Solid State

Solids:

The state of matter in which particles are very closely packed in a definite pattern in long range order and have strong forces of interactions is called solid.

Amorphous solids:

They consist of particles (atoms, ions or molecules) of irregular shape these have short range order, i.e. regular repeating pattern of constituent particles is observed over short distances only. These are isotropic; do not have irregular cleavage, e.g. glass, rubber and plastics.

Crystalline solids:

They consist of regular 3D arrangement of atoms. Ions or molecules and have well defined geometrical shape. These have long range order. These are anisotropic. They have cleavage property and sharp melting point. e.g. quartz diamond graphite, sodium chloride.

Anisotropy:

It is the property due to which crystals show different electrical and optical properties in different planes of the same crystal. Crystalline solids show anisotropy.

Isotropy:

It is the property due to which amorphous substances show identical electrical and optical properties in all directions. Amorphous solids show isotropy.

Crystal:

It is a piece of solid substance with a regular geometrical shape caused by a regular arrangement of atoms, Ions or molecules making up the solid.

Crystal lattice:

A well ordered and regular arrangement of atoms, molecules or ions in the three-dimensional space is called crystal lattice. If the particles are replaced by points, the crystal structure would be an array of points which is called lattice. These points are called lattice points and the lattice is called space lattice.

There are 14 possible three-dimensional crystal lattices called Bravais lattices.

Unit call:

It is portion of crystal lattice which on repetition leads to crystal structure, it has all the characteristics of crystal lattice.

Characteristics of crystal lattice.

- a. The position of particles (atoms, ions or molecules) in crystal lattice is represented by point called lattice point.
- b. Lattice points join together by straight lines to bring out geometry of the lattice.
- c. Each lattice point on corner is shared by 8 unit cells, therefore, contributes 1/8 to each unit cell.
- d. Each lattice point on edge is shared by 4 unit cells, therefore, contributes 1/4 to each unit cell.

e. Each lattice point on face contributes 1/2 to each unit cell because it is shared by two unit cells.

Number of Particles per unit cell (Z):

- In simple cubic, only corners are occupied by particles. Since, each point on a corner is shared by eight unit cells. There are 8 corners. Hence, the number or the particles per unit cell is one $(\frac{1}{8} \times 8 = 1)$. So, Z=1 for simple cubic
- For bcc, 8 lattice points are on the corners contributing $8x\frac{1}{8} = 1$ atom. 1 lattice point is at body centre contributing one atom. Thus total Z = 1+1=2 for bcc element.
- For fcc, 8 lattice points are on the corners contributing $8 \times \frac{1}{8} = 1$ atom. Thus, total Z =1+3 =4 for fcc element or ionic solid.

Voids or holes:

The empty spaces between close packing of its constituting particles are called voids or holes.

Interstitial voids: The vacant spaces in the solid is called interstitial void.

Tetrahebral void:

Void between four touching spheres. It is the void between three spheres in direct contact capped by fourth sphere. Total number of tetrahedral voids is twice the number of particles in a given unit cell.

Octahedral voids: void between six touching spheres in direct contact capped by three more spheres in direct contact. Total number of octahedral voids is equal to the number of particles in a given unit cell.

Close packing:



Crystal Defects or imperfections in crystal or lattice imperfections:

Any irregularities in close packing are called imperfections or crystal defect.

Types of Defects:



Electrical properties:

On the basis of electrical properties, solids are classified into three types:

- (a) Conductor,
- (b) Semiconductor and
- (c) Non-conductor.

According to band theory, it has been suggested that filled band and conduction band are either closely packed or partially overlapped in the case of conductor so that transition of electron takes place easily.

In the case of nonconductor, there is large gap between filled band and conduction band. Hence, transition of electron does not take place.

On the other hand, in the case of semiconductor, there is small gap between filled band and conduction band. Hence, transition of electron takes place slowly.

Conductivity of semiconductor may be increased by the insertion of some other impurities between the gap of filled band and conduction band. This process is called doping. If doping is carried out with element of excess valence electron, the resultant semiconductor is called n-type

semiconductor. For example, Si is doped with As. On the other hand, if doping is carried out with element of less valence electron, the resultant semiconductor is called p-type semiconductor. For example, Si is doped with Ga.

Magnetic properties:

Magnetism is generated due to the spin motion and orbital motion of electrons.

On the basis of magnetic properties, substances may be classified into following types:

- a. Paramagnetic substances,
- b. Diamagnetic substances,
- c. Ferromagnetic substances,
- d. Antiferromagnetic substances and
- e. Ferromagnetic substances.

Paramagnetic substances:

Such types of substances, which are attracted by the external magnetic field, are called paramagnetic substances, e.g. O_2 , Cu^{2+} , Fe^{3+} etc.

Diamagnetic substances:

Such types of substances, which are repelled by the external magnetic field, are called Diamagnetic substances, e.g. TiO₂, Cu⁺, NaCl etc.

Ferromagnetic Substances:

The strong paramagnetic substances, which can be permanently magnetized also, are called ferromagnetic substances e.g. Fe, CrO₂, Co, Ni etc.

Antiferromagnetic Substances:

When magnetic moments are aligned in such a way that net magnetic moment is zero, is called antiferromagnetism. The substances are called antiferromagnetic substances e.g. MnO.

Ferrimagnetic Substances:

When magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers resulting in net magnetic moment is called ferrimagnetism. The substances are called ferrimagnetic substances e.g. Fe_3O_4 , $CuFe_2O_4$ etc.

Solutions

Homogeneous mixture of two or more substances is called solution. It has two components. One of them is called solvent and other is called solute.

Strength of solution:

The amount of solute present in given quantity of solution or in solvent is called strength of solution.

It is measured in following terms:

- a. Mass percentage,
- b. Volume percentage,
- c. Mass by volume percentage,
- d. Parts per Million,
- e. Mole fraction,
- f. Molarity and
- g. Molality.

Mass Percentage:

The amount of solute in gram present in 100 gram of solution is called mass percentage.

$$Mass \% = \frac{Mass of solute (g)}{Mass of solution (g)} \times 100$$

Volume Percentage:

The volume of solute in ml present in 100 ml of solution is called volume percentage.

$$Volume \% = \frac{Volume \ of \ solute \ (ml)}{Volume \ of \ solution \ (ml)} \times 100$$

Mass by volume Percentage:

The mass of solute in gram present in 100 ml of solution is called volume percentage.

Mass by volume
$$\% = \frac{Mass \ of \ solute \ (g)}{Volume \ of \ solution \ (ml)} \times 100$$

Parts per Million (ppm):

The amount of solute present in 10^6 parts of solution is called ppm.

$$ppm \% = \frac{Amount of solute}{total amount of solution} \times 10^6$$

Mole Fraction:

The ratio of the number of moles of a particular component to the total number of moles of the solution i.e. all components is called mole fraction. It is denoted by 'x'.

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It is formulated as:

$$x_A = \frac{n_A}{n_A + n_B}$$
$$x_B = \frac{n_B}{n_A + n_B}$$

Where, n_A and n_B are the respective mole fraction of components A and B. The x_A and x_B are respective mole fraction of the components A and B.

Molarity:

Numbers of moles of the solute present in per liter of the solution is called molarity. It is denoted by 'M'. it is formulated as:

If W_A g of solute of molar mass m_A is present in v ml of the solution, molarity will be:

$$M = \frac{n}{V} = \frac{W_A \times 1000}{m_A \times v}$$

Molality:

Numbers of moles of the solute present in per kilogram of the solvent is called molality. It is denoted by 'm'. It is formulated as:

If W_A g of solute of molar mass m_A is present in W_B of the solvent, molality will be:

$$m = \frac{n}{\text{weight in Kg of solvent}} = \frac{W_A \times 1000}{m_A \times W_B}$$

Solubility:

The maximum amount of solute dissolved in 100 g of solvent to form saturated solution at a given temperature is called solubility.

Solubility of a solid in a liquid:

Ionic compounds are soluble in polar solvents, i.e. in water because they ionize in aqueous solution. Ionic compounds are insoluble in organic solvents because they do not ionize in organic solvents

Effect of temperature:

It has been that if dissolution is endothermic in nature, the solubility of solid in liquid increases with increase in temperature.

On the other hand, if dissolution is exothermic, the solubility of solid in liquid decreases with increase in temperature.

Effect of pressure:

The solubility of solid in liquid is not affected significantly by pressure because solids and liquids cannot be compressed.

Henry's Law:

It states that the solubility of a gas in liquid is directly proportional to the pressure of the gas.

If we use mole fraction of the gas in the solution as a measure of its solubility,

mole fraction of gas in solution \propto partial pressure of the gas

partial pressure of gas in solution = $K_H \times$ mole fraction of gas in solution

or,
$$p = K_H \cdot x$$

Where, K_H = Henry's law constant and x is mole fraction of gas in solution.

Different gases have different $K_{\rm H}$ values at the same temperature. It means $K_{\rm H}$ depends upon nature of the gas

Effect of temperature:

The value of K_H for N_2 and O_2 increases with increase in temperature indicating that the solubility of gases decreases with increase in temperature.

Vapour pressure of a pure liquid.

The pressure exerted by the vapour over the liquid surface is called vapour. It increases with the increase in temperature.

Vapour pressure of solution.

The pressure exerted by the vapour of solvent A and solute B in equilibrium with the liquid phase is called the vapour pressure of solution.

Partial vapour pressure:

The vapour pressure of a component 'A' in solution of A and B is called partial vapour pressure of component A. It is denoted by P_A .

Lowering of vapour pressure:

The vapour pressure of solvent in solution is less than that of pure solvent, when non volatile solute is added to it. The lowering of vapour pressure depends only on the concentration of solute and is independent of its nature. If P_A is vapour pressure of solvent in a solution, P^o_A is vapour pressure of the pure solvent and x_A is mole fraction of solvent, then

$$P_A = x_A P_A^0$$

Ideal solutions:

Those solutions which obey Raoult's law are called ideal solutions. When the forces of attraction between A—A and B—B is similar to A—B, A and B will form ideal solution.

Non-ideal solutions.

Those solutions which do not obey Raoult's law are called non-ideal solution. When forces of attraction between A—A and B—B is different from A—B then A and B form non ideal solutions.

(i) Raoult s law is not obeyed (ii) $\Delta H_{mix} \neq 0$ (iii) $\Delta V_{mix} \neq 0$

For example ethanol and water, chloroform and acetone ethanol are few examples of non-ideal solutions.

Positive Deviation from Raoult s Law

In those non-ideal solutions in which partial pressure of each component A and B is higher than that calculated from Raoult's law show positive deviation. e.g mixture of water and ethanol.

Negative Deviation from Raoult s law

The partial vapour pressure of component A is found to be less than calculated from Raoult's law on adding the second component B and when A is added to B, the partial vapour pressure of component B is found to be less than that calculated from Raoult's law. The total vapour pressure of solution is less than that of ideal solution of same composition. Boiling point of such a solution is relatively higher than the boiling points of A and B respectively. This type of deviation from ideal behaviour is known as negative deviation from Raoult's law. For example, mixture of chloroform and methyl acetate.

Azeotropes:

Liquid mixtures which distill over without changes in composition are called constant boiling mixtures or azeotropic miztures.

Colligative Properties:

Such types of properties of solution, which depend on number of solute particles and independent from the nature of the solute, are called colligative properties. Colligative properties are:

- a. Relative lowering in vapour pressure,
- b. Elevation in boiling point,
- c. Deperssion in freezing point and
- d. Osmotic pressure.

Relative lowering in vapour pressure:

The ratio of lowering in vapour of solution and vapour pressure of pure solvent is called relative lowering in vapour pressure. It is formulated as:

Relative lowering in vapour pressure =
$$\frac{P_A^0 - P_A}{P_A^0}$$

It has following relationship with mole fraction

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{n_A}{n_A + n_B} = \text{mole fraction of solute}$$

Elevation in boiling point:

Boiling point is actually the temperature at which vapour pressure of liquid becomes equal to the atmospheric pressure. After the addition of non-volatile solute to the pure solvent making solution, since, vapour pressure decreases. So, boiling point of the solution increases. It is called elevation in boiling point. It is formulated as:

$$\Delta T_{b} = K_{b} \frac{W_{A} \times 1000}{M_{A} \times W_{B}}$$

Where, ΔT_b = boiling point of pure solution(T_b^0) – boiling point of solvent(T_b)

 K_b = Molal elevation in boiling point constant

 W_A and M_A = weight and molar mass of solute respectively.

 W_B = weight of solvent in gram.

Depression in freezing point:

We know freezing point of the liquid is the temperature at which its vapour pressure in liquid state becomes equal to the vapour pressure of its solid state. After the addition of non-volatile solute to the pure solvent making solution, since, vapour pressure decreases. So, freezing point of the solution decreases. It is called depression in freezing point. It is formulated as:

$$\Delta T_{\rm f} = K_{\rm f} \frac{W_{\rm A} \times 1000}{M_{\rm A} \times W_{\rm B}}$$

Where, ΔT_f = freezing point of pure solution(T_f) – boiling point of solvent(T_f^0)

 K_f = Molal elevation in freezing point constant

 W_A and M_A = weight and molar mass of solute respectively.

 W_B = weight of solvent in gram.

Osmotic pressure:

The spontaneous flow of solvent molecules either from the pure solvent to the solution or from solution of lower concentration to the solution of higher concentration is called osmosis. Osmotic pressure is defined as:

The extra pressure that must be applied to either solution side or to the solution of higher concentration side is known as osmotic pressure. It is denoted by ' π '. It is formulated as:

$$\pi V = nRT \dots \dots \dots (2)$$

or,
$$\pi V = \frac{n}{V}RT \dots \dots (3)$$
$$\pi = CRT \dots \dots \dots (4)$$
or,
$$\pi V = \frac{W_A}{M_A}RT \dots \dots (5)$$

Isotonic solution:

Two or more solution having same osmotic pressure is called isotonic solution.

Hypotonic solution:

The solution having less concentration than the red blood corpuscles (RBC) is called hypotonic solution.

Hypertonic solution:

The solution having higher concentration than the red blood corpuscles (RBC) is called hypertonic solution.

Reverse osmosis:

If extra pressure is applied on either solution side or on solution of higher concentration side and exceeds the osmotic pressure, the osmosis will take place in opposite direction. It is called reverse osmosis.

Van't Hoff Factor:

The ratio of observed colligative property to its theoretical value is known as Van't Hoff factor. It is denoted by 'i'. it is formulated as:

$$i = \frac{obsrved\ colligative\ property}{calculated\ colligative\ property}$$

Since colligative properties are inversely proportional to the molar mass so, it may be formulated as:

$$i = \frac{normal\ molar\ mass}{abnormal\ molar\ mass}$$

Abnormal molar mass:

When molar calculated with the help of colligative property is different from theoretical value is called abnormal molar mass. It is either due to association or due to dissociation.

Association:

When two or more molecules combine together to form a single associated particle, the process is called association. Due to association, number of particle decreases, hence, colligative properties decreases. It increases the molar mass.

