UNIT-1 METALLURGY

1. **What are the differences between minerals and ores?**
   - A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds like oxides, sulphides etc... is called a **mineral**.
   - A mineral that contains a high percentage of metal, from which it can be extracted conveniently and economically are called **ores**.
2. **What are the steps involved in the extraction of pure metals from their ores?**

   (i) Concentration of the ore

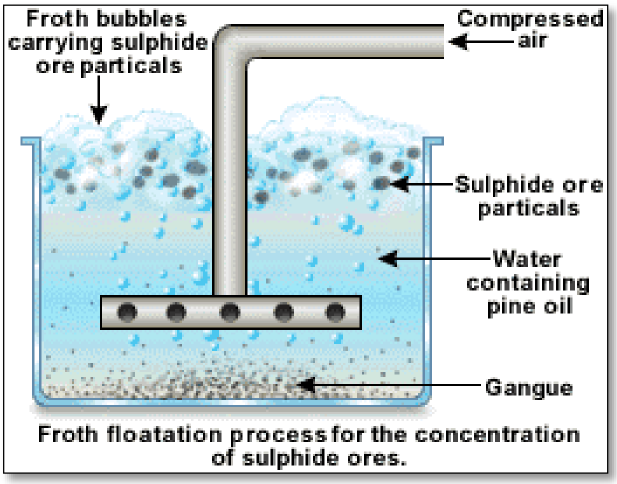
   (ii) Extraction of crude metal

   (iii) Refining of crude metal
3. **What are gangue?**

   Non-metallic impurities, rocky materials and siliceous matter associated with the ores are called gangue.
4. **Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.**

   Sulphide ores can be concentrated by froth floatation method.

   Examples: Galena and Zinc blende.
5. **Write a short note on gravity separation.**
   - ♣ This method is used to concentrate oxide ores. Example: Haematite, tin stone.
   - ♣ The ore having high specific gravity is separated from the gangue that has low specific gravity.
   - ♣ Finely powdered ore is treated with rapidly flowing current of water.
   - ♣ The lighter gangue particles are washed away by the running water.
6. **Write a short note on froth floatation.**



Froth floatation process for the concentration of sulphide ores.

- This method is used to concentrate sulphide ores. Example: galena , zinc blende.
- he crushed ore is suspended in water and mixed with

  Frothing agent : pine oil (or) eucalyptus oil
  Collector : sodium ethyl xanthate

- A froth is generated by blowing air through this mixture.
- The collector molecules attach to the ore particle and make them water repellent. As a result, ore particles wetted by the oil rise to the surface along with the froth.
- The froth is skimmed off and dried to recover the concentrated ore. The gangue particles that are preferentially wetted by water settle at the bottom.

7. Explain the role of depressing agents in froth floatation with an example.

- ❖ When a sulphide ore of a particular metal contains other metal sulphides as impurities, depressing agents such as NaCN, Na_2CO_3 are used to prevent impurities from coming to the froth. For example, Galena (PbS) contains ZnS as an impurity.
- ❖ Sodium cyanide (NaCN) is added to depress the flotation property of ZnS by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of zinc sulphide.

8. What is the principle behind a method called leaching?

- ✓ This method is based on the solubility of the ore in a suitable solvent.
- ✓ The crushed ore is allowed to dissolve in a suitable solvent.
- ✓ Metal is converted to its soluble salt or complex, gangue remains insoluble.

9. Explain how gold ore is leached by cyanide process.

Gold ore is crushed and leached with aerated dilute solution of sodium cyanide.

