaction taking place in a blast furnace
2. At 500 – 800 K



1. At 900 – 1500 K



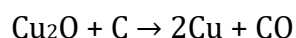
1. Limestone is decomposed to CaO, which removes silicate impurity as slag.



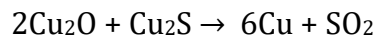
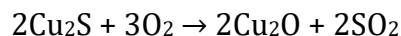
1. Pig iron is the iron obtained from a blast furnace, which contains about 4% carbon and impurities like S, P, Si, Mn in smaller amounts.
2. Cast iron (contains about 3% carbon) is obtained by melting pig iron with scrap iron and coke, using hot-air blast.

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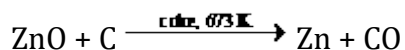
1. **Extraction of copper from cuprous oxide:**



1. Copper matte contains Cu_2S and FeS . It is put in the silica-lined converter to convert the remaining $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$ into metallic copper.

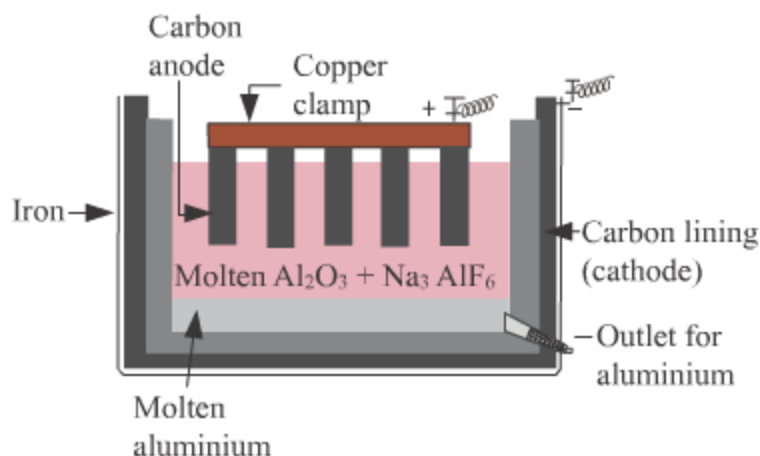


1. Extraction of zinc from zinc oxide:

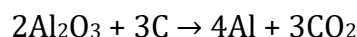


Electrochemical principles of metallurgy: A more reactive metal displaces a less reactive one from its salt solution.

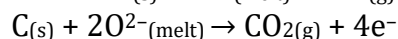
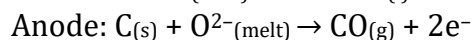
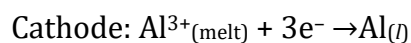
- **Extraction of aluminium:**



1. Purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 to lower the melting point and bring conductivity.
2. The overall reaction –

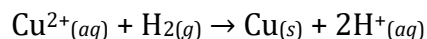


1. This electrolytic process is known as Hall-Heroult process.
2. The electrolytic reactions are – **Jk Study Materials**



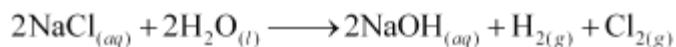
○ **Copper from low-grade ores and scraps:**

Copper is extracted by hydrometallurgy from low-grade ores. The solution containing Cu^{2+} is treated with scrap iron or H_2 .



Extraction of Chlorine from Brine

- oxidation reaction

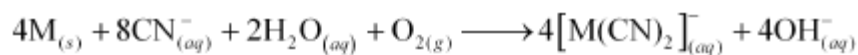


- $E^0 = 2.2 \text{ V}$
- Requires an external emf greater than 2.2 V. But the
- Electrolysis requires an excess potential to overcome some other hindering reactions.

- Electrolysis of molten NaCl produces Na metal in the place of NaOH.

Extraction of Gold and Silver

- Metal is leached with NaCN or KCN.
- Ag is oxidised to Ag^+ and Au is oxidised to Au^+



(M = Ag or Au)



Refining (Purification):

- **Distillation –**

The impure forms of low-boiling metals like zinc and mercury are evaporated to obtain pure metals as distillate.

- **Liquation –**

Low-melting metals (like tin) are separated from higher-melting liquids by allowing them to flow on a sloping surface.