Dissociation:

When a single molecule is decomposed to form two or more particles, the process is called dissociation. Due to dissociation, number of particle increases, hence, colligative properties increases. It decreases the molar mass.

Degree of dissociation

The ratio of number of dissociated molecules to the total number of molecules taken is called degree of dissociation. It is denoted by ' α '.

Degree of association

The ratio of number of associated molecules to the total number of molecules taken is called degree of association. It is also denoted by ' α '.

ELECTROCHEMISTRY

Electrolyte:

Such types of substances, which dissociate to form two or more opposite ions, are called electrolyte. Examples: NaCl, KCl, H₂SO₄, KOH etc.



Degree of Ionisation:

The ratio of number of ions produced to the total number of molecules of electrolyte is called degree of ionization. It is denoted by " α ".

Conductance:

The ease with which current flows through a conductor is called conductance. It is reciprocal of resistance.

$$C = \frac{1}{R}\dots\dots\dots\dots(1)$$

The unit of conductance is Siemens symbolized by "S" or Ohm⁻¹ symbolized by " Ω^{-1} ".

Specific Resistivity:

Suppose a solution is placed between two parallel electrodes having cross sectional area 'A' and distance 'l' apart. Then,

$$R \propto l \text{ and } R \propto \frac{1}{A}$$

Thus,

 $R = \rho \frac{A}{A} \dots \dots \dots \dots \dots (2)$

Where, $\rho = specific resistivity$

The unit of specific resistivity (ρ) is ohm cm. it is defined as:

The resistance when two parallel electrodes are unit distance apart having area of cross sectional area equal to unity is called specific resistivity.

Specific conductance:

The reciprocal of specific resistivity of an electrolytic solution is called specific conductivity or conductivity. It is denoted by ' κ ' pronounced as kappa. It is formulated as:

$$\kappa = C \frac{l}{A} \dots \dots \dots \dots \dots (3) \quad where, C = conductance of solution$$
$$unit of \kappa = ohm^{-1}cm^{-1} \quad or, \qquad Scm^{-1}$$

Molar Conductivity:

The conductivity power of all the ions produced by one mole of an electrolyte in a solution is called Molar conductivity. It is denoted by Λ_m . It is formulated as:

$$\Lambda_{\rm m} = \frac{\kappa}{\rm C} \times 1000 \, \rm Scm^2 mol^{-1} \dots \dots \dots \dots (4)$$

unit of $\Lambda_{\rm m} = ohm^{-1}cm^2 mol^{-1}$ or, $\rm Scm^2 mol^{-1}$

Variation of Conductivity and Molar Conductivity with Concentration or Dilution;

Conductivity always decreases with decrease in concentration both for weak as well as strong electrolyte. It is because number of ions per unit volume that carry the current in a solution decreases on dilution.

On the other hand molar conductivity increases sharply with decrease in concentration in case of weak electrolyte as shown by the following graph. It is because both number of ions as well as mobility of ions increase with dilution. However, in the case of strong electrolyte, number of ions does not increase appreciably on decreasing concentration or increasing dilution, only mobility on ions increases.



Limiting Molar Conductivity:

The molar conductivity at infinite dilution (Concentration is almost zero) is called limiting molar conductivity. It is denoted as " Λ^{0} ".

Cell constant:

The ratio of distance (l) between electrodes to their cross sectional area (A) is called cell constant.

$$Cell constant = \frac{l}{A} in cm^{-1} or in m^{-1} \dots \dots \dots \dots \dots \dots (4)$$

Kohlrausch's Law of Independent Migration:

The law is stated as:

Sum of the molar conductance of all the individual ions produced by an electrolyte at infinite dilution is equal to the molar conductance of the electrolyte at same dilution.

Where, v_+ and v_- are the number of cations and number of anions respectively.

Degree of Dissociation:

The ratio of molar conductivity at a specific concentration 'C' to the molar conductivity at infinite dilution or limiting molar conductivity is called degree of dissociation. It is denoted by ' α '.

$$\alpha = \frac{\Lambda_{\rm m}^{\rm C}}{\Lambda_{\rm m}^{\rm m}} \quad or, \alpha = \frac{\Lambda_{\rm m}^{\rm C}}{\Lambda_{\rm m}^{\rm 0}} \dots \dots \dots \dots \dots \dots \dots \dots \dots (7)$$

Law of Electrolysis:

There are two laws of electrolysis given by Faraday, which are called Faraday's law of electrolysis.

Faraday's First Law:

The mass of substance deposited during the electrolysis is directly proportional to the quantity of electricity passed. It is called Faraday's 1st law of electrolysis.

$$m \propto Q \quad \dots \dots \dots \dots \dots \dots (8)$$

If 'I' current in ampere is passed for 't' second, the quantity of electricity will express as:

$$Q = It$$

Thus, $m \propto It$ or, $M = ZIt \dots \dots \dots (9)$

Where, Z = Electrochemical equivalent, which is defined as:

The amount of substance deposited in grams when one ampere of current is passed for one second is called electrochemical equivalent.

Faraday's Second Law:

If same charge is passed through different electrolytes of cells those connected in a series, the mass of substance deposited will be proportional to their equivalent weights.

Suppose W_1 , W_2 and W_3 are weights of substances and E_1 , E_1 and E_1 are their equivalent weights of three different substances respectively.

Electromotive Force:

The energy per unit of charge passing through the cell is called electromotive force. It is measured in volts with the help of voltmeter, which does not have internal resistance.

Salt Bridge:

The 'U' shaped tube filled with agar-agar paste containing electrolyte having ions of equal mobolities like KCl or KNO₃ is called salt bridge.

Electrolytic Cell:

The cell in which electrolysis is carried out to convert electrical energy into chemical energy by passing electric current through the solution or molten state of electrolytes is called electrolytic cell.

Galvanic Cell / Voltaic Cell:

The cell in which electricity is generated at the cost of chemical energy is called galvanic cell.

Daniel Cell:

Is consists of a zinc rod dipped in 1M zinc sulphate solution and a copper rod in 1M copper sulphate solution. Both the solutions are kept apart by taking $ZnSO_4$ in a porous pot and putting in a bath of copper sulphate solution. Both electrolytes are connected by a salt bridge.

Electrode potential:

The capacity of an electrode to undergo oxidation or reduction is called electrode potential. It is of following two types:

- a. Oxidation Potential and
- b. Reduction Potential.

Reduction potential is conventionally called electrode potential. For a general reaction is denoted as:

$E_M{}^{n+}\!/_M\!.$

Standard Electrode Potential:

The electrode potential of an electrode, which is in contact with its ions having concentration 1molL^{-1} is coupled with standard hydrogen electrode is called standard electrode potential. It is denoted by $E_{M^{n+}/M}^{0}$.

Standard Hydrogen Gas Electrode:

It consists of Pt-wire coated with finely divided platinum black containing pure hydrogen gas at 1 atm and solution of HCl (1M) so as to maintain the equilibrium between H^+ and H_2 gas. Platinum black catalyses the reaction involved in cell. It is used reference electrode. Conventionally, its electrode potential is 0.00 volt.

Cell Potential:

The difference in electrode potential of cathode and anode is called cell potential. Thus;

Electrochemical Series:

On the basis of standard electrode potential elements have arranged in a particular series, which is called electrochemical series.

Nernst Equation:

The equation that gives the relationship between electrode potential and concentration of metal ions is called Nernst equation.

Nernst equation for the following reaction

 $M^{n+}(Aq) + ne \longrightarrow M_{(S)}$ may be written as:

For a particular cell:

Products of electrolysis:

The products of electrolysis depend upon the nature of electrolyte as well as nature of the electrodes.

If the electrolytic solution has single type of cation and single type of anion, the cation is deposited at cathode while anion is deposited at anode. If the solution has more than one type of cation and anion, in such case, the cation that has higher electrode potential get reduced or deposited at cathode. On the other hand, the anion that has lower electrode potential get oxidized or deposited at anode. It is the case where electrode is almost inert say platinum or gold. If the electrodes are reactive and may participate in chemical reaction, the products will be different as in the case of inert electrodes.

Electrolysis of Molten NaCl:

At anode: Cl ⁻ \longrightarrow 1/2 Cl _{2 (s)} + e ⁻	At cathode: I	Na⁺ +	e —	→ Na _(s)
Electrolysis of Aqueous NaCl:				
It contains Na^+ , H^+ , Cl^- and OH^- ions.				
At anode: Cl ⁻ \longrightarrow 1/2 Cl _{2 (s)} + e ⁻	At cathode: H⁺	+	e ⁻ >	1/2H _{2 (g)}
Primary cells:				

The cell in which electrical energy is generated by the chemical reaction occurring in the cell and can't be recharged again is called primary cell. Examples: dry cell, Daniel Cell and mercury cell.

Secondary cells:

The cells which are used again and again by recharging it are called secondary cell. It used for storing electricity. Examples: lead storage battery and nickel-cadmium cell.

Fuel Cells:

Electrical cells, which are manufactured to convert the energy of the combustion of fuels directly into electrical energy, are called fuel cells. The most successful fuel cell uses the reaction of hydrogen with oxygen to form water. It has been used for electric power in the Apollo space program. The reaction occurring in this cell may be shown as:

At anode: $2H_{2(g)}$ + $2OH^{-}(aq.) \rightarrow 4H_{2}O + 4e^{-}$ At cathode: O_{2} + $2H_{2}O + 4e^{-} \rightarrow 4OH^{-}$ Net Reaction: $2H_{2} + O_{2} \rightarrow H_{2}O$

Dry cell / Leclanche Cell:

It is a type of primary cell. In this cell, Zn-container acts as anode while graphite electrode acts as cathode, which is surrounded by powdered MnO_2 . Since the space between electrodes is filled with a moist paste of NH_4Cl and $ZnCl_2$, which acts as electrolyte, so it is called dry cell. Cell reaction may be shown as:

At anode: $Zn \longrightarrow Zn^{2+} + 2e^{-}$ At cathode: $2MnO_2 + 2NH_4^+ + 2e^{-} \longrightarrow 2MnO(OH) + 2NH_3$ Net reaction: $Zn + 2NH_4^+ + 2MnO_2 \longrightarrow Zn^{2+} + 2MnO(OH) + NH_3$

Mercury cell:

It is also a type of primary cell, which gives constancy of voltage. It has Zn-Hg amalgam as anode, a paste of HgO and carbon as cathode. The paste of KOH and ZnO acts as electrolyte.

Lead Storage Battery:

It is a type of secondary battery. It has lead anode and a grid of lead packed with lead dioxide as cathode. A 38% aqueous solution of H_2SO_4 acts as electrolyte.

Nickel-Cadmium Cell:

Corrosion:

The deterioration of metals either by loss or gain of electrons is called corrosion. Tarnishing of silver, rusting of iron and formation of blue precipitate on copper surface are example of corrosion.

Hydrogen Economy:

Hydrogen has highest calorific value among all the fuels. It can be used in vehicles to prevent the pollution from petrol and diesel. Hydrogen is present in natural gas. it may be obtained by the photolysis of water on large scale. Thus hydrogen as a fuel will help to improve the economy of our country.

CHEMICAL KINETICS

Rate of Reaction:

The decrease in concentration of reactant or increase in concentration of product in per unit time is called rate of reaction.

$$rate of reaction = -\frac{[reactant]_{T_{f}} - [reactant]_{T_{i}}}{T_{f} - T_{i}}$$

$$or, \quad rate of reaction = -\frac{\Delta[reactant]}{\Delta T} \dots \dots \dots \dots (1)$$

$$where, \Delta[reactant] = change in concentration of reactant$$

$$rate of reaction = \frac{[product]_{T_{f}} - [product]_{T_{i}}}{T_{f} - T_{i}}$$

$$or, \quad rate of reaction = \frac{\Delta[product]}{\Delta T} \dots \dots \dots (2)$$

Average Rate:

The rate of change of concentration of reactant or product during infinitesimal small time interval is called instantaneous rate of reaction.

instantaneous rate of reaction =
$$\pm \frac{dc}{dt}$$

Where, dc is the infinitesimal change in the concentration of reactant or product during infinitesimal time interval "dt" after time "t" i.e. between t and t + dt. Instead of expressing instantaneous rate by $\pm \frac{dc}{dt}$, we may also expressed it by $\frac{dx}{dt}$, where "dx" is infinitesimal small amount of reactant consumed or product formed during infinitesimal small time interval "dt" from "t".

Rate Law or Rate Equation:

The expression which relates the rate of a reaction with concentration of the reactants is called rate law or rate equation. For a general reaction:

$$A + B \rightarrow Product$$

 $\frac{dx}{dt} = K[A]^n [B]^m \dots \dots \dots \dots (3)$

Where, K = proportionality constant called rate constant and n + m = Order of reaction.

Thus order of reaction may be defined as: "sum of the exponents of the concentration terms of reactants in rate lay expression"

Molecularity:

Total number of atoms, ions or molecules of the reactants involved in a reaction is called molecularity. It is always in whole number. It can't be zero.

Zero Order Reaction:

Such types of reaction for which rate of reaction does not change with the concentration of the reactants is called zero order reaction.

First Order Reaction:

Such types of reaction, for which rate of reaction increases same number of fold (times) as the number of fold by which concentration of reactant is increased, is called first order of reaction. Expression for rate constant of first order reaction is:

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \dots \dots \dots \dots \dots \dots \dots \dots \dots (4)$$

Where, a = initial concentration of reactant and a-x = final concentration of reactant.

Half life of a Reaction:

The time taken for a reaction when half of the concentration of reactant has reacted is called half life of reaction. It is denoted by $t_{1/2}$. If K be the rate constant, for first order reaction it is expressed as:

Pseudo First Order Reaction:

Such types of reaction, which looks like second order but it is actually first order, is called pseudo first order reaction. For example: acidic hydrolysis of ethyl acetate.

Unit of Rate constants:

Units of rate constants for reaction of different order has different. It is generally expressed as:

unit of rate constant =
$$\left[\frac{1}{unit of concentration}\right]^{n-1} \times time^{-1}$$

or, unit of rate constant = $\left[\frac{1}{\frac{mol}{lite}}\right]^{n-1} \times second^{-1}$
or, unit of rate constant = $\left[\frac{liter}{mol}\right]^{n-1} \times second^{-1}$

For first order reaction,

unit of rate constant = $second^{-1}$

For second order reaction,

For third order reaction,

unit of rate constant =
$$liter^2 mol^{-2}second^{-1}$$

Elementary Process:

Some reactions, which occur in more than one step, each step is called elementary process or elementary reaction. The slowest step is called rate determining step.

Collision theory:

It is based on kinetic theory of gases. According to this theory chemical reaction takes place as a result of collision between reacting molecules. On the basis of this theory, rate of reaction may be expressed as:

Rate of reaction =
$$PZe^{\frac{-Ea}{RT}}$$
.....(6)

Where, P = Probability factor, Z = Collision frequency, $E_a = collision$ frequency, R = gas constant and T = Temperature.