Gold is converted into a soluble cyanide complex. The gangue, aluminosilicate remains insoluble.

$$4Au + 8CN^- + O_2 + 2H_2O \longrightarrow \underset{\substack{\text{Auro cyanide} \\ \text{(a soluble complex)}}}{4\,[Au(CN)_2]^-} + 4OH^-$$

Gold can be recovered by reacting the deoxygenated leached solution with zinc. This process is called **cementation**.

$$2\left[Au(CN)_2\right]^- + Zn \longrightarrow \left[Zn(CN)_4\right]^{2-} + 2Au\downarrow$$

10. Explain how pure alumina is obtained by alkali leaching.

- When bauxite ore is heated with NaOH, it forms soluble sodium meta-aluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \xrightarrow[35atm]{470-520K} \underset{\substack{\text{Sodium meta aluminate} \\ \text{(soluble)}}}{2Na\left[Al(OH)_4\right]}$$

- Impurities, Iron oxide and Titanium oxide are left behind.
- This hot solution is neutralised by passing CO_2, to the form hydrated Al_2O_3.

$$2Na\left[Al(OH)_4\right] + 2CO_2 \longrightarrow \underset{\text{Hydrated alumina}}{Al_2O_3.\ xH_2O} + 2NaHCO_3$$

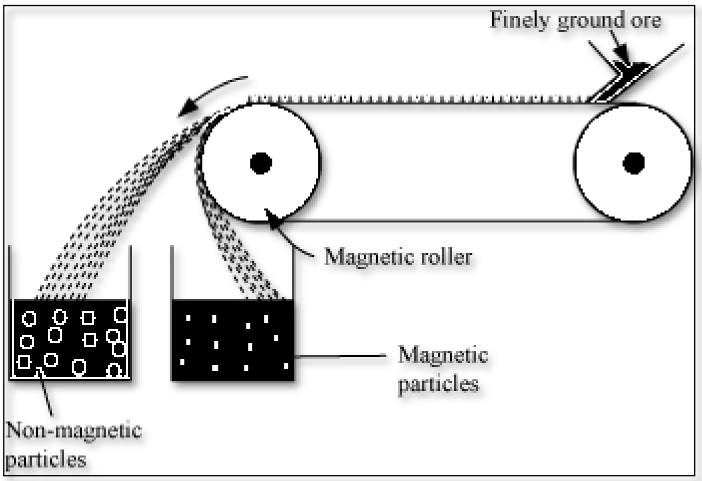
- This precipitate is filtered off and heated to 1670 K to get pure alumina Al_2O_3.

11. What is acid leaching?

Sulphide ores are leached with hot aqueous sulphuric acid. In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.

$$\underset{\substack{\text{sulphide}\\(\text{insoluble})}}{2ZnS} + 2H_2SO_4 + O_2 \longrightarrow \underset{\substack{\text{sulphate}\\(\text{soluble})}}{2ZnSO_4} + 2S + 2H_2O$$

12. Write a short note on magnetic separation.



- The crushed ore is poured on to an electromagnetic separator consisting of a belt moving over two rollers of which one is magnetic.
- The magnetic particles of the ore is attracted towards the magnet and collected as a heap close to the magnetic region, while the nonmagnetic particles collected as a separate heap away from the magnetic region.
- This method is applicable to ferromagnetic ores. For example, Pyrolusite (magnetic) is separated from siliceous impurities (non-magnetic).

13. What is roasting?

The process in which the concentrated ore is heated in the presence of excess oxygen is called roasting. During Roasting sulphide ores are converted into their oxides.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

14. What is Calcination?

The process in which the concentrated ore is heated in the absence of oxygen is called Calcination. During calcination Carbonate ore is converted into its oxide.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

15.What is smelting? Explain with an example.

Smelting is the process in which crude metal is obtained from its ore by heating beyond its melting point with reducing agents such as C, CO , Al etc.,Usually smelting is carried out in the presence of a flux.

For example, the oxide of iron can be reduced by carbon monoxide as follows.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

The ore is smelted with basic flux limestone (CaO).

The silica gangue present in the ore is acidic in nature, it combines with limestone (CaO) form calcium silicate (slag).

$$\underset{(\text{flux})}{CaO} + \underset{(\text{gangue})}{SiO_2} \longrightarrow \underset{(\text{slag})}{CaSiO_3}$$

16.What is flux?

A chemical substance that combines with gangue to form an easily fusible slag is called a flux.