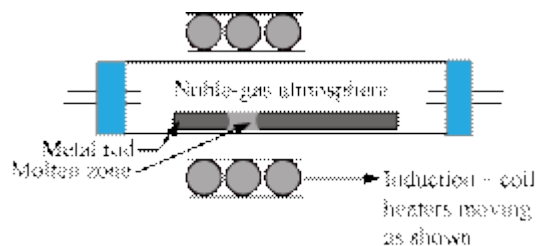
- **Electrolytic refining –**

Anode: $\text{M} \rightarrow \text{M}^{n+} + n\text{e}^-$

Cathode: $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}$

- Impure metal is taken as anode and a strip of pure metal is taken as cathode.
- Copper and zinc are refined by this process.
- Anode mud obtained during electrolytic refining of copper contains antimony, selenium, tellurium, silver, gold and platinum.

- **Zone refining –**



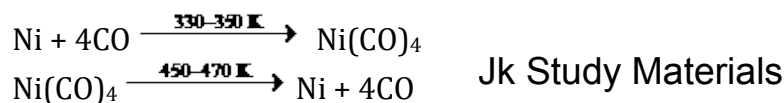
- Principle – The impurities are more soluble in the molten state than in the solid state of a metal.
- Germanium, silicon, boron, gallium, indium are refined by this process.

- Vapour-phase refining –**

Requirements –

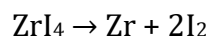
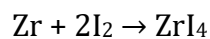
- The metal should form a volatile compound with an available reagent.
- The volatile compound should be easily decomposed so that it can be recovered easily.

- Mond process for refining nickel:



- van Arkel method for refining zirconium (Zr) or titanium (Ti):

Used for removing oxygen and nitrogen present as impurities

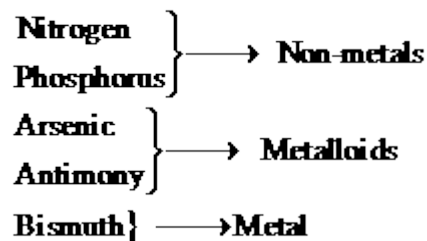


- Chromatographic methods:**

- Principle – Different components of a mixture are differently adsorbed on an adsorbent.
- Chromatography involves a mobile phase and a stationary phase.
- There are several chromatographic techniques –
- Paper chromatography
- Column chromatography
- Gas chromatography

The p-Block Elements

Group 15 elements:



- The valence shell electronic configuration is $ns^2 np^3$.
- Nitrogen differs in chemical properties from other elements of the group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of d -orbitals.
- They exhibit two oxidation states, +3 and +5. Heavier elements exhibit mainly +3 oxidation state due to inert pair effect.

The main use of nitrogen is in the manufacture of ammonia

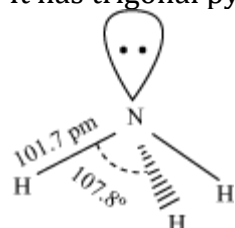
Ammonia

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- On a small scale, ammonia is obtained from ammonium salts, which decompose when treated with caustic soda or lime. It forms metal salt, water, and ammonia gas.

Ammonia can also be prepared by treating metal nitrides with warm water.

- It has trigonal pyramidal structure with nitrogen atom at the apex.



- **Forms**

- Dry ammonia gas (gaseous ammonia)
 - Liquid ammonia (liquified ammonia)
 - Liquor ammonia fortis (saturated solution of ammonia in water)
 - Laboratory bench reagent (dilute solution of liquor ammonia)
- On large scale, ammonia is obtained by **Haber's process**.

- Raw material: Mixture of hydrogen and nitrogen gases in the ratio 3:1
- Pressure: 200 atm to 900 atm pressure
- Temperature: 450 – 500°C
- Catalyst: Finely divided iron
- Promoter: molybdenum or Al₂O₃

- **Properties:**

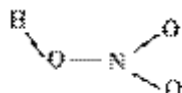
- It is a colourless non-poisonous gas with a characteristic pungent odour.
- It is lighter than air and extremely soluble in water because of hydrogen bonding.
- It can be liquefied when cooled to 10 ° C under pressure of 6 atm. It forms white crystals on cooling.
- It has basic nature because of the presence of lone pair of electrons.
- It acts as a reducing agent.
- Inhaling this gas causes irritation to the eyes and respiratory system.