Activation Energy:

The minimum required energy by a reactant for the completion of reaction is called activation energy at a given temperature.

Threshold Energy:

The minimum energy that the reacting species must possess in order to undergo effective collision to complete the reaction is called threshold energy.

Effective collision:

The collision that is responsible for the formation of product is called effective collision.

Collision Frequency:

The number of effective collisions that take place in per second in per unit volume of reaction mixture is called collision frequency. It is denoted by 'Z'

Activated Complex:

Reacting molecules combine together to form a highly energetic species before the formation of product. This species is called activated complex.

Thermo chemical Reaction:

Those reactions, which are initiated by heat energy, are called thermo chemical reaction.

Factors Affecting the Reaction:

Following factors affect the rate of reaction:

- a. Nature of reactant,
- b. Physical state,
- c. Surface area,
- d. Concentration,
- e. Catalyst and
- f. Temperature.

It has been observed that rate of reaction becomes two or three times when temperature is increased by 10 0 C. The ratio of rate constant at two different temperatures differed by 10 0 C is called temperature coefficient. It is denoted by " μ ". It is formulated as:

SURFACE CHEMISTRY

It includes three topics say Adsorption, Catalysis and Colloids.

Adsorption:

The accumulation or deposition of a substance at the surface of other substance is called adsorption.

The substance, which get adsorb, is called *adsorbate*. On the other hand, the substance on the surface of which adsorption take place is called *adsorbent*.

Desorption:

The detachment or removal of adsorbate molecules from the surface of adsorbent is called desorption.

Absorption:

The process through which a substance is uniformly distributed throughout the bulk of the solid is called absorption.

Sorption:

The process in which both adsorption and absorption both take place simultaneously is known as sorption.

Mechanism of Adsorption:

A molecule in the interior of the substance is surrounded by other molecules uniformly from all sides. Consequently, this molecule will be attracted by other molecules from all sides equally. The molecule say "A" will therefore experience balance force of attraction. The net attractive force exerting on this molecule will be zero. Now let us consider a molecule say "B", which is at the surface of the substance. It is surrounded by other molecule from all sides but from the above of the surface. Consequently, this molecule experience unbalanced force of attraction.



The resultant force that would tend to pull the molecule inward is called *inward* pull or *residual* force. Due to this inward pull adsorption takes place.

Thermodynamics of Adsorption:

According to thermodynamics, for a process to be spontaneous ΔG should be negative. Further, we know.

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

Adsorption is exothermic in nature i.e. it occurs with decrease in ΔH value. Further, during adsorption, adsorbate molecules are attached to the surface of adsorbent. So, ΔS is also negative in sign. Therefore, ΔG will be negative only when the magnitude of ΔH must be greater than that of T ΔS for the adsorption to be spontaneous.

Types of Adsorption:

On the basis of force of attraction between adsorbate and adsorbent, adsorption is classified into following two types:

- a. Physisorption / Physical adsorption and
- b. Chemisorptions / Chemical adsorption.

Physisorption	Chemisorption
It is due to Vander wall's force of attraction.	It is due to chemical bond formation.
It is usually multilayered.	It is unimolecular layered.
Enthalpy of adsorption is low (20-40kJmol ⁻¹).	Enthalpy of adsorption is low (20-40kJmol ⁻¹).
It is reversible in nature.	It is irreversible in nature.
It is not specific in nature.	It is highlyt specific in nature.
More easily liquefiable gases are adsorbed readily.	Gases, which can react with the adsorbent, show chemisorptions.
No appreciable activation energy is required.	High activation energy is required.
Low temperature is favourable.	High temperature is favourable.

Factors Affecting the Adsorption:

Following factors affect the adsorption.

- a. Surface area,
- b. Nature of the adsorbent or adsorbate,
- c. Temperature and
- d. Pressure.

Adsorption Isotherm:

The graphical representation of variation in the amount of adsorption or gas adsorbed by the adsorbent with respect to pressure at constant temperature is called adsorption isotherm.

If x is the gas adsorbed on the 'm' mass of the adsorbent at constant temperature, according to the Freundlich adsorption isotherm, we may write.

Eq.1 is the mathematical form of Freundlich adsorption isotherm.

Taking logarithm on both sides of Eq.1, then we get;

$$\log \frac{x}{m} = \log K + \frac{1}{n}P \dots \dots \dots \dots \dots \dots \dots \dots (2)$$

Eq.2 is another form of Freundlich adsorption isotherm. It is in the form of straight line equation. When a graph is plotted between logx/m and logP, following straight line should be obtained.

Although, the equation is followed at lower pressure however, as pressure is increased more and more, the equation is failed.

When adsorption takes place from solution, the term pressure is replaced by the concentration.

$$\frac{x}{m} = KC^{1/n} \dots \dots \dots \dots \dots \dots (3)$$
$$\log \frac{x}{m} = \log C + \frac{1}{n}P \dots \dots \dots \dots \dots (4)$$

where,
$$C = concentration$$

Applications of adsorption:

Following applications should be listed.

- a. In production of high vacuum,
- b. In gas masks,
- c. In control of humidity,
- d. In removal of colouring materials from solution,
- e. In heterogeneous catalysis, in separation of inert gases and
- f. In chromatographic analysis.

CATALYSIS

Catalysis:

The substances, which can increase the rate of reaction, are called *catalyst*. The process is called catalysis. In the following reaction, MnO₂ acts as catalyst.

 $2\text{KCIO}_3 \xrightarrow{\text{MnO}_2} 2\text{KCI} + 3\text{O}_2$

In *Haber process* of NH₃, divided Fe and Mo are used, in *Ostwald's process*, Platinised asbestos and in *Contact process* of sulphuric acid, platinised asbestos or V_2O_5 are used.

Promoters:

The substances, which itself is not a catalyst but increases the activity of catalyst, are called promoters. In Haber process of ammonia, Fe acts as catalyst where, Mo acts as promoter.

$$N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$$

Types of catalysis:

There are following two types of catalysis.

- a. Homogeneous catalysis and
- b. Heterogeneous catalysis.

Homogeneous catalysis:

The catalytic process, in which both reactant and catalyst are in same physical state, is called homogeneous catalysis.

$$2SO_{2g} + 3O_{2g} \xrightarrow{NO_{g}} 2SO_{3}$$

$$C_{12}H_{22}O_{11(aq.)} + H_{2}O_{(1)} \xrightarrow{H_{2}SO_{4}(1)} C_{6}H_{12}O_{6} + C_{6}H_{12}O_{6}$$

Mechanism:

Catalyst combines with reacting molecules to form an intermediate of higher energy. This highly energetic species readily decomposed to form desired product.

Heterogeneous catalysis:

The catalytic process, in which both reactant and catalyst are in different physical states, is called homogeneous catalysis.

Mechanism:

The mechanism governs the principle of adsorption. It involves in following five steps:

- a. At first diffusion of the reactants to the surface of the catalyst takes place.
- b. Adsorption of the reacting molecules at the surface of the catalyst takes place.
- c. Chemical reaction takes place through the formation of intermediate at the surface of catalyst.
- d. Desorption of the products from the surface of catalyst takes place.
- e. Diffusion of the products from the catalytic surface takes place.

Important features of catalyst:

- i. It takes participate in reaction without consumption in its amount.
- ii. Very small quantity of catalyst is sufficient for the vast amount of reaction.
- iii. It does not initiate the reaction. It only increases the rate of reaction.
- iv. Larger the surface area, greater will be the activity of catalyst.
- v. Catalysts are selective in nature.

$$CO + H_2 \xrightarrow{Vi} CH_4 + H_2O$$

$$CU + H_2 \xrightarrow{Cu} H_3C - OH$$

$$CU + HCHO$$

Shape Selective Catalysis:

Such types of catalysis, which depends on the porous nature of the catalyst and size of the reactant and product, are called shape selective catalysis.

Zeolite is one of the best examples of shape selective catalyst.

Enzyme Catalysis:

Such types of catalyst, which increase the rate of biochemical reactions occurring in living thing, are called enzyme or biocatalyst. The process is called enzyme catalysis. Some examples are:

Important features of Enzyme catalysis:

- i. Most highly efficient
- ii. Highly specific in nature,
- iii. Having optimum temperature,
- iv. Having optimum pH,
- v. Increasing activity in presence of activators and co-enzymes and
- vi. Influence of inhibitors and poisons.

Mechanism of Enzyme Catalysis:

It is suggested that enzymes possess number of characteristic shape and active groups say $-NH_2$, -COH, -SH, -OH etc. the reacting molecules having complementary shape fit into these cavities like a particular key fit into a particular lock key. Thus an activated complex is formed, which readily decomposed to a desired product. It is called key lock mechanism.

COLLOIDS

Colloid/Dispersion medium/Dispersed phase:

The heterogeneous mixture of two or more substances, which looks like homogeneous, is called colloid. One of the components having size in the range in between 10^{-7} cm to 10^{-5} cm is known as *dispersed phase*. Other component is known as *dispersion medium*.

Classifications of Colloids:



• On the Basis of Physical State of Dispersed phase and Dispersion medium:

Colloids	Dispersed Phase	Dispersion Medium	Examples	
Foam	Gas	Liquid	Soap leather	
Solid foam	Gas	Solid		
Liquid aerosol	Liquid	Gas	Fog, cloud, mist	
Emulsion	Liquid	Liquid	Milk, cream	
Gel	Liquid	Solid	Jellies, curd, cheese	
Aerosol	Solid	Gas	Smoke	
Sol	Solid	liquid	Gold sol, sulfur sol	
Solid sol	solid	Solid	Minerals, gem	

• On the basis of interaction between dispersed phase and dispersion medium:

There are following two types of colloids.

- a. Lyophilic Colloids and
- b. Lyophobic Colloids.
- *Lyohilic colloids:* (Lyo = solvent and phile = to love)

Such types of colloids that are formed simply by bringing the dispersed phase in contact of dispersion medium are called lyophillic colloids.

When dispersion medium is water, it is especially called hydrophilic (Hydro = water) colloids. Preparation and precipitation of lyophilic colloids are reversible in nature i.e.

colloidal state \rightleftharpoons precipitates

Therefore it is sometimes also called reversible or resoluble colloids.

• *Lyphobic Colloids*: lyophobic (Lyo = solvent, Phobic = to hate)

If dispersion medium is water, lyphobic colloids are especially called hydrophobic colloids. Since in this case dispersed phase has not great affinity for its dispersion medium, lyophobic colloids cannot be prepared simply by bringing dispersed phase in contact with dispersion medium.

Lyophobic colloids are also caleed irreversible colloids as it is irreversible in nature.

Preparation of Colloids:

• By chemical methods:

$$\begin{split} & As_2O_3 + 3H_2S \rightarrow As_2S_{3as\ a\ sol} + 3H_2O \quad Double\ decomposition \\ & SO_2 + 2H_2S \rightarrow 3S_{as\ a\ sol} + 2H_2O \quad Oxidation \\ & 2AuCl_3 + 3HCHO + 3H_2O \rightarrow 2Au_{as\ a\ sol} + 3HCOOH + 6HCl \quad Reduction \\ & FeCl_3 + 3H_2O \rightarrow Fe(OH)_{3as\ a\ sol} + 3HCl \quad Hydrolysis \end{split}$$

• By electrical disintegration or Bredig's Arc method:

In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat vapourises the metal, which then condenses to form colloids.

• *Peptization:*

The process of converting a precipitate into colloids by shaking it with dispersion medium in presence of some electrolyte is called peptization.

Purification:

Removal of impurities from colloidal solution is known as purification. It is carried out by:

- a. Dialysis,
- b. Electrodialysis and
- c. Ultrafiltration.

Dialysis:

The removing of impurities from a colloidal solution by means of diffusion through a semi permeable membrane or through parchment paper is called dialysis.

When dialysis is carried out in presence of electric field, it is specially called electodialysis.

Ultrfiltration:

When filtration is carried out by using specially prepared filter paper that can allowed the solute particles through it, is known as ultrfiltration.

- Properties of Colloids:
- *Heterogeneity:*

Colloidal system is a heterogeneous mixture of two or more components namely dispersed phase and dispersion medium.

• *Filtrability*:

Dispersed phase of colloids can pass through ordinary filter paper but it may be filtered by ultrafilter paper.

• Visibility:

Size of the dispersed phase is less than 200 m μ , which is shortest than the wavelengths of visible light (400 m μ). Hence, colloidal particles are neither visible with naked eye nor with simple microscope. However it is visible with ultramicroscope.

• Surface Tension and Viscosity:

Lyophilic sols show higher viscosity and lower surface tension while lyophobic sols have lower viscosity and higher surface tension.

• Colligative Properties:

Colloids have less value of colligative properties than that of true solution.

• *Kinetic Properties:*

Zsigmondy observed that dispersed phase of colloids were in constant motion having no definite path but travelling in zigzag direction.

It is called Brownian movement in honour of botanist Robert Brown. Brownian movement is defined as:

The continuous and zigzag movement of the dispersed phase in colloids is called Brownian movement.

Brownian movement is independent from the external influence and also independent from the nature of dispersed phase. Smaller the size of dispersed phase, greater is its movement and less viscous the colloids.

Due to unequal bombardment of the dispersed particles by the particles of dispersed medium, colloids show Brownian movement.

• Optical Properties (Tyndall Effect):

The scattering of incident light by colloidal particles is known as Tyndall effect.

The wavelength of the incident light remains almost unchanged in Tyndall effect.

The causes of Tyndall effects are:

- a. The size of the dispersed phase and wavelength of used light are almost comparable and
- b. Appreciable difference in refractive index of dispersed phase and dispersion medium.

Intensity of the scattered light increases, when wavelength of the light decreases.

• Electrical Properties:

It is observed that dispersed particles carry an electric charge. Charge on dispersed particles may be positive or negative. Some examples of positive and negative colloids are:

Positive Colloids Negative Colloids

Metal hydroxide, Ag, Au, Pt, Metal sulphides

The causes of charge are:

- a. Due to capture of electron by colloidal particles and
- b. Due to preferential adsorption of ions.

Due to electrically charged nature, colloids attract ions of opposite nature. In this way, two layers of ions are formed. One of them is called fixed layer and other is called diffused layer.

• Electrokinetic Potential/Zeta Potential:

The potential difference between fixed layer and diffused layer of opposite charges is called Electrokinetic potential or zeta potential.

• Electrophoreses:

The movement of colloidal particle towards a particular electrode under an applied electric field is known as electrophoresis.

When electrophoresis is prevented by any means, movement of dispersion medium takes place. It is specially called electro osmosis.

• *Coagulation or Precipitation:*

The settling of colloidal particles is called coagulation of the sol.

It may be carried out by any of the following means:

- a. By electrophoresis,
- b. By mixing two oppositely charged colloids,
- c. By boiling,
- d. By persistent dialysis and
- e. By addition of electrolytes.
- Stability of colloids:

The presence of equal and similar charges on colloidal particle is responsible for the stability of colloids. The repulsive nature of the force between similar charged colloidal particles prevents them from coagulation, which gives the stability of the colloids.