17.What is slag? Explain with an example.

An easily fusible substance obtained when the ore is heated with flux is called a slag.

Examples:

$$FeO + SiO_2 \longrightarrow FeSiO_3(\text{slag})$$

18.What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3?

In the extraction of Iron from its oxide ore Fe_2O_3 (haematite ore), lime stone is added as a basic flux to remove acidic SiO_2 present as gangue.

$$\underset{\substack{(\text{flux})\\ \text{basic}}}{CaO} + \underset{\substack{(\text{gangue})\\ \text{acidic}}}{SiO_2} \longrightarrow \underset{(\text{slag})}{CaSiO_3}$$

19.Describe the role of Silica in the extraction of copper.

Silica SIO_2 is an acidic flux, it is used to remove basic oxide FeO formed during the extraction of copper from copper pyrite.

$$\underset{\substack{(gangue)\\ basic}}{FeO} + \underset{\substack{(flux)\\ acidic}}{SiO_2} \longrightarrow \underset{(slag)}{FeSiO_3}$$

20.What kind of metal oxides are reduced by carbon?

The oxides of metals which do not form carbides with carbon are reduced by carbon.

$$ZnO + C \longrightarrow Zn + CO$$

21. What kind of metal oxides are reduced by hydrogen?

The oxides of metals having less electropositive character than hydrogen are reduced by hydrogen.

$$Ag_2O + H_2 \longrightarrow 2Ag + H_2O$$

22. Write a note on Aluminothermite process.

- Metal oxides such as Cr_2O_3 can be reduced by an aluminothermite process.
- The metal oxide is mixed with Aluminium powder in a fire clay crucible.
- The reduction process is initiated by an ignition mixture (Mg + BaO2).

$$\underset{\text{(Barium peroxide)}}{BaO_2} + Mg \longrightarrow BaO + MgO \quad \Delta H = -852 kJmol^{-1} (\text{»}2400^0C)$$

- During the above reaction a large amount of heat is evolved which facilitates the reduction.

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$$

23. Explain Auto-reduction with an example.

Roasting of some of the ores give the crude metal. In such cases, the use of reducing agents is not necessary. For example, mercury is obtained by roasting cinnabar.

$$HgS + O_2 \xrightarrow{\text{Roasting}} Hg + SO_2$$

24. Give the limitations of Ellingham diagram.

- It gives information about the thermodynamic feasibility of a reaction. It does not tell anything about the rate of the reaction.
- It does not give any idea about the possibility of other reactions that might be taking place.
- The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the products which is not always true.

25. Explain the electrometallurgy of aluminium. (Hall-Herold process)

cathode : an iron tank lined with carbon.
anode : carbon blocks
electrolyte : molten cyrolite + 20% alumina +10% $CaCl_2$
Temperature : >1270 K

$CaCl_2$ decreases the melting point of the mixture.

≈ The chemical reactions involved in this process are as follows.

Ionisation of alumina : $Al_2O_3 \xrightarrow{\Delta} 2Al^{3+} + 3O^{2-}$
Reaction at cathode : $2Al^{3+} + 6e^- \longrightarrow 2Al$
Reaction at anode : $6O^{2-} \longrightarrow 3O_2 + 12e^-$

- ≈ Since carbon acts as anode the following reaction also takes place on it.

$$C + O^{2-} \longrightarrow CO + 2e^-$$

$$C + 2O^{2-} \longrightarrow CO_2 + 4e^-$$

- ≈ Due to the above two reactions, anodes are slowly consumed during the electrolysis.
- ≈ Pure aluminium is formed at the cathode and settles at the bottom.

26.Explain the principle of electrolytic refining with an example.

- ≈ The crude metal is refined by electrolysis in an electrolytic cell.
- ≈ Electrolytic refining of silver can be carried out as follows.