- **Uses:**

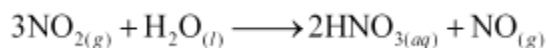
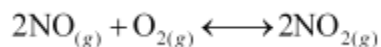
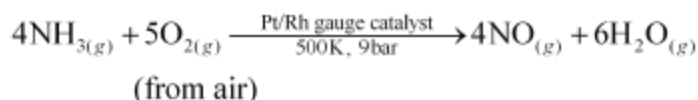
- Due to high dielectric constant, ammonia is a good solvent for ionic compounds.
- It is used as a cleaning agent for removing grease in dry cleaning.
- It is used in the manufacturing of artificial silk.
- It is used as laboratory reagent.

- Nitric acid (HNO₃)

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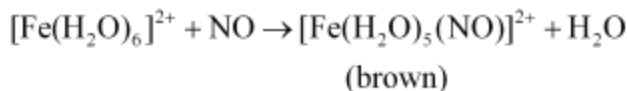
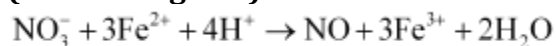


1. Preparation: Ostwald's process

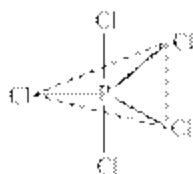


- **Detection of the presence of nitrate:**

(Brown ring test)



- Phosphorus exists as P_4 in elemental form.
- Allotropic forms of phosphorus:**
 - White phosphorus
 - Red phosphorus
 - Black phosphorus (α -block phosphorus and β -block phosphorus)
- Phosphorus forms two types of halides, PX_3 ($X = F, Cl, Br, I$) and PX_5 ($X = F, Cl, Br$).
- The structure of PCl_5 is trigonal bipyramidal



- Phosphorus forms a number of oxoacids such as ortho-phosphoric acid (H_3PO_4), ortho-phosphorus acid (H_3PO_3), hypo-phosphorus acid (H_3PO_2).
- The oxoacids containing P – H bond are strong reducing agents.

Group 16 elements: (known as chalcogens)

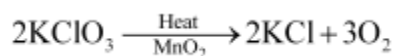
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Oxygen
Sulphur
Selenium
Tellurium
Polonium

- The valence shell electronic configuration is $ns^2 np^4$.

Like nitrogen, oxygen differs from other elements of the group due to its small size and high electronegativity

1. Preparation:



- Three stable isotopes – ^{16}O , ^{17}O , ^{18}O

Uses

- In normal respiration and combustion

- As an oxidant (in liquid state) for propelling rockets
- In oxyacetylene welding
- In the manufacture of many metals (particularly steel)
- Oxygen cylinders are used in hospitals, high altitude flying and mountaineering.

Acidic oxides – Combine with water to give an acid

Example – SO_2 , Cl_2O_7 , CO_2 , N_2O_5

Basic oxides – Combine with water to give bases

Examples – Na_2O , CaO , BaO

Amphoteric oxides – Show the characteristics of both acidic as well as basic oxides

React with both acids and alkalies

Example – Al_2O_3

Neutral oxides – Neither acidic nor basic

Examples – CO , NO , N_2O

Ozone (O_3) is an allotropic form of oxygen. It is a powerful oxidising agent.

• Sulphur –

Allotropic forms of sulphur:

1. Rhombic sulphur (α – sulphur)
2. Monoclinic sulphur (β – sulphur)

Both rhombic and monoclinic sulphur exist as S_8 molecules.

Oxides of sulphur – SO_2 , SO_3

Sulphur Dioxide

- In laboratory, sulphur dioxide is prepared by treating sulphites of active metal with dilute sulphuric acid.
- It causes headache when inhaled in small amount while it might prove fatal in large amounts.
- It is a pungent smelling gas, which is soluble in water.
- It is heavier than air and its boiling point is 263 K.
- It is neither combustible nor does it support combustion. Also, it has both acidic and bleaching properties.
- It reacts with alkalis such as sodium hydroxide. When sulphur is present in limited amount, it forms their respective soluble sulphites and water, but when sulphur is present in excess amount, it forms their respective metal hydrogen sulphites.