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• Protective action:
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Lyophilic colloids have unique property of protecting lyophobic colloids. When lyophilic colloids are added to the lyophobic colloids, the lyophilic particles form a layer around the lophobic particles and thus protect the lyphobic particle from electrolytes. The used lyophilic colloids are specially called *protective colloids*.

• Hardy-Schultz rule:

When excess of an electrolyte is added the colloidal particles are coagulated. Greater the valency of the ion of the electrolyte, greater is the power of coagulation. It is called Hardy-Shultz rule.

In coagulation of negative colloids, according to Hardy-Schultz rule the power of coagulation is:

 $Al^{3+} > Ba^{2+} > Na^+$

In coagulation of negative colloids, according to Hardy-Schultz rule the power of coagulation is:

 $[Fe(CN)_6]^{4-} > PO_4^{3-} > Cl^{-}$

EMULSION

The liquid-liquid colloidal system is called *emulsion*. One of the liquids is water. It is of following two types:

- 1. Oil dispersed in water (O/W) and
- 2. Water dispersed in liquid (W/O).

Emulsions of the type oil in water are unstable and sometime they are separate into two layers on standing. For stabilization of such types of emulsion, a third component is added, which is called *emulsifying agent*. Emulsifying agent forms an interfacial layer between suspended particles and the medium.

The principal emulsifying agents for oil in water type of emulsions are proteins, gums natural and synthetic soaps. The emulsifying agents for water in oil type of emulsions are metal salts of fatty acids (such as oleic acid, palmitic acid, stearic acid etc.), long chain alcohol, lampblack etc.

Like other colloids emulsion also shows general properties of colloids such as electrical properties, kinetic properties, optical properties colligative properties etc.

• Applications of colloids:

Colloids have many applications in our daily life as well as in industry.

- 1. Foods: Many of our foods such as milk, a protein-casein, cream, fruit jellies, eggs etc. are colloidal in nature.
- 2. Medicines: Most medicines are emulsions, which are colloids. It has been observed that in colloidal form they are more effective and more easily assimilated.
- 3. Industrials goods: many industrial goods like paints, varnishes, enamels, celluloses, resins, gums and flues etc are colloidal in nature.
- 4. Sewage disposal: Sewage water consists of dust particles, rubbish, mud etc are of colloidal in nature.
- 5. Artificial rain:
- 6. Formation of deltas:
- 7. Cleansing action of soap.

General Principles and Processes of Isolation of Elements

Minerals:

The naturally occurring chemical substances in the earth crust, which are obtained by mining, are known as minerals.

Ores:

Such types of ores, from which elements may be extracted or isolated with easily, in short period and with economically, are called ores. Thus all ores are mineral but reverse is not true.

		1		.0		n
Nativ	Sulphurise	Oxides	Carbonate	Nitrates	Phosphates	Halides
e Ores	d and				and	
	Arsenical				Silicates	
	Ore					
Ag,	Galena	Haematite	Magnesite (MgCO ₃),	Chile	Willemite	Common salt
Au, P,	(PbS), Zinc	$(Fe_2O_3),$	Lime stone (CaCO ₃),	saltpetre	$(Zn_2SiO_4),$	(NaCl), Horn
Hg etc	blende	Magnetite	dolomite (CaCO ₃ .	(NaNO ₃)	Fluor-	silver (AgCl),
are	(ZnS),	$(Fe_{3}O_{4}),$	MgCO ₃), Calamine	and Salt	apatite	Carnallite
presen	Cinnabar	Limonite	$\{CuCO_3Cu(OH)_2\},\$	petre	$[3Ca_3(PO_4)_2]$	(KCl.MgCl ₂ .6H ₂
t in	(HgS),	$(Fe_2O_3.3H_2O)$	Azurite	(KNO ₃)	.CaCl ₂],)
Free	Argentite or		$\{Cu(OH)_2.3CuCO_3\},\$		Felspar	Fluorspar (CaF ₂)
states.	Silver	Corundum	Cerussite (PbCO ₃)	$\mathbf{N}\mathbf{N}$	(KAlSi ₃ O ₈ ,	and Cryolite
Their	glance	$(Al_2O_3),$	and Siderite (FeCO ₃)		Asbestos	$(Na_3AlF_6).$
free	(AgS), Iron	Diaspore			[CaMg ₃ .(Si	
state is	pyrite (Fes ₂)	$(Al_2O_3.H_2O)$			O ₃) ₄]	
called	and Copper	Bauxite				
native	pyrites,	$(Al_2O_3.2H_2O)$				
ores.	Copper	Cassiterire or				
	glance or	Tin stone				
	Chalcocite	(SnO ₂)				
	$(Cu_2S).$					

Gangue:

The undesired impurities associated with ores are called gangue or matrix.

Flux:

The substances, which are mixed with concentrated ores that combine to form fusible material, are called flux.

 $Gangue + Flux \rightarrow Slag$

Fluxes are classified as acidic flux (silica, borax) and basic flux (limestone, magnesite, ferric oxide).

$$SiO_2 + CaO \rightarrow CaSiO_3$$

 $MgCO_3 + SiO_2 \rightarrow MgSiO_3 + CO_2$

Metallurgy:

The whole process to extract or to obtain an element from their ores in pure form is known as metallurgy. Following processes are used for metallurgical process of an element.



Gravity Separation:

It is based on the specific gravities of the gangue particle and ores particles. Generally heavier ores like oxide and carbonate ores are concentrated by this method.

Electromagnetic Separation:

It is based on magnetic properties of the ores particles and gangue particles. When either ore gangue particles are magnetic in nature, this method will use.

Froth Floatation Process:

This method is based on the preferential wetting properties of the ores with frothing agent and water. The frothing agent pine oil, froth stabilizers (cresol and aniline) and collecting agent sodium ethyl xanthate are used. This method is used for the concentration of lighter ores say sulphide ores. In order to separate, two sulphide ores depressant say NaCN, which selectively prevents the coming of one ore with the froth, is used.

Calcination:

Heating of ores below its fusion temperature in absence of air is known as calcination. It expels organic matter, moisture from hydrated oxides and CO₂ from carbonates, making ores porous.

 $\begin{array}{c} Al_2O_3.\,2H_2O \rightarrow Al_2O_3+2H_2O\\ 2Fe_2O_3.\,3H_2O \rightarrow 2Fe_2O_3+3H_2O\\ CaCO_3 \rightarrow CaO+CO_2 \end{array}$

Roasting:

Heating of ores either alone or with other material below its fusion temperature and in presence of air is known as roasting. In roasting, definite chemical change like oxidation, chlorination takes place.

$$2ZnS + 3O_2 \rightarrow 2ZnO + SO_2$$
$$PbS + 2O_2 \rightarrow PbSO_4$$
$$Ag_2S + 2NaCl \rightarrow 2AgCl + Na_2S$$

Both clacination and roasting are carried out in *reverberatory* furnace.

Leaching:

It is used when only ore is soluble in a suitable solvent and impurities remain insoluble in same solvent. Al, Ag and Au are concentrated by this method.

Leaching of Al:

$$\begin{split} Impure \left(Al_2 O_{3(S)}\right) + 2NaOH_{(aq)} + 3H_2 O_{(l)} &\to 2Na[Al(OH)_4]_{(aq)} + Impurities \\ 2Na[Al(OH)_4]_{(aq)} + CO_{2(g)} &\to Al_2 O_3. xH_2 O_{(S)} + 2NaHCO_{3(aq)} \\ Al_2 O_3. xH_2 O_{(S)} + CO_{2(g)} &\to Al_2 O_{3(S)} + xH_2 O_{(g)} \quad at \ 1470 \ K \end{split}$$

Leaching of Ag and Au:

In this case dilute solution of NaCN is used. The process is called Mac-Arthur Forrest cyanide process. The reactions involved in the process may be shown as:

$$Impure(4M) + 8NaCN + 2H_2O_{(l)} + O_2 \rightarrow 4Na[M(CN)_2] + NaOH with Impurities$$
$$2Na[M(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + M \downarrow$$

Smelting:

It involves the reduction of ore to the molten metal at high temperature. For less electropositive metals like Pb, Zn, Fe, Sn etc powerful reducing agent like C, H_2 , CO, water gas, Na, K, Mg and Al etc are used.

	Smelting
Carbon reduction process: Oxides of less electropositive metals are reduced with coal or coke	Gold-Schmidt alumino-thermic process: Oxides of very high M.P. metals are reduced by heating mixture of thermite and ignition mixture. Ignition mixture = Mg-Powder+BaO ₂ Thermite = AI-Powder + Mixture of oxide ore

Self Reduction/Air Reduction Process:

The sulphide ores of less electropositive metals like Hg, Pb, Cu etc are heated in air. Some part of the ores is converted into oxide or sulphate, which then reduced with remaining part of the sulphide to form reduced metal.

 $(1.) 2HgS + 3O_2 \rightarrow 2HgO + SO_2$ $2HgS + HgO \rightarrow 3Hg + SO_2$ $(2.) 2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ $2Cu_2O + Cu_2S \rightarrow 6CuO + SO_2$

Electrolytic Reduction:

The oxides of the highly electropositive metals like Na, K, Mg, Ca, al etc are reduced by electrolytic reduction.

Hydrometallurgy:

It is based on the principle that more electropositive metals can displace less electropositive metals from its salt solution.

Amalgamation:

It is used for the extraction of noble metals like Ag, Au etc from their native ores. The ore is brought in contact of mercury to obtain amalgam, which upon distillation form Hg-vapour and metal.

Refining:

Liquation:

It is based on the differences in fusibility of the metal (more fusible) and impurities (less fusible). It is employed for the refining of Bi, Cd, Hg etc.

Distillation:

It is based on the M.P. of the metal and impurities. It is employed for the refining of Zn and Hg. *Pyrometallurgical Process:*

The method is employed when impurities have greater affinity for oxygen. Fe, Cu, Ag etc are refined by this method.

Electrolytic Refining:

In this method impure metal is made to act as anode and a strip of same pure metal is made to act as cathode. The salt of the same metal is used as electrolyte. The pure metal is deposited at cathode.



Flow Sheet for the Extraction of Copper:

Copper pyrites (CuFeS₂)
Concentration by froth floatation
Roasting in Reverberatory furnace

$$S + O_2 \longrightarrow SO_2$$

 $2As + 3O_2 \longrightarrow As_2O_3$
 $2CuFeS_2 \longrightarrow Cu_2S + 2FeS + SO_2$
Roated Ore + Silica
Smelting in Blast furnace
 $2FeS+3O_2 \longrightarrow 2FeO + 2SO_2$
 $FeO + 3SiO_2 \longrightarrow FeSiO_3$
Matte (Cu₂S + FeS) mixed with silica
Bessemerisation in Bessemer
converter in presence of air
 $2FeS+3O_2 \longrightarrow 2FeO + 2SO_2$
 $FeO + 3SiO_2 \longrightarrow FeSiO_3$
 $2Cu_2S + 3O_2 \longrightarrow 2FeO + 2SO_2$
 $FeO + 3SiO_2 \longrightarrow FeSiO_3$
 $2Cu_2O + Cu_2S \frac{Self}{16} + 6Cu + SO_2$
Blister Copper
Electrolytic Refining
Cathode = Impure Cu-Plate
Electrolytic Refining
Cathode = Impure Cu-Plate
Electrolyte = CuSO_4 + H_2SO_4
Pure Cu (99.99%) at cathode

Extraction of Iron:

Important ores: Magnetite, haematite, limonite, siderite, iron pyrites, chalcopyrites. Concentration: by gravity separation followed by magnetic separation and then ore is calcinated/ roasted.

Smelting:

The calcinated ore is mixed with lime stone and coke in the ration 8:1:4 and introduced in a blast furnace for smelting. Pig iron is obtained by following reaction.

In combustion zone:

$$\begin{array}{ccc} \mathcal{C} + \ \mathcal{O}_2 \rightarrow \ \mathcal{C}\mathcal{O}_2 \\ \mathcal{C}\mathcal{O}_2 + \mathcal{C} \rightarrow \ 2\mathcal{C}\mathcal{O} \ at \ 1500^\circ \mathrm{C} \end{array}$$

In reduction zone:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \text{ at } 300 - 400^{\circ}\text{C}$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2\text{ at } 500 - 600^{\circ}\text{C}$$

$$FeO + CO \rightarrow Fe \text{ (spongy)} + CO_2 \text{ at } 700^{\circ}\text{C}$$

Slag formation zone:

$$CaCO_3 \rightarrow CaO + CO_2 \text{ at } 1000^{\circ}C$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$

The impurities silicates, phosphates and manganates are reduced to Si, P and Mn respectively. These are partly absorbed by spongy iron and partly by slag.


The p-Block Elements

The group of elements for which last electron enters into outermost p-subshell are called p-block
elements. The maximum possible number of electrons in p-subshell is six. So, there are six groups
in p-block. The p-block elements are:

					He
					$1s^2$
В	С	Ν	0	F	Ne
$[He]2s^22p^1$	$[He]2s^22p^2$	$[He]2s^22p^3$	[He]2s ² 2p ⁴	$2s^22p^5$	$2s^22p^6$
Al	Si	Р	S	Cl	Ar
$[Ne]3s^23p^1$	$[Ne]3s^23p^2$	$[Ne]3s^23p^3$	[Ne]3s ² 3p ⁴	3s ² 3p ⁵	3s ² 3p ⁶
Ga	Ge	As	Se	Br	Kr
$[Ar]3d^{10} 4s^24p^1$	$[Ar]3d^{10} 4s^2 4p^2$	$[Ar]3d^{10}4s^24p^3$	$[Ar]3d^{10}4s^24p^4$	$4s^24p^5$	$4s^24p^6$
In Sn		Sb	Te	Ι	Xe
$[Kr]4d^{10}5s^25p^1$	$[Kr]4d^{10}5s^25p^2$	$[Kr]4d^{10}5s^25p^3$	[Kr]4d ¹⁰ 5s ² 5s ² 5p ⁴	$5s^25p^5$	$5s^25p^6$
T1	Pb	Bi	Ро	At	Rn
$[Xe]4f^{14}5d^{10}6s^{2}6p^{1}$	$[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$	$[Xe]4f^{14}5d^{10}6s^26^3$	$[Xe]4f^{14}5d^{10}6s^{2}6p^{4}$	$6s^26p^5$	6s ² 6p ⁶
Nh	Fl	Ms	Lv	Og	Ts
[Rn] $5f^{14}6d^{10}7s^27p^1$ [Rn]		[Rn]	$[Rn] 5f^{14}6d^{10}7s^27p^4$	$7s^27p^5$	$7s^27p^6$
	$5f^{14}6d^{10}7s^27p^2$	$5f^{14}6d^{10}7s^27p^3$		·····P	···· · F

General Characteristics:

• Atomic and Ionic Radii:

Atomic size increases from top to bottom in the group while it decreases from left to right in a period.