Anode : Impure silver rod
Cathode : Pure silver strip
Electrolyte : Acidified aqueous solution of silver nitrate

When a current is passed through the electrodes,

At anode : $Ag \longrightarrow Ag^+ + e^-$

At cathode : $Ag^+ + e^- \longrightarrow Ag$

27.Explain the principle involved in zone refining.

- ❖ **Principle**: The principle involved in Zone refining is fractional crystallisation. When the molten impure metal is allowed to solidify, the impurities prefer to be in the molten region.
- ❖ **Process:**
  - Impure metal is taken in the form of a rod.One end of the rod is heated using a mobile induction heater which results in melting of the metal on that portion of the rod.
  - When the heater is slowly moved to the other end the pure metal crystallises while the impurities will move on to the adjacent molten zone.
  - As the heater moves further away, the molten zone containing impurities also moves along with it.The process is repeated several times in the same direction to get high purity.
  - This process is carried out in an inert gas atmosphere to prevent the oxidation of metals. Ge, Si and Ga are refined by this process.

28.Give the basic requirement for vapour phase refining.

(i) Metal must be able to form a volatile compound with the particular reagent.

(ii) The volatile compound must decompose to give the pure metal.

29.How is nickel refined by Mond's process?

- Impure nickel is heated in a stream of carbon monoxide at 350 K.
- Nickel reacts with CO to form a highly volatile nickel tetracarbonyl.
- The solid impurities are left behind.

$$\underset{(\text{impure})}{\text{Ni}} + 4\text{CO} \xrightarrow{350\text{K}} \text{Ni}(\text{CO})_4$$

- Nickel tetracarbonyl is decomposed at 460 K to get pure Nickel.

$$\text{Ni}(\text{CO})_4 \xrightarrow{460\text{K}} \underset{(\text{Pure})}{\text{Ni}} + 4\text{CO}$$

30.Explain how Titanium is refined by Van-Arkel method.

- Impure Titanium is heated in an evacuated vessel with iodine at 550 K to form the volatile titanium tetra-iodide (TiI_4).

$$\text{Ti} + 2\text{I}_2 \xrightarrow{550\text{K}} \text{TiI}_4 \uparrow$$

- Impurities do not react with Iodine and are left behind.
- When TiI4 vapour is passed over a tungsten filament at 1800 K, it decomposes to give pure titanium which deposits on the filament.

$$\text{TiI}_{4(\text{v})} \xrightarrow[\text{» 1800K}]{\text{W filament}} \text{Ti} + 2\text{I}_2$$

31.List the uses of Aluminium.

s.no	Items	Uses
1	Aluminium	Sinks, cooking vessels. Reactors, refrigerators, gas pipelines. Electric cables.
2	Al foils	Wraps for food items
3	Aluminium alloys	(Al-Cu), (Al-Mn), (Al-Mg), (Al-Si) alloys are light weight and strong. They are used in design of aeroplanes and vehicles.

32.List the uses of Zinc.

s.no	Items	Uses
1	Zinc	is used in the galvanisation of iron and steel. Galvanisation protects them from rusting and corrosion.
2	ZnO	Paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles etc.
3	ZnS	Luminous paints, fluorescent lights and x-ray screens.

33.List the uses of Iron.

s.no	Items	Uses
1	Iron &its alloys	Bridges, electricity pylons, bicycle chains, cutting tools and rifle barrels.
2	Iron & its alloys	Magnets
3	Stainless steel	Architecture, bearings, cutlery, surgical instruments
4	Nickel steel	Cables, automobiles and aeroplane parts.
5	Chrome steel	cutting tools and crushing machines

34.List the uses of copper.

s.no	Items	Uses
1	Cu-Au alloy	Coins and jewellery
2	Cu alloys	wires, water pipes, electrical parts

35.List the uses of gold.

s.no	Items	Uses
1	Gold	coinage, as standard for monetary systems
2	Au-Cu alloy	jewellery
3	Gold plated metals	watches, artificial limb joints, dental filling etc.,
4	Gold nanoparticles	solar cells , catalysts

UNIT-2 P-BLOCK ELEMENTS-I

1. **Why group 18 elements are called inert gases? Write the general electronic configurator of group 18 elements.**

   18th group elements have completely filled p orbitals, they are more stable and they have least reactivity, hence they are called inert gases.