- It reduces chlorine water to hydrochloric acid and forms sulphuryl chloride with dry chlorine gas.
- Moist sulphur dioxide behaves as a reducing agent.

Sulphuric Acid

- Concentrated sulphuric acid is known as oil of vitriol. It occurs in free state in hot water of sulphur springs. In combined state, it occurs as mineral sulphates.
- Sulphuric acid is prepared by contact process. It involves burning of a pure and dry mixture of two parts of sulphur or sulphide ores and one part of air in the presence of vanadium pentoxide or platinised asbestos as catalyst.
- Chemical reactions of H_2SO_4 are because of its
 1. low volatility
 2. strong acidic character
 3. strong affinity for water
 4. ability to act as an oxidising agent
- Dilute sulphuric acid reacts with active metals, metal oxides, metal hydroxides, metal carbonates, metal sulphites to form their respective metal sulphates and acid sulphates.
- Because of low volatility, it can be used for the manufacture of more volatile acids from their corresponding salts.
- It is a strong dehydrating agent. Because of its strong affinity for water, sulphuric acid removes water from hydrated salts and organic compounds.
- Concentrated sulphuric acid is a moderately strong oxidising agent and can oxidise both metals and non-metals.

Fluorine
Chlorine
Bromine
Iodine
Astatine

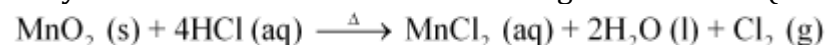
- The valence shell electronic configuration is $ns^2 np^5$.
- They have very high electronegativity.
- The common oxidation state is -1 . However, $+1$, $+3$, $+5$ and $+7$ oxidation states are also exhibited.

- Fluorine show anomalous properties in the group due to its very small size.
- Chlorine has an atomic number 17 and an atomic mass of 35.5 u.
- It does not occur in free state as it is highly reactive in nature.

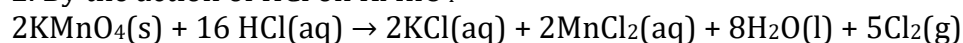
Manufacture of chlorine:

- **Laboratory methods of preparation of chlorine**

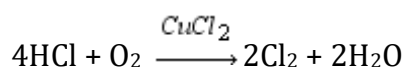
1. By the oxidation of conc. HCl and manganese dioxide (MnO₂)



2. By the action of HCl on KMnO₄



- **Deacon's process:**



Physical properties of chlorine:

- It is a greenish yellow gas.
- It has a pungent smell.
- It has a slight sour taste.
- It is fairly soluble in water.
- It is 2.5 times heavier than air.
- It is poisonous in nature. When inhaled, it causes severe headache accompanied by cough and breathlessness.

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Chemical properties of chlorine:

- Chlorine gas is non-combustible.
- Chlorine reacts with water to form hypochlorous acid.
- It reacts with burning sodium to form sodium chloride.
- When white phosphorus comes in contact with chlorine, it melts and spontaneously catches fire to form dense white fumes.
- It has strong affinity for hydrogen.
- It reacts with slaked lime to give bleaching powder.

- HOCl releases nascent oxygen, which is responsible for oxidising and bleaching action.
- Bleaching effect of Cl₂ is permanent. It bleaches vegetable or organic matter in the presence of moisture.

Hydrogen Chloride

- In laboratory, hydrogen chloride gas is prepared by heating sodium chloride with concentrated sulphuric acid.
- It is also prepared by burning hydrogen gas in the atmosphere of chlorine gas or by exposing hydrogen gas and chlorine gas to diffused sunlight.
- It is colourless and pungent-smelling with sour taste and a very irritating odour.
- It is extremely soluble in water.
- Hydrogen chloride is neither combustible nor does it support combustion.
- On heating at above 500°C, it dissociates into hydrogen and chlorine.
- On mixing with ammonia gas, it forms dense white fumes due to formation of ammonium chloride.