• Ionization enthalpy/ Electron gain enthalpy/ Electronegativity:

Usually I.E, E.a. and E.N.
$$\propto \frac{1}{Radius}$$

Order of electronegativity, $F > 0 > Cl > N$

- Physical properties:
- 1st I.P. of nitrogen is greater than that of oxygen but 2nd I.P. of oxygen is greater than that of nitrogen.

Nitrogen has half filled electronic configuration $(2s^22p^3)$, which is comparatively more stable than oxygen that has one electron more than half filled $(2s^22p^4)$. Hence, 1st I.P. of nitrogen is greater than that of oxygen.

During the removal of 2^{nd} electron, oxygen has half filled $(2s^22p^3)$ but nitrogen has one electron less $(2s^22p^2)$ than half filled. Hence, 2^{nd} I.P. of oxygen is greater than that of nitrogen.

- Inert pair effect
- Chlorine has higher electron affinity than fluorine.

Due to extremely smaller size, there is very strong electronic repulsion in fluorine. Hence fluorine has not greater attraction for added electron. On the other hand, this repulsion is less in larger

chlorine. Hence chlorine has comparatively greater attraction for added electron. It is this reason chlorine has higher electron affinity than fluorine.

• Nitrogen exists in diatomic form while phosphorus exists in tetratomic form.

Due to smaller size nitrogen forms effective $p_{\pi}-p_{\pi}$ bonding. Hence, it exists in diatomic form. On the other hand, due to larger size, phosphorus does not form effective $p_{\pi}-p_{\pi}$ bonding. However, in order to minimize electronic repulsion phosphorus forms single bond and exists in tetratomic forms.

• Oxygen exists in diatomic form while sulfur exists in octatomic form.

Due to smaller size, oxygen forms effective $p_{\pi}-p_{\pi}$ bonding. Hence, it exists in diatomic form. On the other hand, due to larger size, sulfur does not form effective $p_{\pi}-p_{\pi}$ bonding. However, in order to minimize electronic repulsion sulfur forms single bond and exists in octatomic forms.

• Nitrogen shows only trivalency while phosphorus shows trivalency as well as pentavalency.

Due to absence of d-subshell nitrogen is unable to extent its valency. On the other hand, due to presence of d-subshell, phosphorus is able to extent its valency and it shows trivalency as well as pentavalency.

• Allotropic forms of phosphorus



Allotropic forms of Sulphur:

Sulphur exists in octatomic form in crown shaped. In gaseous state it exists in S_2 form, which is paramagnetic in nature. The rings of sulphur from 6-20 atoms have been synthesized.

Rhombic Sulphur (α-sulphur)	Monoclinic Sulphur (β-sulphur)
It is yellow in colour	It is colourless.
Insoluble in water.	Soluble in CS_2 .
Soluble in CS ₂ , dissolves to some	
extent in benzene, alcohol, ether.	

• Chemical properties:

- Members of nitrogen family react with hydrogen to form corresponding compounds say ammonia (Azine, NH₃), Phosphine (PH₃), Arsine (AsH₃), stilbine (SbH₃) and bimusthine (BiH₃).
- As size of the element increases, bond length (E–H) increases, this weakens the bond strength. So thermal stability of the molecules decreases. Due to this fact, dissociation of hydrogen increases. Hence, reducing property of the compounds increases.
- As size of the element increases, electron density on element decreases so, basic character decreases. (*NH*₃ >*PH*₃ *AsH*₃ >*SbH*₃ >*BiH*₃).
- Due to presence of lone pair of electrons, all hydrogen compounds of this family behave as Lewis base. As we go down the group, electronegativity decreases so, distance of bonded electrons from central element increases. Due to this fact the distance bended pair of electrons decreases, this decreases the bond pair-bond pair repulsion. Hence, bond angle decreases. $(NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3)$
- *NH*₃ has higher boiling point than PH₃.

Ammonia molecules are associated with intermolecular H-bonding, which is absent in phosphine molecules. It is this reason ammonia has higher boiling point than phosphine.

• H₂O exists in liquid state while H₂S exists in gaseous state.

Due to intermolecular H-bonding, water molecules associated with each other and hence exist in liquid state. On the other hand, due to absence of H-bonding, H_2S exists in gaseous state.

• *HF exists in liquid state while HCl exists in gaseous state.*

Due to intermolecular H-bonding, molecules of hydrogen fluoride associated with each other and hence, they exist in liquid state. On the other hand, due to absence of H-bonding, HCl exists in gaseous state.

• Acidic character of hydra acids:

As we go from left to right in a period, electronegativity increases. It increases the capacity of element to attract the bonded electrons towards itself. Consequently, to release H^+ ion increases. Thus acidic character increases. (NH₃ < H₂O < HF)

As we go down the group, size of the element increases. It increases the bond length and decreases the bond strength. Due to this fact, capacity to release H^+ ion increases. Thus, acidic character increases. ($H_2O < H_2S < H_2Se < H_2Te < H_2Po$ & HF < HCl < HBr < HI)

• Nitrogen forms five types of oxides say N_2O , NO, N_2O_3 , NO_2 , N_2O_4 and N_2O_5 .

Out of them, only N_2O_3 and NO_2 are coloured solid and gas respectively. Others are colourless. The oxide NO_2 contains a free unpaired electron. In order to pair it, the molecule is dimerised to form N_2O_4 . Only one oxide i.e. N_2O_5 is lack of nitrogen-nitrogen direct bond.

• Both PCl₃ and PCl₅ hydrolyse in presence of moisture giving fume of HCl. Reactions are:

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$
$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

• In PCl₅, the hybridization of phosphorus is sp³d giving trigonal bipyramidal structure. In this structure, three equatorial chlorines are equivalent where as remaining two axial chlorines are equivalent. In order to minimize repulsion, the bonds of axial chlorines are elongated.



- In the solid state of PCl₅, the two molecules of it decompose to form tetrahedral [PCl₄]⁺ and octahedral [PCl₆]⁻. Due to presence of ionic constituent particles, the PCl₅ shows ionic character in its solid state.
- Sulphuric acid violently reacts with water.

In order to prepare aqueous solution of sulphuric acid, care must be taken that concentrated acid is slowly added into water with constant stirring.

• Sulphuric acid has strong affinity for water. Hence, it shows charring with carbohydrate.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

• Oxidizing power of halogens:

As electronegativity of the halogens increases, oxidizing character of the halogens increases. It is this reason lighter halogens replaces heavier halogens from their salt.

$$F_{2} + 2X^{-} \longrightarrow 2F^{-} + X_{2} \text{ Where, } X = CI, Br, I$$

$$CI_{2} + 2X^{-} \longrightarrow 2CI^{-} + X_{2} \text{ Where, } X = Br, I$$

$$Br_{2} + 2I^{-} \longrightarrow Br^{-} + I_{2}$$

Fluorine oxidizes water to oxygen while chlorine and bromine itself are oxidized by water as oxygen is less electronegative than water but more electronegative than others.

 $2F_2 + 2H_2O \rightarrow 4H^+ + 4F^- + O_2$ $X_2 + H_2O \rightarrow HX + HOX Where, X = Cl, Br$

- Due to smaller size, fluorine experiences greater lone pair-lone pair repulsion. Hence, F–F bond is comparatively weaker and fluorine has less bond energy or bond dissociation energy.
- Interhalogen compounds:

Halogens form four different types of interhalogen compounds say X^IX, X^IX₃, X^IX₅, X^IX₇. All interhalogen compounds are hydrolyzed to form halide of smaller halogens i.e. halogens of higher electronegativity and hypohalite (from X^IX), halite (from X^IX₃), halate (from X^IX₅) and perhalate (from X^IX₇) of higher halogens i.e. halogens of lower electronegativity. For example;



• *Inertness of 18th group elements:*

Partly due to completely filled outermost shell and partly due to higher I.P. and very higher positive electron gain affinity, elements of 18th group are almost inert.

• Partial hydrolysis of XeF₆ gives oxyfluorides say XeOf₄ and XeO₂F₂.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

 $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

• Complete hydrolysis of XeF_4 and XeF_6 give xenon trioxide (XeO₃). $6XeF_6 + 12H_2O \rightarrow Xe + 2XeO_3 + 24HF + 3O_2$

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

• Oxy acids of phosphorus:



Metaphosphoric acid may exist in cyclic form or in polymeric open chain form.



• Oxy acids of Sulphur:

Sulphur forms four different types of oxy acids say –ous acids, –ic acids, thionic caids and peroxy acids.



• Oxy acids of halogens:

Oxy acids of halogens	Oxy	acids	of	halogens	
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Hapohalous	Hypoflourous	Hypochlorous	Hypobromous	Hypoiodous
acids (HOX)	acid (HOF)	acid (HOCl)	acid (HOBr)	acid(HOI)
Halous acids		Chlorous acids	Bromous acid	
(HOXO)		(HOClO)	(HOBrO)	
Halic acids		Chloric acid	Bromic acid	Iodic acid
(HOXO ₂)		(HOClO ₂)	(HOBrO ₂)	(HOIO ₂)
Perhalic		Perhloric acid	Perbromic acid	Periodic acid
acids		(HOClO ₃)	(HOBrO ₃)	(HOIO ₃)
(HOXO ₃)				

• Preparation of Dinitrogen:

In lab, nitrogen is prepared by the reaction of ammonium chloride and sodium nitrite.

$$NH_4Cl + NaNO_2 \rightarrow N_2 + 2H_2O + NaC_2$$

By the thermal decomposition of ammoniumdichromate, sodium azide or barium azide:

$$(NH)_2 Cr_2 O_7 \rightarrow N_2 + 4H_2 O + Cr_2 O_3$$
$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$
$$2NaN_3 \rightarrow 2Na + 3N_2$$

Preparation of Dioxygen:

By heating potassium chlorate, oxygen is prepared as:

$$2\text{KCIO}_3 \xrightarrow{\Delta} 2\text{KCI} + 3\text{O}_2$$

It may be prepared by the thermal decomposition of oxides of metals of low reactivity.

$$2Ag_2O \rightarrow 4Ag + O_2$$

$$2Pb_3O_4 \rightarrow 6PbO + O_2$$

$$2HgO + 2Hg + O_2$$

$$2PbO_2 + 2PbO + O_2$$

In presence of MnO₂, hydrogen peroxide is also decomposed to form dioxygen.

$$H_2 O_2 \rightarrow 2H_2 O + O_2$$

On large scale, it prepared from air.

Dioxygen is a colourless, odourless and tasteless gas. Its solubility in water is 3.08cm³ in 100cm³ at 293K, which is just sufficient for the vital support of aquatic life.

• Preparation of Chlorine:

 $(a.) MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$ $(b.) KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$ $(c.) 4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O (CuCl_2 catalyst, Deacon process)$ (d.) by the electrolysis of brine i.e. concentrated NaCl solution.

It is a greenish yellow gas with pungent and suffocating odour. It reacts with ammonia as:

$$\begin{array}{l} {NH_3}_{excess} + Cl_2 \rightarrow NH_4Cl + N_2 \\ {NH_3} + Cl_{2}_{excess} \rightarrow NCl_3 + 3HCl \end{array}$$

It reacts with cold and dilute sodium hydroxide as:

 $NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$

It reacts with hot and conc sodium hydroxide as:

$$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

It reacts with slaked lime to form bleaching powder.

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

• Preparation of Ammonia:

Small quantity of ammonia is formed by the hydrolysis of urea as:

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

By the reaction of ammonium salt with caustic soda or lime:

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$
$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

On large scale, ammonia is manufactured by Haber's process.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 46.1 K Jmol^{-1}$$

Ammonia is colourless gas with pungent odour. Its respective freezing point and b.p. are 198.4K and 239.7 K. Due presence of lone pair of electrons on nitrogen, ammonia acts Lewis acid and a better ligand in coordination chemistry.

• Preparation of Phosphine:

$$\begin{array}{c} Ca_3P_2+6H_2O\rightarrow Ca(OH)_2+2PH_3\\ Ca_3P_2+6HCl\rightarrow 3CaCl_2+2PH_3\\ In \ lab:\ P_4+3NaOH+3H_2O\rightarrow 3NaH_2PO_2+2PH_3 \end{array}$$

It is colourless gas with rotten fish smell. It is highly poisonous. It explodes in contact with traces of oxidizing agents like HNO_3 , Cl_2 etc.

• Preparation of PCl₃ and PCl₅:

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + S_2Cl_2$$

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

$$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$$

PCl₃ ahs pyraimidal shape while PCl₅ has trigonal bipyramidal geometry.

• Preparation of Hydrogen chloride:

In laboratory, it is prepared as:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$
 at 420 K
 $NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$ at 823 K

It is colourless and pungent smelling gas. It is easily liquefied to a colourless liquid (b.p., 189 K) and freezes to a white crystalline solid (f.p., 159 K). Its aqueous solution is called hydrochloric acid. Mixture of three parts of concentrated HCl and one part of concentrated HNO₃ is called aqua regia, which is used for dissolving noble metals. Hydrochloric acid decomposes salts of weaker acids say carbonates, hydocarbonates (bicarbonates) and sulphites.

• Preparation of Ozone:

It is prepared by passing dry stream of oxygen slowly through a silent electrical discharge.

$$3O_2 \rightarrow 2O_3 \quad \Delta H^0 = +142 k Jmol^{-1}$$

It is pale blue gas. It is dark blue in liquid and violet black in solid. It is harmless in small concentration. In high concentration, breathing becomes uncomfortable gives rise to headache and nausea. It has angular shape in following resonating structures.

When ozone reacts with an excess KI solution buffered with a borate buffer (pH, 9.2), iodine is liberated that can be titrated against a standard solution of sodium thiosulphate.

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

• Preparation of Sulphurdioxide:

Sulphur burns in air or oxygen to form SO₂ along with SO₃.

$$S + O_2 \rightarrow SO_2 + SO_3$$

In lab, it is prepared by treating sulphite with dil.H₂SO₄.

$$SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O$$

Industrially, it is produced by roasting of sulphide ore.

$$4FeS_2+11O_2\rightarrow 4Fe_2O_3+8SO_2$$

It is colourless gas with pungent odour. It is highly soluble in water. It behaves as it is anhydride of sulphurous acid. It decolourises acidified potassium permanganate solution.

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

This reaction is used for the test of SO₂ gas.

• Preparation of Nitric acid:

Lab Method: $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

Commercially, it is prepared by Ostwald's process. It involves in following steps.