   The general electronic configuration is $ns^2\ np^6$

2. **Write a short note on anomalous properties of the first element of p-block.**

   The following factors are responsible for this anomalous behaviour of first member of each group.

   1. Small size of the first member.
   2. High ionisation enthalpy and high electronegativity.
   3. Absence of d orbitals in their valance shell.

3. **What is inert pair effect?**

   In p- block elements, while moving down a group, the outer s electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding. This effect is known as inert pair effect.

4. **List the Uses of boron.**

   1. ${}_5B^{10}$ is used as moderator in nuclear reactors as it absorbs neutrons.
   2. Amorphous boron is used as a rocket fuel igniter.
   3. Boron is essential for the cell walls of plants.

5. **What are borax beads? (or) what is borax bead test? How is it useful in identifying transition metal ions?**

   On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$\underset{\text{Borax}}{Na_2B_4O_7.10H_2O} \xrightarrow[-10H_2O]{\Delta} \underset{\substack{\text{sodium}\\\text{tetra borate}}}{Na_2B_4O_7} \xrightarrow{\Delta} \underset{\substack{\text{sodium meta}\\\text{borate}}}{2NaBO_2} + \underset{\substack{\text{Boric}\\\text{anhydride}}}{B_2O_3}$$

(Borax bead)

   The metaborates of many transition metals have characteristic colours. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed

6. **List the Uses of borax.**
    1. Borax is used for the identification of coloured metal ions.
    2. In the manufacture of optical and borosilicate glass, enamels and glazes for pottery
    3. It is used as a flux in metallurgy.
    4. It acts as a preservative.
7. **Why is boric acid considered as a weak acid? (or) Is boric acid a protic acid? Explain.**

    It is a very weak monobasic acid and, it cannot release H^+ ions, but it accepts hydroxyl ion.

    $$B(OH)_3 + 2H_2O \longrightarrow H_3O^+ + \left[B(OH)_4\right]^-$$
8. **How will you identify borate radical?**

    When boric acid or borate salt is heated with ethyl alcohol in presence of conc. sulphuric acid, an ester, trialkylborate is formed.

    $$\underset{\text{boric acid}}{B(OH)_3} + \underset{\text{Ethanol}}{3C_2H_5OH} \xrightarrow[\Delta]{\text{conc } H_2SO_4} \underset{\text{Triethyl borate}}{B(OC_2H_5)_3} + 3H_2O$$

    The vapour of this ester burns with a green edged flame and this reaction is used to identify the presence of borate radicals.
9. **List the Uses of boric acid.**
    1. Boric acid is used in the manufacture of pottery glasses, enamels and pigments.
    2. It is used as an antiseptic and as an eye lotion
    3. It is used as a food preservative.
10. **What is hydroboration reaction?**

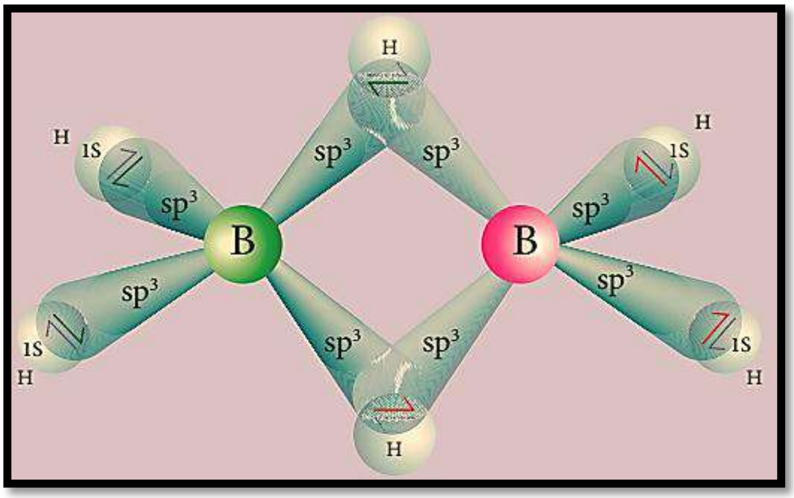
    Diborane adds on to alkenes and alkynes in ether solvent at room temperature. This reaction is called hydroboration. it undergoes anti Markovnikov addition.