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- Aqueous solution of hydrogen chloride is called **hydrochloric acid**.
- It is prepared by dissolving hydrogen chloride in water.
- It reacts with metals to form respective chlorides and hydrogen gas.
- **Aqua regia** is a mixture of 3 parts of concentrated hydrochloric acid and 1 part of concentrated nitric acid. It is a very corrosive acid and is the only known acid that can dissolve gold.
- Halogens form a number of oxoacids.

Halic (I) acid (Hypohalous acid)	HO₂F (Hypo-fluorous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (III) acid (Halous acid)	–	HOClO (Chlorous acid)	–	–
Halic (V) acid (Halic acid)	–	HOClO ₂ (Chloric acid)	HOBrO ₂ (Bromic acid)	HOIO ₂ (Iodic acid)
Halic (VII) acid	–	HOClO ₃ (Perchloric acid)	HOBrO ₃ (Perbromic acid)	HOIO ₃ (Periodic acid)

(Perhalic acid)				
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- Halogens form a number of inter-halogen compounds (compounds formed by two different halogens).

Type	Formula	Structure
XX'_3	ClF ₃	Bent T-shaped
	BrF ₃	Bent T-shaped
	IF ₃	Bent T-shaped
	ICl ₃	Bent T-shaped
XX'_5	IF ₅	Square pyramidal
	BrF ₅	Square pyramidal
	ClF ₅	Square pyramidal
XX'_7	IF ₇	Pentagonal bipyramidal

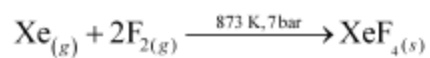
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Helium
Neon
Argon
Krypton
Xenon
Radon

- The valence shell electronic configuration is $ns^2 np^6$. (Exception: Helium $\rightarrow 1s^2$)
- **Physical Properties**
 - Monoatomic
 - Colourless, odourless, and tasteless
 - Sparingly soluble in water
 - Low melting and boiling points.
- **Xenon-Fluorine Compounds**



(Xe in excess)



(1:5 ratio)



(1:20 ratio)

Structure

- $\text{XeF}_2 \longrightarrow$ Linear
- $\text{XeF}_4 \longrightarrow$ Square planar
- $\text{XeF}_6 \longrightarrow$ Distorted octahedral

Xenon-Oxygen Compounds

XeO_3 has a pyramidal

XeOF_4 has a square pyramidal

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Coordination Compounds

Coordination compounds:

These are the complex compounds in which transition metal atoms are bound to a number of anions or neutral molecules.

Postulates of Werner's theory of coordination compounds:

- In coordination compounds, there are two types of linkages (valences) – primary and secondary.
- The primary valences are ionisable and are satisfied by negative ions.
- The secondary valences are non-ionisable and are satisfied by negative ions or neutral molecules. The secondary valence is equal to the coordination number of a metal and remains fixed for a metal.
- Different coordination numbers have characteristic spatial arrangement of the ions or groups bound by the secondary linkages.

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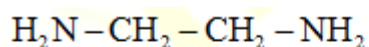
Difference between a double salt and a complex:

- In water, a double salt dissociates completely to give simpler ions. Examples of double salt: carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), Mohr's salt [$\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$]
- Complex ions do not dissociate further to give simpler ions. For example, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

Ligands:

Ions or molecules bound to the central metal atom or ion in the coordination entity