 $\begin{array}{ll} Step: I & 4NH_3+5O_2 \rightarrow 4NO+6H_2O\\ Step: II & 2NO+5O_2 \rightarrow 2NO_2+6H_2O\\ Step: III & 3NO_2+H_2O \rightarrow 2HNO_3+NO \end{array}$

It is colourless liquid (f.p. =231.4K and b.p. =355.6K). In aqueous, it behaves as strong acid. In nitric acid, oxidation state of nitrogen is +V, which is highest for it. Hence, it acts strong oxidizing agent.

$$\begin{array}{l} 3Cu + 8HNO_{3_{dil.}} \rightarrow 3Cu(NO_{3})_{2} + 2NO + 4H_{2}O \\ 4Zn + 10HNO_{3_{dil.}} \rightarrow 4Zn(NO_{3})_{2} + N_{2}O + 5H_{2}O \\ Cu + 4HNO_{3_{Conc.}} \rightarrow Cu(NO_{3})_{2} + 2NO_{2} + 2H_{2}O \\ Zn + 4HNO_{3_{Conc.}} \rightarrow Zn(NO_{3})_{2} + 2NO_{2} + 2H_{2}O \\ I_{2} + 10HNO_{3} \rightarrow 2HIO_{3} + 10NO_{2} + 4H_{2}O \\ C + 4HNO_{3} \rightarrow CO_{2} + 4NO_{2} + 2H_{2}O \\ S_{8} + 48HNO_{3} \rightarrow 8H_{2}SO_{4} + 48NO_{2} + 16H_{2}O \\ P_{4} + 20HNO_{3} \rightarrow 4H_{3}PO_{4} + 20NO_{2} + 4H_{2}O \end{array}$$

Nitrate ion is tested by brown ring test. It is carried out by adding ferrous sulphate solution to an aqueous solution containing nitrate ion taken in test tube. Thereafter, concentrated H_2SO_4 is added along the side of the test tube. A brown ring at the interface between the solution and H_2SO_4 layer is formed, which indicate the presence of nitrate ion.

$$\begin{split} NO_3^- + 3Fe^{2+} + 4H^+ &\rightarrow NO + 3Fe^{3+} + 2H_2O \\ NO + [Fe(H_2O)_6]^{2+} &\rightarrow [Fe(H_2O)_5(NO)]_{brown}^{2+} + H_2O \end{split}$$

• Preparation of Sulphuric acid

It is prepared by the contact process. It is completed in following steps.

$$\begin{array}{ll} Step: I & 4FeS_2 + 11O_2 \rightarrow 4Fe_2O_3 + 8SO_2\\ Step: II & 2SO_2 + O_2 \rightarrow 2SO_3 & in \ presence \ of \ V_2O_5 catalyst\\ Step: III & SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \ (Oleum) \end{array}$$

Finally, oleum is diluted to obtain sulphuric acid.

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

It is colourless, dense and oily liquid. It is diprotic acid. Hence, it forms two types of salt say normal sulphate and acidic sulphate. In sulphuric acid oxidation state of sulphur is +VI, which is highest for it. So, it acts as oxidizing agent.

$$Cu + 2H_2SO_4 \ conc. \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \ conc. \rightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4 \ conc. \rightarrow CO_2 + 2SO_2 + 2H_2O$$

It is used to prepare more volatile acids say hydrohalic acids and nitric acid.

 $2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4$ (where, X = F, Cl and NO_3)

The d-Block Elements/Transition Metals

Transition Metals:

The group of elements for which last electron enters into inner d-subshell or d-subshell of penultimate shell i.e. (n-1)d subshell, where n= outermost shell, are collectively called d-block elements. They are also called transition metals. It is defined as:

The elements having incompletely filled (n-1)d subshell either in its elemental state or in its common oxidation state are called transition metals. Zn, Cd and Hg are pseudo transition metals. *Classification:*

On the basis of entrance of last electron in d-subshell, transition metals are classified into following series:

The D block elements with their outermost electronic configuration										
3d-series	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
1 st series	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^{1}$	$3d^{10}4s^2$
4d-series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
2 nd series									-	
5d-series	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg
3 rd series							\sim			-
6d-series	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
4 th series				_					-	

The D-block elements with their outermost electronic configuration

Atomic size:

Among transition metals the last electron enters into (n-1)d subshell as we go from left to right. Since, size of the d-subshell is larger than the s and p-subshell so electron density will become comparatively less. Consequently, nuclear charge will become more effective to attract the outermost shell. Hence atomic size decreases from left to right. This decrease in size is called dorbital contraction.

Atomic size decreases from Sc to Cr. It almost remains same for Fe, Co, Ni. Cu and Zn are bigger in size because larger electron repulsion between paired electrons, which expands the size.

Ionic size for divalent cations decreases from Sc to Cu.

Ionization Energy:

Due to irregular variation in atomic size, there is slight and irregular variation in ionization energy for transition metals.

The I.E. for 5d series of transition metals is higher than 3d and 5d series of transition metals due to lanthanoid contraction.

Oxidation State:

Due to very less energy gap between (n-1)d and ns subshell (n-1)d electrons participate in chemical reaction along with ns electrons. Hence, transition metals show variable oxidation state. The variable oxidation states are differed by unity. It is due to (n-1)d electrons participate in chemical reaction one by one.

Oxidation States of 3d series of Transition Metals

							1		
Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^{1}$	$3d^{10}4s^2$
+III	+II	+I	+II						
	+III	+II							
	+IV								
		+V	+V	+V	+V				
			+VI	+VI	+VI				
				+VII					

Melting and Boiling Point:

Transition metals generally have higher M.P. and B. P. because of strong metallic bond. Zn, Cd and Hg are volatile metals due to bigger in size and having weaker metallic bonding. In these cases there is absence of d_{π} - d_{π} bonding.

It is the same reasons that transition metals have very higher enthalpy of atomization.

Electrode Potential:

Due to higher value of I.E., higher value of heat of sublimation and lower value of heat of hydration, transition metals have lower value of electrode potential.

Complex Formation:

Transition metals form many coordination compounds or complex compounds. It is due to the following reasons:

- a. They have smaller atomic size,
- b. They have incompletely filled (n-1)d electrons and
- c. They show variable oxidation state.

Catalytic Property:

Most transition metals and/or their compounds act as catalyst. The causes behind it are:

- a. They have larger surface area,
- b. They have incompletely filled (n-1)d electrons and
- c. They show variable oxidation state.

Paramagnetic Nature of the Compounds:

Most compounds of the transition metals are paramagnetic nature. It is because of the presence of unpaired electrons in their incompletely filled (n-1)d subshell. The magnetic moment may be calculated by using following formulae:

$$\mu_s = g_s \sqrt{S(S+1)} \ B.M.$$

Where,
$$g_s = 2$$
 and $S \frac{n}{2}$ and $n =$ number of unpaired electrons

By using this, the above formula may be written as:

$$\mu_s = g_s \sqrt{n(n+2)} \ B.M.$$

Colour of the Compounds:

With some exceptions most compounds of transition metals are coloured. The colour of the compounds is either due to:

- a. The $d \rightarrow d$ transition or due to
- b. Charge transfer.

Interstitial Compounds:

Transition metals form more or less interstitial compounds non stoichiometric compounds. It is because during crystallization they have some void in which smaller atoms like C, H, N, B etc can fit into it.

Alloy formation:

They form many alloys, which is formed by the mixing of two or more molten metal's followed by cooling. Hence, alloys are considered as homogeneous mixture of two or metals.

Potassium dichromate (K₂Cr₂O₇):

Method of Peparation: $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2Cr_2O_4 + 2Fe_2O_3 + 8CO_3$ $2Na_2Cr_2O_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ $Na_2Cr_2O_7 + 2KCI \longrightarrow K_2Cr_2O_7 + 2NaCI$

It is orange crystal solid. Its colour depends on pH of the solution. It is highly soluble in water. Both chromate ion and dichromate ion are interconvertible into each other depending on pH of the solution.



Chemical Properties:

In potassium dichromate, oxidation state of chromium is +VI, which is highest for it. Hence, potassium dichromate acts as oxidizing agent.

(a.)
$$Cr_2O_7^- + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + I_2 + 7H_2O$$

(b.) $Cr_2O_7^- + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$
(c.) $Cr_2O_7^- + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

Uses:

It is used as an oxidizing agent. It is used for tanning of leather. It is used as disinfectant. It is used in volumetric analysis. It is used in chromyl chloride test.

Potassium permanganate (KMnO₄):

Method of preparation:

 $2MnO_2$ + 4KOH + O_2 \longrightarrow $2K_2MnO_4$ + $2H_2O$

 $4H^{+}$ + $3MnO_{4}^{-}$ ----- $2MnO_{4}^{-}$ + MnO_{2} + $2H_{2}O$

Physical Properties:

It is purple crystalline solid. It is less soluble in water. It is stored in dark coloured bottle because it gets decomposed in presence of sunlight. Its magnetic moment is temperature dependent. *Chemical properties:*

In potassium permanganate, oxidation state of manganese is +VII, which is highest for it. Hence, potassium permanganate acts as oxidizing agent.

(a.) MnO_4^- + 5Fe²⁺ + 8H⁺ \longrightarrow Fe³⁺ + Mn²⁺ + 4H₂O

(b.) $2MnO_4^- + 10l^- + 16H^+ \longrightarrow 2Mn^{2+} + 5l_2 + 8H_2O$

Uses:

It is used as oxidizing agent in organic chemistry. It is used as bleaching agent. It is used for preparation of oxygen. It is used as disinfectant.

The f-Block Elements/Inner Transition Metals

The group of elements for which last electron enters into (n-2)f subshell i.e. f-subshell of antepenultimate shell are collectively called f-block elements. Because of their position they are called inner transition metals. They are also called rare earth metals because are rarely found in earth crust.

The f-block elements are classified into following two types in account of entrance of last electron in which sub shell.

- a. The 4f-series (Lanthanoid series) and
- b. The 5f-series (Actinoid series).

The lanthanoid series:

- The fourteen elements after La₅₇ are called lanthanoid in which 4f subshell is progressively filled with general electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.
- Among lanthanoids only Pm₍₆₁₎ is radioactive.
- There is steady decrease in their atomic size with increase in atomic number due to poor shielding effect of f-electrons. It is called lanthanoid contraction.
- Due to similar ionic size they occur together and hence their separation becomes difficult.
- The common oxidation state of lanthanoids is +III. However, Ce shows +IV where as Eu and Yb shows +II oxidation state. It is because of their full filled and half filled electronic configuration.
- Most lanthanoids forms coloured compounds due to presence of unpaired electrons, which participate in f→f transition.
- Due to presence of unpaired electrons, their compounds are paramagnet in nature.
- They are highly reactive and electropositive. The Eu is most and Yb is least reactive.



The Actinoids series:

- The fourteen elements after Ac₈₉ i.e. from Th₉₀ to Lr₁₀₃ are collectively called actinoids in which 5f subshell is progressively filled.
- All of them are radioactive.
- The elements after U₉₂ are called *transuranic* elements. They are synthetic or man-made.
- There is steady decrease in their atomic size with increase in atomic number from Th₉₀ to Lr₁₀₃ due to poor shielding effect of f-electrons. It is called actinoid contraction.
- The common oxidation state of lanthanoids is +III. However, they also show +II, +IV, +V and +VI oxidation states.
- Most lanthanoids forms coloured compounds due to presence of unpaired electrons, which participate in f→f transition.
- Due to presence of unpaired electrons, their compounds are paramagnet in nature.
- Most elements form coloured compounds.
- They form oxo-cation in higher oxidation state loke NpO⁺, UO_2^{2+} etc.

Coordination compounds

Molecular Salts/Addition Salts:

Molecular salts or addition salts are usually formed by the reaction or mixing of two or more simple salts. It has two types say double salts and complex salts.

- Those which lose their identity in solution *Double Salts* say carnallite, Mohr salt, potash alum etc.
- Those which retain their identity in solution *Complex Salts/Coordination compounds* say potassium hexacyanoferrate(III), *cis*-platin etc.

Coordination Compounds:

It contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules.

Coordination Sphere or Coordination Entity:

The square bracket part containing central metal atom or ion and ligands is called coordination sphere or entity.

Central Metal Atom or Ion:

The metal ion surrounded by ligands and written in coordination sphere i.e. in square bracket is called central metal atom or ion.

Ligands (Ligation = linking):

A molecule, ion or groups that coordinate to the central metal ion and present with it in square bracket is called ligand.

Types of ligands:



Chelate:

When bidentate or polydentate ligands combine with central metal atoms or ion, cyclic coordination compound is formed. The compound is called chelate.

Such ligands are called chelating agent or chelate ligand.



Ambidentate Ligand:

The ligands, which can link through the metal two different donor site but through on site at a time, are called ambidentate ligands. Some of them are NO_2^- , SCN^- , CN^- etc.

Donor Atom or Site:

An atom of the ligand, which is directly attached to the central metal, is called the donor atom or site.

Coordination Number:

The number of donor site in a particular coordination compound is called coordination number of the central atom in a given complex compound.

Werner's Theory:

According to this theory:

- * Metal ion may have two types of valencies say primary valency and secondary valency.
- * Primary valency, which is also called counter ion, is ionisable whereas secondary is non ionisable.
- * Secondary valencies are satisfied by anions or neutral molecules, commonly known as *Ligands*. These secondary valencies have fixed arrangement in space around the central metal ion and the arrangement is retained even in the solution.
- * Number of bond formed between the metal ion and ligand gives the coordination number, and number of ligands gives the coordination number if the ligands are monodentate (Mono = one, Dentate = teeth).
- * Most common coordination number is four and six. If the coordination number is four the complex is either tetrahedral or square planar whilst when coordination number is six then the complex is octahedral.

Isomerism:



Ionization Isomerism:

Two or more isomers, which form different ions upon dissociation, are called ionization isomers of each other. The phenomenon is called ionization isomerism.

For example; [Co(NH₃)₅SO₄]Br and [Co(NH₃)₅Br]SO₄ are ionization isomers. *Solvate Isomerism:*

It is a special type of ionization isomerism. It is defined as:

Two or more isomers, out of which one forms at least one solvent molecule upon dissociation, are called solvate isomers of each other. The phenomenon is called solvate isomerism. If solvent molecule is water, the isomer is called *hydrate isomer* and phenomenon is called *hydrate isomerism*.

For example; $[Cr(H_2O)_6]Cl_3$ and $[Co(H_2O)_5Cl]Cl_2H_2O$ are solvate or hydrate isomers.

Linkage Isomerism:

Such type of isomers, in which same ligand has different linking with metal atom or ion, is called linkage isomer. The phenomenon is called linkage isomerism. It is possible only when complexes have ambidentate ligands. The complexes $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$ are linkage isomer of each other.

Coordination Isomerism:

The isomers having different ligands in their coordination sphere are called coordination isomer of each other and the phenomenon is called coordination isomerism. It is possible only when complexes have at least two different coordination spheres.

The complexes $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are coordination isomer of each other.

Geometrical Isomerism:

Two or more isomers having different arrangements of ligands with a particular plane are called geometrical isomer of each other. The phenomenon is called geometrical isomerism. When two similar ligands are in same side of the plane, the isomer is called *cis*-isomer. On the other hand, if similar ligands are in different sides, the isomer is called *trans*-isomer.

Tetrahedral complexes do not show geometrical isomerism as in this case ligands are at equidistant. However, tetrahedral and octahedral complexes show geometrical isomerism.