    $$B_2H_6 + 6RCH = CHR \xrightarrow{\text{ether}} 2B(RCH - CH_2R)_3$$
11. **List the Uses of diborane.**
    - Diborane is used as a high energy fuel for propellant.
    - It is used as a reducing agent in organic chemistry.
    - It is used in welding torches.
12. **How is borazole prepared?**

    Diborane reacts with ammonia at higher temperatures give borazine (or) borazole. It is known as Inorganic benzene because of its structural resemblance with benzene.

    $$3B_2H_6 + 6NH_3 \xrightarrow[\text{closed vessel}]{180\text{-}190^0C} 2\ \underset{\text{Borazole}}{B_3N_3H_6} + 12H_2 \uparrow$$

13.Describe the structure of diborane.



- In diborane, the boron is sp^3 hybridised, three of the four sp^3 hybridised orbitals contains single electron and the fourth orbital is empty.
- Two hybridised orbitals of each boron overlap with the two H atoms to form four terminal 2c-2e bonds.
- The 3c-2e B-H-B bond formation involves overlapping the half-filled hybridised orbital of one boron, the empty hybridised orbital of the other boron and the half-filled 1s orbital of hydrogen. The bridging hydrogen atoms are in a same plane.
- In diborane two BH_2 units are linked by two bridged Hydrogens. There are eight B-H bonds. However, it contains only 12 valance electrons and are not sufficient to form normal covalent bonds.

14.**Write a note on McAfee process.**

$AlCl_3$ is obtained by heating a mixture of alumina and coke in a current of chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

15.How is potash alum prepared?

- The Alunite (or) alum stone is $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$.
- When alum stone is treated with excess of sulphuric acid, the aluminium hydroxide is converted to aluminium sulphate.

$$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3 + 6H_2SO_4 \xrightarrow{\Delta} K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$

- A calculated quality of potassium sulphate is added and the solution is crystallized to generate potash alum.

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \xrightarrow{\Delta} K_2SO_4.Al_2(SO_4)_3.24H_2O$$

- It is purified by recrystallisation.

16.List the Uses of potash alum.

- It is used for purification of water.
- It is used for water proofing and textiles.
- It is used in dyeing, paper and leather tanning industries.
- It is employed as a styptic agent to arrest bleeding.

17.What is catenation? Bring out the reasons for an extreme tendency of carbon for catenation.

Catenation is an ability of an element to form chain of atoms. The following conditions are necessary for catenation.

a. The element should have its valency greater than or equal to 2.
b. The element should have an ability to bond with itself.
c. The self-bond must be as strong as its bond with other elements.
d. Kinetic inertness of catenated compound towards other molecules.

Carbon possesses all the above properties and forms a wide range of catenated compounds.

18.Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on their physical properties?

❖ **Graphite**:

Graphite is the most stable form of carbon at normal temperature and pressure. It is soft and conducts electricity.

Structure of graphite:

- It is composed of two dimensional flat sheets of carbon atoms.
- Each sheet is a hexagonal net of SP^2 hybridised carbon atoms with a C-C bond length of 1.41 Å. The distance between successive sheets is 3.40 Å. The successive carbon sheets are held together by weak van der Waals forces.
- Each carbon atom forms 3 σ bonds with three neighboring carbon atoms and the fourth electron present in the unhybridized p orbital forms a π-bond.
- These π electrons are delocalized over the entire sheet which is responsible for its electrical conductivity. It is used as a lubricant either on its own or as a graphited oil.