- **Didentate –**

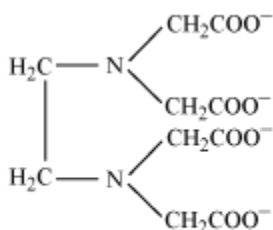


Ethane-1,2-diamine



Oxalate

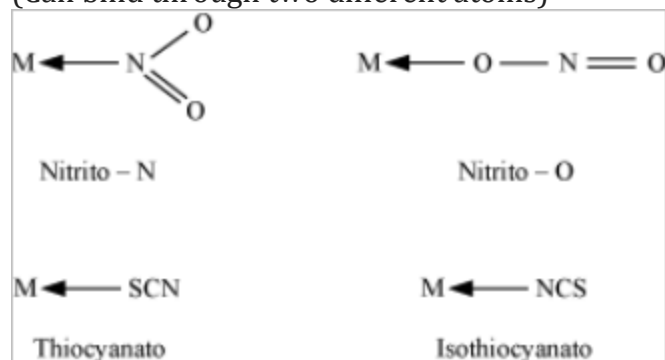
- **Polydentate –**



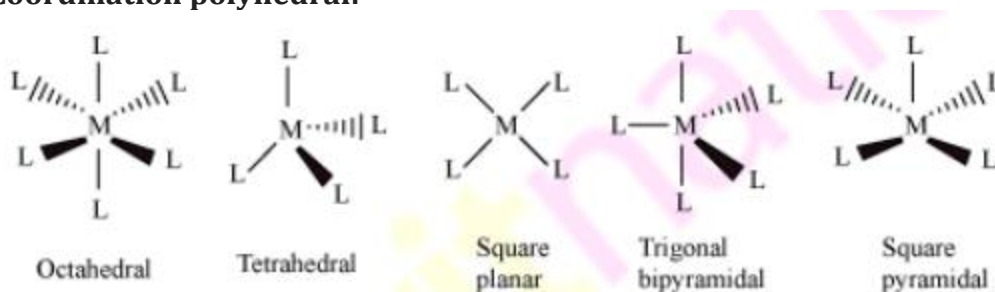
Ethylenediaminetetraacetate (EDTA^{4-})

- Ambidentate -**

(Can bind through two different atoms)



Coordination number: Number of ligands bonded directly to the metal
Coordination polyhedral:



Homoleptic and heteroleptic complexes:

- Homoleptic complexes: In these complexes, the metal is bound to only one kind of donor group, e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Heteroleptic complexes: In these complexes, the metal is bound to more than one kind of donor groups, e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

Naming of mononuclear coordination compounds:

- The cation is named first in both positively and negatively charged coordination entities.

- The ligands are named in alphabetical order, before the name of the central atom/ion.
- Names of the anionic ligands end in -o.

[Exceptions: aqua (H_2O), ammine (NH_3), carbonyl (CO), nitrosyl (NO)]

- To indicate the number of the individual ligands, the prefixes mono-, di-, tri-, etc., are used. If these prefixes are present in the names of ligands, then the terms bis-, tris-, tetrakis-, etc., are used.
- Oxidation state of the metal is indicated in Roman numerals, in parentheses.
- If the complex ion is cation, then the metal is named as the element.

If the complex ion is anion, then the metal is named with '-ate' ending.

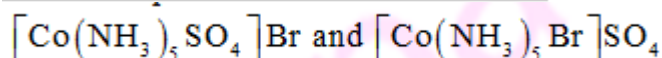
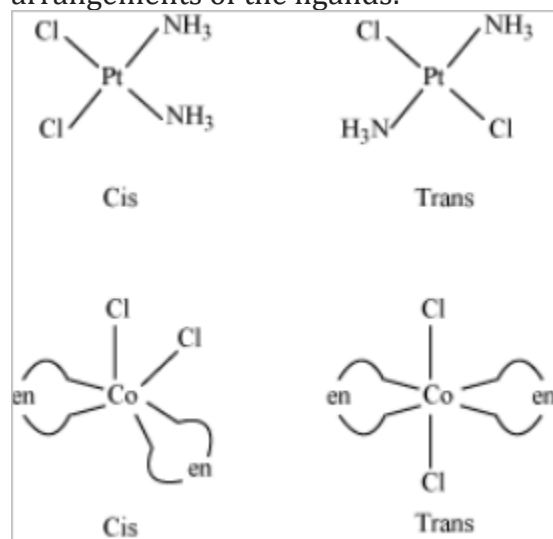
- The neutral complex molecule is named as the complex cation.