Octahedral complexes of the type Ma_3b_3 exist in *fac*-isomer and *mer*-isomer. When three similar ligands are at same three triangular face, the isomer is called *fac*-isomer (fac stands for facial). If all three similar ligands are at meridonial position, the isomer is called *mer*-isomer (mer stands for meridonial).



Optical isomerism:

Like organic compounds, coordination compounds also exhibit optical isomerism and they exist in dextrorotatory (d or +) and laevorotatory (l or -) two forms.

Valence Bond Theory:

This theory was developed by Linus Pauling. The main features of this theory are the consideration of covalent nature of bonding between the ligand and metal ion.

There are following assumptions of valence bond theory:

- Metal or metal ions make available number of vacant atomic orbital equal to its coordination number.
- These atomic orbitals hybridize together to form equal number of equivalent hybrid orbitals.
- Ligand must contain at least one lone pair of electron on its sigma (σ)-orbital.
- Filled σ-orbitals of the ligands overlap with vacant hybrid orbital of metal to form ligand to metal σ-bond.
- Type of hybridization involved in the formation of the complex decides the geometry of the complex.
- If inner d-orbitals participate in hybridization, inner orbital complex is formed. Participation of outer d-orbitals in hybridization forms outer orbital complexes.
- Presence of unpaired electron makes the complex paramagnetic and if all the electrons are paired then the complex is diamagnetic.
- Hund's rule is applied for the arrangement of the electron of the non bonded atomic orbitals.
- The π -bonds may be of L \rightarrow M and M \rightarrow L. Formation of L \rightarrow M, π -bonds decreases the stability of the σ -bonds where as formation of M \rightarrow L, π -bonds increase the stability of the σ -bonds.

Limitations of Valence Bond Theory:

The main limitation of valence bond theory is it itself dependence upon the magnetic properties of the complexes. There are following limitations may be illustrated behind the valence bond theory;

- VBT fails to explain the actual geometry of the complex, when two or more geometry are possible for same magnetic properties.
- This theory does not explain the colour and spectra of the complex.
- It fails to describe the reaction shown by the complexes.
- It doesn't consider any excited state of the complex and therefore fails to explain the thermodynamic properties of the complex.
- The VBT does not properly explain the role of ligands in the formation of complexes.
- The VBT fails to explain the position of ligands in the spectrochemical series.

Crystal Field Theory:

The main feature of this theory is the consideration of ionic nature of metal-ligand linking and splitting of sub orbit. There are following assumptions of this theory are as below:

- This theory considers that the metal-ligand bonding in metal complexes purely ionic in nature.
- Ligands are either anionic or neutral. Non ionic ligands are considered as point negative charged where as neutral ligands is point negative dipole.
- Metal ions are positively charged and ligands are either point negative charged or point negative dipole, between them there exist electrostatic force of attraction.
- Interaction between the metal d-electrons and ligands is purely repulsive in nature.
- Five d-orbitals of the free metal ion remain in degenerate state but these orbitals split in different sets when ligands surrounds metal ion and form a complex.
- The difference in energy between upper energy level and lower energy level is called crystal field splitting energy (Δ).
- By comparing Δ and pairing energy high spin and low spin nature of the complex is predicted.
- Splitting follows the Bari Centre rule i.e. the centre of gravity of splitted orbitals remain same as it was the unsplitted orbital

Splitting of d-orbitals:

In octahedral complex formation, ligands approach the metal along the axis whereas in tetrahedral complex formation ligands approach the metal just about between the axes. It is this reason, energy of two d-orbitals is raised while energy of three d-orbitals is decreased in octahedral field. It is reversed in tetrahedral field, as ligands approach the metal are reversed manner. Splitting may be shown as:



Limitations of CFT

- Position of the ligand in the spectrochemical series cannot be explained by CFT.
- Several spectroscopic methods such as ESR, NMR etc confirms the covalent nature of the bonding in the complexes.
- Inter electronic repulsion of the free metal ion decreases when it forms a complex. It is called cloud expanding or *Nephelauxetic effect*. It can be considering the metal-ligand orbital overlap. Overlapping is possible in the case of covalency which is not allowed the CFT. Therefore, it fails to explain Nephelauxetic effect.
- It fails to explain the charge transfer spectra.
- Explanation of anti ferromagnetism by super exchange mechanism required the use of metal-ligand orbital overlap. It is not allowed under the CFT and hence, cannot be explained by CFT.

HALOAKANES AND HALOARENES

Haloakanes and Haloarenes:

Halogens derivatives of hydrocarbons are called haloalkanes where as halogens derivatives of aromatic hydrocarbons are called haloarenes.

Classifications:



b. From alkene



Physical Properties:

Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher members are either gases or solids. They have higher boiling points than that of hydrocarbons of similar molar mass. As size and molar mass of the alkyl halides increase, boiling point increases. Boiling point decreases with increase in branching for isomeric alkyl halides. Bromo, iodo, polychloro derivatives of hydrocarbons have higher density than that of water. Haloalkanes are slightly soluble in water. Solubility decreases with increase in carbon chain.

Chemical properties:

Haloderivatives of hydrocarbons show following types of chemical reactions.



Substitution Reaction:

The reaction in which an atom or group is replaced by some other is known as substitution reaction. On the basis of kinetics, it is further classified into two types say *U*nimolecular *N*ucleophilic Substitution (S_N1) reaction and Bimolecular *N*ucleophilic Substitution (S_N2) reaction.



Reactivity of alkyl halide towards substitution reaction:

Reactivity of alkyl halide towards $S_N 1$ reaction is $3^0 > 2^0 > 1^0 >$ Methyl Halide. Reactivity towards $S_N 2$ reaction is just reverse as $3^0 < 2^0 < 1^0 <$ Methyl halide.

Elimination Reaction:

Alkyl halides exhibit elimination in which hydrogen (from β -position) and halogen (from α -position) atoms are removed from adjacent position to form corresponding alkene. The reaction is also called dehydrohalogenation process. Reactivity towards dehydrohalogenation is:

 $R-F < R-Cl < R-Br < R-I \text{ and } 3^0 > 2^0 > 1^0.$

Saytzeff's Rule:

More substituted alkenes are formed as a major product in a particular elimination reaction. E1 reaction always follows Saytzeff's rule. However, it is followed in E2 reaction if antiperipanar β -hydrogen is available in such position.



Formation of Grignard Reagent:

Allyl halides react with magnesium in presence of dry ether in anhydrous condition to form alkyl magnesium halide. It is called Grignard reagent in honour of its inventor Victor Grignard.

Electrophilic Substitution Reaction:

The substitution by an electrophile is called Electrophilic substitution reaction. It is the characteristics of aromatic compounds. Aryl halides exhibit Electrophilic substitution reaction at ortho and para position with slower reactivity than benzene as halogens are ortho/para directing and ring deactivating group. Some characteristics Electrophilic substitution reactions are:

(i.) Halogenation





F. C. alkylation may be carried out by using alcohol or alkene in acidic medium.



F. C. acylation may be carried out by using acid anhydride.

ALCOHOLS, PHENOLS AND ETHERS

Types of Alcohols:



(e.) By using Grignard reagent:

Formaldehyde forms 1[°] alcohol while other aldehydes form 2[°] alcohol. Ketones form 3[°] alcohol.

(f.) By the hydrolysis of alkene:

$$R \longrightarrow CH_2 \xrightarrow{H_3O^+} R \longrightarrow CH_3 \text{ More substituted alcohol} HO$$

(g.)By hydroboration-oxidation of alkene:



Physical Properties:

Lower alcohols are liquid due to presence of intermolecular H-bonding while higher alcohols are solid in state. Lower members have pleasant smell but burning taste. Higher members are odourless and tasteless. Lower alcohols are soluble in water as they can form intermolecular H-bonding with water. As number of hydroxyl group increases, solubility increases. Solubility decreases with increase in carbon chain. Alcohols have higher melting and boiling point than those of alkanes, alkenes, alkyl halides and ethers of similar molar mass.

Chemical properties:





Preparation of Phenol:

Phenol is used to make thermosetting plastic like Bakelite, urea-formaldehyde resin. The 0.2 % solution of phenol is used as antiseptic while it 2% solution acts as disinfectant.







Physical Properties:

Phenol is colourless liquid. It is soluble in water as it forms intermolecular H-bonding. It is acidic in nature as its conjugate base phenoxide ion is resonance stabilized base. It is toxic in nature and shows antiseptic properties.

Chemical Properties:







Ethers are extensively used as solvents because they are almost inert. Some of them are used as anesthetic in their pure form. It is used in perfumes.



Methods of Preparation:

(i.) By dehydration of alcohols: comparatively at lower temperature. less hindered alcohols are used to minimise the formation of side product alkene. $_{H_2SO_4}$

$$H_3C$$
 OH $\xrightarrow{\text{or, }H_3PO_4}$ H_3C O CH₃ + H₂O

(ii.) Williamson's Synthesis:



Physical properties:

Lower members like dimethyl ether and ethyl methyl ether are gases while higher members are colourless, pleasant smelling and low boiling volatile liquids. The boiling points of ethers increase with increase in molar mass. They are sparingly soluble in water but readily soluble in organic solvents.

Chemical properties:



When less quantity of hydrohalic acid is used, halide of less substituted alkyl is formed.

(iii.)
$$H_3C \frown O^{CH_3} + H \longrightarrow H_3C \frown H_3C \frown H_3C \frown OH$$

Less

Electrophilic substitution on aromatic ring:

Alkoxy groups are considered as ortho/para directing and ring activating group as they donate its lone pair of electrons to the aromatic ring especially at ortho/para positions.

(i.) Nitration:



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FeCl₂



ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Functional groups:

These compounds belong to carbonyl compounds. The functional group of the compounds is:



Methods of Preparations for Aldehydes and Ketones:







(viii.) From organometallic compounds:



Physical Properties:

Formaldehyde is gas while acetaldehyde is a volatile liquid at room temperature. Other aldehydes and ketones are either liquid or solid at room temperature. Aldehydes and ketones are polar in nature. Therefore their boiling points are higher than that of non-polar compounds say hydrocarbons and ethers of comparable molar masses. They have lower boiling points than that of alcohols and carboxylic acids as they possess intermolecular H-bonding. The lower members say methanol, ethanol and propanone are miscible with water as they form intermolecular H-bonding with water. However, solubility decreases with increase in carbon chain.

Chemical Properties:





When two different aldehyde or ketones participate in aldol reaction, it is called crossed aldol reaction.

(vi.) Cannizzaro's reaction: two or more aldehydes or ketones lack of α -hydrogen are refluxed then one of the molecules is reduced to form alcoholand other oxidized to form corresponding acid.



When two different aldehydes and ketones lack of α -hydrogen participate in Cannizzaro's reaction, it is specially called crossed Cannizzaro's reaction.

(vii.) Electrophilic substitution reaction: aldehydic and ketonic groups act as Meta directing and ring deactivating group.



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CARBOXYLIC ACIDS:

Carboxyl group (–COOH) containing carbon compounds are called carboxylic acids. Some of them are:

Methods of Preparation:

(i.) By the oxidation of alcohols and aldehydes:



Physical Properties:
Aliphatic carboxylic acids up to nine carbon atoms are colourless liquid with unpleasant odour. Higher carboxylic acids are waxy solids. Carboxylic acids have higher boiling points even than alcohols of similar molar mass. It is due to carboxylic acids form very strong intermolecular Hbonding. Its hydrogen bonding is so strong that carboxylic acids exist in dimeric form even in vapour phase. They are soluble in water because they form intermolecular H-bonding with water. Solubility of carboxylic acids in water decreases with increase in carbon chain (Hydrophobic in nature).

Acidic properties:

Carboxylic acids loose H⁺ ion and form resonance stabilized conjugate base i.e. carboxylate ion indicating acidic character.



Acidic character decreases with increase in +I effect and +M effect. It decreases with increase in -I effect and -M effect.

CICH₂COOH>CH₃COOH and HCOOH>CH₃COOH FCH₂COOH>CICH₂COOH>BrCH₂COOH>ICH₂COOH



Chemical Properties:

(1.) Esterification in acidic medium. In basic medium, ester doesn't form.

$$H_{A}^{O} + H_{O} - R^{1} \xrightarrow{H_{3}O^{+}} R \xrightarrow{O} - R^{1} + H_{2}O$$

(ii.) Formation of anhydrife in presence of dehydrating agent say H_2SO_4 or P_2O_5 .



(iii.) Formation of amide.

(iv.) Formation of acid chloride:



(v.) Decarboxylation to form hydrocarbon containing less number of carbon.

$$R \xrightarrow{\text{NaOH/CaO}} R \xrightarrow{\text{NaOH/CaO}} R \xrightarrow{\text{H}} \text{H} \text{Na}_2\text{CO}_3 \text{ Kolbe's electrolysis}$$

(vi.) Rdeduction:



(vi.) Hell-Volhard-Zelinsky (HVZ) reaction: α -Halogenation process:



Electrophilic Substitution Reaction:

Carboxyl group acts as ring deactivating and meta directing group towards electrophilic substitution reaction.



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AMINES

4.2.1. Amines: Classification

Amines are the derivatives of ammonia (NH₃). Successive replacement of the hydrogens by alkyl groups, aryl groups or cycloalkyl groups leads to amines. Thus amines are classified as:

- a. Primary (1^0) amine,
- b. Secondary (2^0) amine and
- c. Tertiary (3^0) amine.

Quaternary nitrogen compounds are positively charged species. It is called quaternary ammonium salt.

1 able:-2.1			
1 ⁰ amine	2^0 amine	3 ⁰ amine	4 ⁰ ammonium salt
RNH ₂	R ₂ NH	R ₃ N	R4N ⁺
CH ₃ NH ₂	(CH ₃) ₂ NH	(CH3)3N	(CH ₃) ₄ N ⁺
CH ₃ CH ₂ NH ₂	(CH ₃ CH ₂) ₂ NH	(CH ₃ CH ₂) ₃ N	$(CH_3CH_2)_4N^+$

Amines may be classified on the basis of presence of alkyl or aryl group.

- a. Aliphatic amines,
- b. Aromatic amines and
- c. Heterocyclic amines.

4.2.3. Methods of Preparation:

a. Amonolysis of alkyl halides:

When alkyl halide is heated with ammonia or alcoholic ammonia at 100 0 C in a sealed tube, we get mixture of 1⁰, 2⁰, 3⁰ amines, quaternary ammonium salt and salts of 1⁰, 2⁰ and 3⁰ amines. Hence, this method is not useful for the preparation of an amine. However, use of excess NH₃ results 1⁰ amine.

$$R \xrightarrow{X} H NH_3 \xrightarrow{\Delta} R \xrightarrow{NH_3^+} X^- \xrightarrow{NaOH} R \xrightarrow{NH_2^-} R$$

b. The Gabriel synthesis:

Treatment of phthalimide with potassium hydroxide forms potassium phthalimide. After the heating of this potassium salt with an alkyl halide and followed by hydrolysis, it forms primary amine.



c. Reduction of Nitro Compounds:

By the reduction of nitro group, we can prepare both aliphatic and aromatic primary amines.

Reduction of the nitro group may be accomplished by using hydrogen in presence of metal such as Ni, Pt or Pd; Sn/HCl, SnCl₂/HCl, Zn/HCl or Fe/HCl.



d. Reduction of nitriles:

When nitriles are reduced with Na in ethanol, corresponding amines are formed. This reaction is called Mendius reaction.



This reaction may be accomplished with Raney nickel or LiAlH₄ in ether.

e. Hofmann Rearrangement:

When a primary amide is heated with sodium hypo bromide or bromine and base (NaOH or KOH), it converts into primary amine with loss of one carbon atom. The reaction is called Hofmann rearrangement.

(f.) Reduction of amides:



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Physical properties:

Lower amines like methyl amine, ethyl amine, dimethyl amine and trimethyl amine are gases at room temperature. Higher amines are colourless liquid. Amines of higher molecular mass are solids. Volatile amines usually have unpleasant odour.

The 1^{0} and 2^{0} amines have higher boiling point than that of 3^{0} amines of similar molar mass.

 CH₃CH₂CH₂CH₂-NH₂
 (CH₃CH₂)NH
 CH₃CH₂-N(CH₃)₂

 B.P.; 77.8 ^oC
 B.P.; 56.3 ^oC
 B.P.; 37.5 ^oC

All amines $(1^0, 2^0 \text{ and } 3^0)$ have higher boiling point than that of alkanes of comparable molar mass. 1^0 and 2^0 amines have higher boiling point than ethers of comparable molar mass, because they can form intermolecular hydrogen bonding but ethers do not. However, amines have lower boiling point than alcohols and carboxylic

acid. Amines are soluble in water because they can form intermolecular hydrogen bonding. As hydrocarbon chain is hydrophobic in nature so, solubility decreases with increase in length of hydrocarbon chain.

Basic Properties:

Amines have lone pair of electrons for protonation. So, they act as Lewis base.

$$R-\dot{N}H_2 + \dot{H}^{\dagger} \longrightarrow R-NH_2$$

Alkanaminium

a. Aliphatic amines are stronger base than ammonia.

Due to electron releasing nature i.e. +I effect of the alkyl group, electron density on nitrogen is greater. The increased electron density on nitrogen in aliphatic amines is more available for proton.

$$R \xrightarrow{H^+} R \xrightarrow{H^+} R$$

Further, +I effect of alkyl group stabilizes the conjugate acid of alkyl amine. It is this reason aliphatic amines are stronger base than ammnonia.

On the other hand, introducing successive alkyl groups, basic strength increases. But the increment becomes smaller and smaller, which is changed on going from 2^0 to 3^0 . Observed orders are:

 $2^0 > 1^0 > 3^0 > NH_3$ for methyl amines

 $2^0 > 3^0 > 1^0 > NH_3$ for ethyl amines

b. Aromatic amine is weaker base than aliphatic amine.

In the case of aromatic amine, lone pair of electrons of nitrogen takes part in resonance with π -electrons of benzene ring.



Chemical Properties:

a. Reaction with alkyl halides:

Primary amines react with alkyl halide to form secondary amine, which further react with alkyl halide to form tertiary amines. The tertiary amine reacts with alkyl halide to form quaternary ammonium salt.



If amine is used in excess, monoalkylation is favoured.

b. Reaction with acid chloride:

Primary amines and secondary amines react with acid chloride in presence of tertiary amine or pyridine to form secondary and tertiary amide respectively.



c. Carbyl amine reaction:

Primary amines, aliphatic and aromatic both react with chloroform in presence of potassium hydroxide to form its corresponding isocyanide with foul odour.



Due to foul odour of isocyanide, this reaction is used for the test of primary amine. This reaction is used to distinguish it from 2^0 and 3^0 amines.

d. Reaction with benzene sulphonyl chloride: Primary and secondary amines react with benzene sulphonyl chloride to form N-substituted and N,N-disubstituted benzene suphonamides respectively.



Due to absence of hydrogen on nitrogen, tertiary amine does not react with benzene sulphonyl chloride. This reaction is also used for the distinguishing primary, secondary and tertiary amine. It is called Hinsberg test.

e. Reaction with nitrous acid:

(a.) Aliphatic primary amines react with nitrous acid to form its corresponding alcohol.

$$H_{3}C \longrightarrow NH_{2} \xrightarrow[0-5 \circ C]{NaNO_{2}, HCl} H_{3}C \longrightarrow OH + N_{2} + NaCl + H_{2}O$$

Ethanamine Ethanol

Aromatic primary amines form diazonium salt.



Secondary amines and tertiary amines react with different manner.

Electrophilic Substitution reaction:

The -NH₂ group acts as orto/para directing and ring activating group.



BENZENEDIAZONIUM CHLORIDE

Methods of Preparation:

Aniline reacts with freshly prepared nitrous acid at 0-5 °C to form benzenediazonium chloride.



BIOMOLECULES



Carbohydrates:

The optically active polyhydroxy aldehydes and ketones are called carbohydrates.

Sugars:

Due to sweet test, carbohydrates are commonly called sugars. Some of the sugars reduce Tollen's reagent and Fehling solution due to presence of free aldehydic or ketonic group. they are called *Reducing Sugar*.

On the other hand, some of the sugars do not reduce Tollen's reagent and Fehling solution due to absence of free aldehydic or ketonic group. They are called *Non-Reducing Sugar*.

Structure of Glucose:

The molecular formula of glucose ($C_6H_{12}O_6$) is confirmed by mass spectrometry. By the formation of n-hexane with HI, the arrangement of six carbons in straight chain is confirmed. Presence of carbonyl group is confirmed as it forms oxime with hydroxyl amine and cyanohydrin with hydrogen cyanide. It forms gluconic acid containing same number of carbon with bromine water indicating presence of aldehydic group. Acylation of glucose forms pentaacetate derivative, which confirms the five hydroxyl group. Since glucose is stable so, all hydroxyl groups are at different five carbon atoms. Glucose forms glucaric acid with oxidation of nitric acid having same number of carbon atoms.

Although, glucose has aldehydic group however, it doesn't give 2,4-DNP test, doesn't form addition product with hydrogen sulphite, pentaacetate of glucose doesn't react with hydroxyl amine. Glucose is found to exist in two different crystalline form say α -form and β -form.

On the basis of above facts, E. Fischer gave the following structures of glucose.



Both α -glucose and β -glucose are anomers of each other. Since they are differing at C-1 so, this carbon-1 is called anomeric acroon.

Structure of Fructose:

All things of fructose are same as that of glucose. But fructose and ketonic carbonyl group instead of aldehydic carbonyl group. Its cyclic structure is in furanose form. The structures are:





Proteins:

Proteins are the polymers of polypeptides, which itself consists of amino acids linked by peptide bonds, which is an amide bond. The organic acids containing amino group as well as carboxylic group are called amino acids. In proteins, α -amino acids are present. Among twenty amino acids ten amino acids are essential, which are required to take with diet and rest amino acids are non essential. Out of total amino acids, only glycine is optically inactive. Amino acids exists in zwitter ionic form in aqueous solution

Structure of Proteins:



Denaturation of Proteins:

When proteins are allowed to change in temperature or pH change, its natural properties like biological activity, three dimensional structures are changed. It is called denaturation of proteins.

Enzymes:

The substances, which change the rate of biochemical reactions, are called enzymes. Enzymes are very specific for a particular reaction and for a particular substrate. They are named either after the compound upon which they work or after the reaction, where they are used, say maltase, invertase, zymase, oxireductase etc.

Enzymes work on the basis of key-lock mechanism.

Vitamins:

Organic compounds those are required in the diet to perform specific biological functions for normal maintenance of optimum growth and health of the organism. The fat soluble vitamins are vit-A, vit-D, vit-E and vit-K. The water soluble vitamins are vit-B group and vit-C.

Nucleic Acids:

There are two nucleic acids; say deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA exists in double helical structure while RNA exists in single helical structure.

Nucleic acids are the polymer of nucleotide, which itself consists nucleoside and phosphate. Each nucleoside consists of deoxyribose (ribose in RNA) sugar and base. There are mainly two types of bases purine and pyrimidine. Adenine and guanine belongs to purine while cytosine, thymine and uracil are the pyrimidine bases. Composition of DNA is: *2-deoxyribose, adenine, guanine, thymine* and *cytosine* while composition of RNA is: *ribose, adenine, guanine, uracil* and *cytosine*.

POLYMERS

The regular repeating process of many small molecules to form a large molecule by linking together is called polymerization. The products are called polymers.

polymerisation n M -M-M-M-M-M-Polymer Monomer



Types of Synthetic Polymers:

On the basis of method of preparation synthetic polymers may be classified into following types:

- a. Chain growth polymers and
- b. Step growth polymers.

Chain Growth Polymers:

Such types of synthetic polymers, which are made by addition of monomers to the end of a growing chain is called Chain growth or addition polymers. For example;



The monomer of chain growth polymers is either ethylene or substituted ethylene. Hence these polymers are also called *vinyl polymers*.

Types of Polymerization Reactions:

On the basis of formation of intermediate during polymerization, mechanism may be classified as:

- a. Free radical polymerization,
- b. Cationic polymerization and
- c. Anionic polymerization.

Free Radical Vinyl Polymerization:

Initiation step:

In this mechanism a radical initiator is added to the monomer.

$$R \xrightarrow{O} \xrightarrow{O} R \xrightarrow{Peroxide} 2 R \xrightarrow{O}$$

$$R^{-0}$$
 H_2C $X \rightarrow R^{-0}$ CH^{-1}_{X}

Propagation step:

In this step radical of monomer reacts with another monomer to form a new subunit, which propagates the chain.



Termination Step:

Finally, propagation step is terminated by any one of the following ways.

By the chain combination:



Styrene, vinyl acetate, vinyl chloride, acrylonitrile and 1,3-buadiene undergo radical polymerization. When a propagating site abstracts a hydrogen atom from a chain, branching of the polymer chain is observed.

Unbranched chains can pack together more closely. So, it is also known as High Density Polyethylene (HDP). It is relatively hard plaster. On the other hand, branched chains are not so closely packed. So, it is called Low Density Polyethylene (LDP). It is flexible in nature.

Condensation or Step Growth Polymerisation:

Such types of polymers which are formed by the intermolecular reaction of bifunctional molecules with the elimination of small molecules such H₂O, alcohol or HCl etc are called *step growth polymers or condensation polymers*. The process is called *step growth polymersation*.



On the basis of presence of functional group, step growth polymers may be classified as:

- Polyesters, a.
- b. Polyamides,
- Phenol-formaldehyde resin and c.

Polyesters:

The step growth polymers in which the monomers are joined together by ester groups are called polyesters. Dacron is an example of polyesters.



Polyamide:

The step growth polymers in which monomers are joined together by amide groups are called polyamides. Polyamides are commonly known as nylon. Nylon-6 and nylon-6,6 are the common examples of polyamides. The starting material of nylon-6 is ε-caprolactam.



Azepan-2-one or, caprolactam

Nylon-6,6 is formed by two different bifunctional monomers say adipic acid and hexane-1,6-diamine.



Bakelite:

The polymer formed by the polymerization of phenol and formaldehyde either in acidic or in basis medium, is called Bakelite.



Now when novolac is heated with formaldehyde, cross linking infusible solid mass is formed. It is called Bakelite.



Melamine-Formaldehyde Polymer:

It is formed by the condensation of melamine and formaldehyde.



Copolymer:

When more than one different monomer is allowed to polymerization, the process is called copolymerization. The polymer is called copolymer.



Rubber:

Natural rubber is the polymer of isoprene (2-methyl-1,3-butadiene). It is very soft and hence can't be used. It is subjected to vulcanization in which natural rubber is heated with 5% sulphur.

Synthetic rubbers are neoprene, Buna-S and Buna-N. Neoprene is the polymer of chloroprene (2-Chloro-1,3-butadiene).

Biodegradable Polymers:

Those polymers, which are decomposed by microorganisms and hence do not create pollution, are called biodegradable polymer. Poly β -hydroxybutyrate-co- β -hydroxyvalerate (PHBV) is an example of biodegradable polymer.



Nylon-2-nylon-6:

Nylon-2-nylon-6 is a polyamide copolymer of glycine and aminocaproic acid, which is a biodegradable polymer.



CHEMISTRY IN EVERY DAY LIFE

• Drugs/Medicines:

Chemical substances used for the treatment of diseases and for reducing pain are called drugs or medicines.

• *Chemotherapy:*

The branch of chemical science in which chemicals are used in treatment of diseases is called chemotherapy.

Classifications of Drugs: **Classifications of Drugs** On the Basis of On the Basis of On the Basis On the Basis of Pharmacological effect **Drug Action** of Structure Molecular Targets Antacids Antihistamines Antifertility Tranquilizers Antimicrobials Disinfectants Analgesics Antiseptics Non-narcotic Narcotic Drug Target Interactions: Classifications of Drugs Receptors as drug Target Enzyme as drug Target **Drug-Enzyme Interactions** Catalytic Action of Enzymes Competitive Inhibitors Allosteric Site When preferentially react 'When react at different at active site of enzyme" site other than active site in such a way that shape of the active site of enzyme is changed " Chemicals in Food: Chemicals in Food Food Preservatives Artificial Sweetening Agents NaCl, Aspartame (100), Sugar, Saccharin (550), Vegetable Oils, Sucrolose (600) and PhCOONa. Alitame (2,000) Salts of Sorbic Acid and Salts of Propanoic Acid

• Cleansing Agents:



• Analgesics:

The drugs, which relieve or decrease painwithou causing unconsciousness, paralysis or mental confusion, are known as analgesics. Aspirin, analgin, saridon, anacine, aspro etc. are examples.

• Antiseptics:

The drugs, which are used to kill or prevent the growth of micro-organisms, are known as antiseptics.

• Antacids:

The drugs, which remove the excess acid and raise the pH to appropriate level in stomach, are called antacids. Milk of magnesia, magnesium carbonate, magnesium trisilicate, aluminium hydroxide gel, sodium bicarbonate and aluminum phosphate are common antacids. Cematidine, rantitidine (zantac) are also examples of antacids.

• Antihistamines:

The drugs, which are used to cure allergy, are called antihistamines. It is also called ant-allergic drugs.

Diphenylhydramine, chloropheniramine, promethazine, bromopheniramine (dimetapp) and terfenadine (seldane) etc are examples of antihistamine.

• Antifertility:

These drugs are used to control the birth of the child.

• Tranquilizers:

These drugs are used to cure mental diseases. They act on higher centers of central nervous system. They are also called antidepressants or psychotherapeutic drugs.

Equanil, calmpose, tofranil, veronal, amytal, valium, serotonin, cocaine, barbituric acid, luminal, seconal, iproniazid and pheneizine are examples of tranquilizers.

• Antimicrobials:

The drugs, which are used to control microbial diseases, are antimicrobials.

• Disienfectants:

These drugs kill microorganisms but are not safe for contact with living tissues.