Isomerism in coordination compounds:

- **Stereoisomerism –**

Geometrical isomerism:

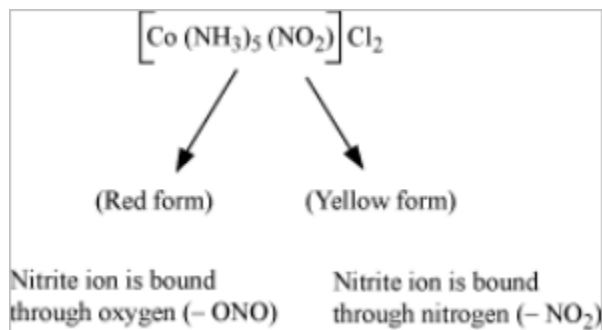
This type of isomerism arises in heteroleptic complexes due to different geometric arrangements of the ligands.



- **Optical isomerism:**

Optical isomers (enantiomers) are mirror images which cannot be superimposed on one another.

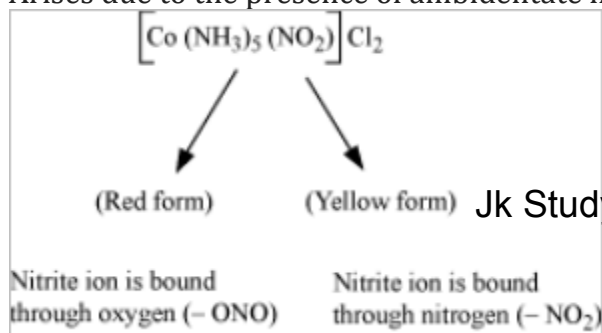
- The molecules or ions which cannot be superimposed on their mirror images are called **chiral** or **optically active**.



- Structural isomerism –**

- Linkage isomerism:**

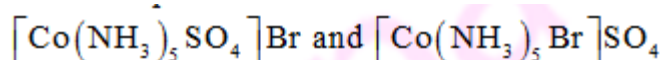
Arises due to the presence of ambidentate ligand



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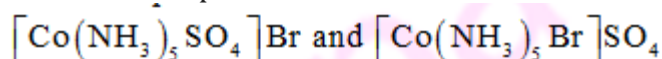
- Coordination isomerism:**

Arises due to the interchange of ligands between cationic and anionic entities of different metal ions



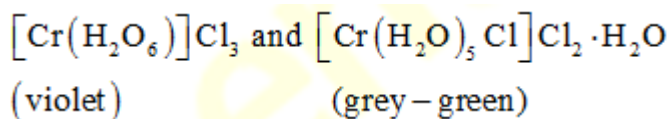
- Ionisation isomerism:**

Arises due to the interchange of ligands between the inside and the outside of the coordination sphere



- Solvate isomerism (Hydrate isomerism when solvent is water):**

Arises depending upon whether a solvent molecule is directly bonded to the metal ion or is present as a free solvent molecule.



Valence bond theory:

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

- **Inner-orbital or low spin or spin-paired complexes:** Complexes that use inner d -orbitals in hybridisation, e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$
- **Outer-orbital or high spin or spin-free complexes:** Complexes that use outer d -orbitals in hybridisation, e.g., $[\text{CoF}_6]^{3-}$

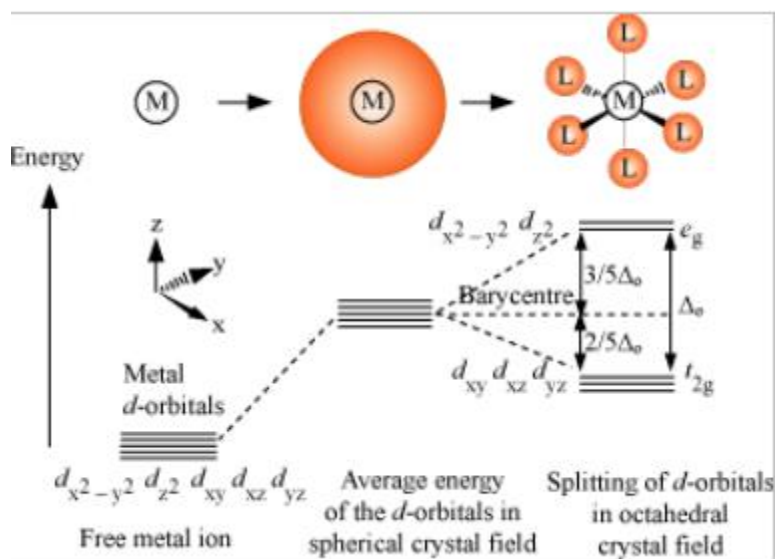
Limitations of valence bond theory:

- A number of assumptions are involved.
- Quantitative interpretation of magnetic data is not given.
- The exhibition of colour by coordination compounds is not explained.
- The thermodynamic or kinetic stabilities of coordination compounds are not quantitatively interpreted.
- Whether a complex of coordination number 4 is tetrahedral or square planar cannot be exactly predicted.
- Weak and strong ligands cannot be distinguished.

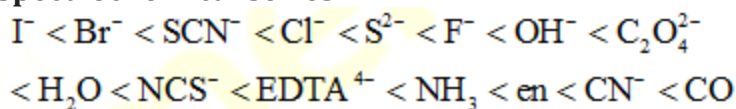
Crystal-field theory:

[Crystal-field splitting is the splitting of the degenerate energy levels due to the presence of ligands.]

- Crystal-field splitting in octahedral coordination entities:



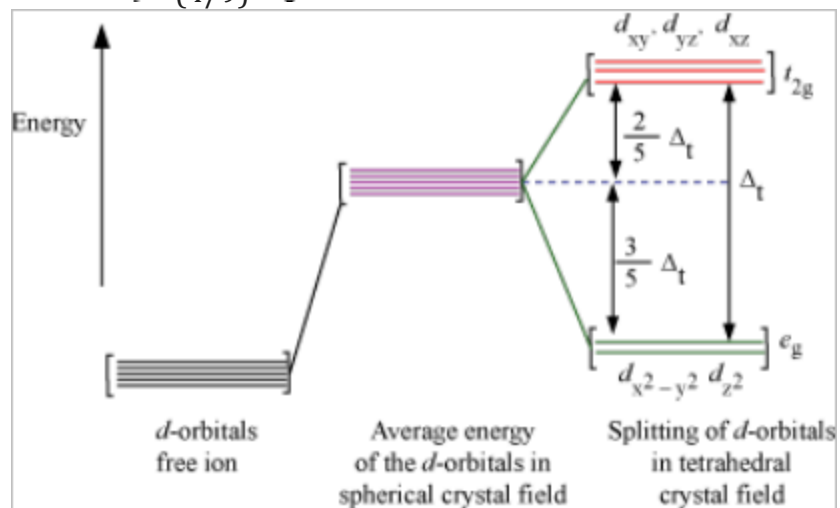
- Spectrochemical series:**



- Ligands for which Δ_o (crystal-field splitting) $< P$ (pairing energy) are called **weak-field** ligands, and form **high-spin** complexes.
- Ligands for which Δ_o (crystal-field splitting) $> P$ (pairing energy), are called **strong-field** ligands, and form **low-spin** complexes.

- Crystal-field splitting in tetrahedral coordination entities:

$$\Delta_t = (4/9) \Delta_o$$



Colour in coordination compounds:

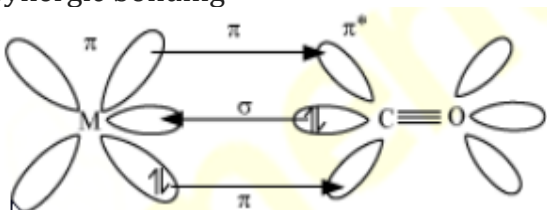
The colour of the coordination compounds is attributed to $d-d$ transition of electrons.

Limitations of the crystal-field theory:

- Anionic ligands are assumed to exert the greatest splitting effect. But the anionic ligands are found at the lower end of the spectrochemical series.
- Crystal-field theory does not take into account the covalent character of bonding between ligand and the central metal atom.

Bonding in metal carbonyls:

- Synergic bonding –



Stability of coordination compounds:

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \dots K_n$$

Where,

$\beta \rightarrow$ Overall stability constant

$K \rightarrow$ Stepwise stability constant

Applications of coordination compounds in Study Materials

- EDTA is used in the treatment of lead poisoning.
- Cis-platin is used in the treatment of cancer.