❖ **Diamond**:

- Diamond is the hardest form of carbon. In diamond each carbon atom is sp^3 hybridised and to four neighboring carbon atoms by σ bonds with a C-C bond length of 1.54 Å.
- There is no free electrons for conductivity.it used for sharpening hard tools, cutting glasses, making bores and rock drilling.

19.**Write a note on the following:**

(i) fullerene **(ii) carbon nano tubes** **(iii) graphene**

(i) Fullerenes:

- ✓ fullerenes exist as discrete molecules such as C_{32}, C_{50}, C_{60}, C_{70}, C_{76} etc.. they have cage like structures.
- ✓ C_{60} Molecule is called Buckminster fullerene or Bucky balls. It has a fused ring structure consists of 20 six membered rings and 12 five membered rings.
- ✓ Each carbon atom is SP^2 hybridised and forms three σ bonds & a delocalized π bond giving aromatic character to these molecules. The C-C bond distance is 1.44 Å and C=C distance 1.38 Å.

(ii) Carbon nanotubes:

Carbon Nano tubes have graphite like tubes with fullerene ends. Along the axis, they are stronger than steel and conduct electricity. They are used in Nano scale electronics, catalysis, polymers and medicine.

(iii) Graphene:

Graphene has a single planar sheet of sp^2 hybridised carbon atoms that are densely packed in a honeycomb crystal lattice.

20.Write a note on industrial Preparation of carbon monoxide.

$$2C + \underset{(air)}{\underline{O_2 + N_2}} \longrightarrow 2CO + N_2$$

The mixture $(CO + N_2)$ is called producer gas. It is passed through a solution of CuCl under pressure to get $CuCl(CO).2H_2O$. At reduced pressures this solution releases the pure carbon monoxide.

21.How is propanal prepared by Oxo process?

$$CO + C_2H_4 + H_2 \longrightarrow CH_3CH_2CHO$$

22.Write a note on Fisher Tropsch synthesis.

$$nCO + (2n+1)H_2 \xrightarrow[50atm]{500-700K} \underset{Alkane}{C_nH_{(2n+2)}} + nH_2O$$

$$nCO + 2nH_2 \xrightarrow[50atm]{500-700K} \underset{Alkene}{C_nH_{2n}} + nH_2O$$

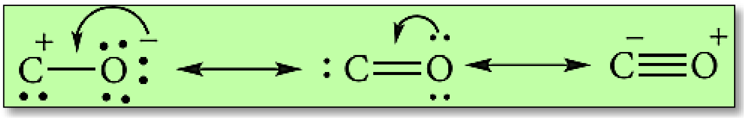
23.List the uses of carbon monoxide.

1. water gas$(CO+H_2)$and producer gas$(CO+N_2)$are used as industrial fuel.
2. CO is a good reducing agent.
3. CO is used as a ligand and forms carbonyl compound with transition metals

24.Give the structure of CO and CO_2.

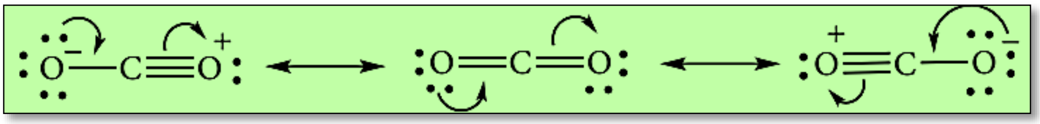
Structure of CO:

It has a linear structure. In carbon monoxide, three electron pairs are shared between carbon and oxygen. The C-O bond distance is 1.128 Å.



Structure of CO_2:

Carbon dioxide has a liner structure.In this molecule there is one C-O sigma bond. In addition there is 3c-4e bond covering all the three atoms.



25.List the Uses of carbon dioxide

1. CO_2 is used to produce an inert atmosphere for chemical processing.
2. It is important for photosynthesis.
3. It is used as fire extinguisher and as a propellant gas.
4. It is used in the carbonated beverages and in the production of foam.

26.**List the characteristics of silicones.**

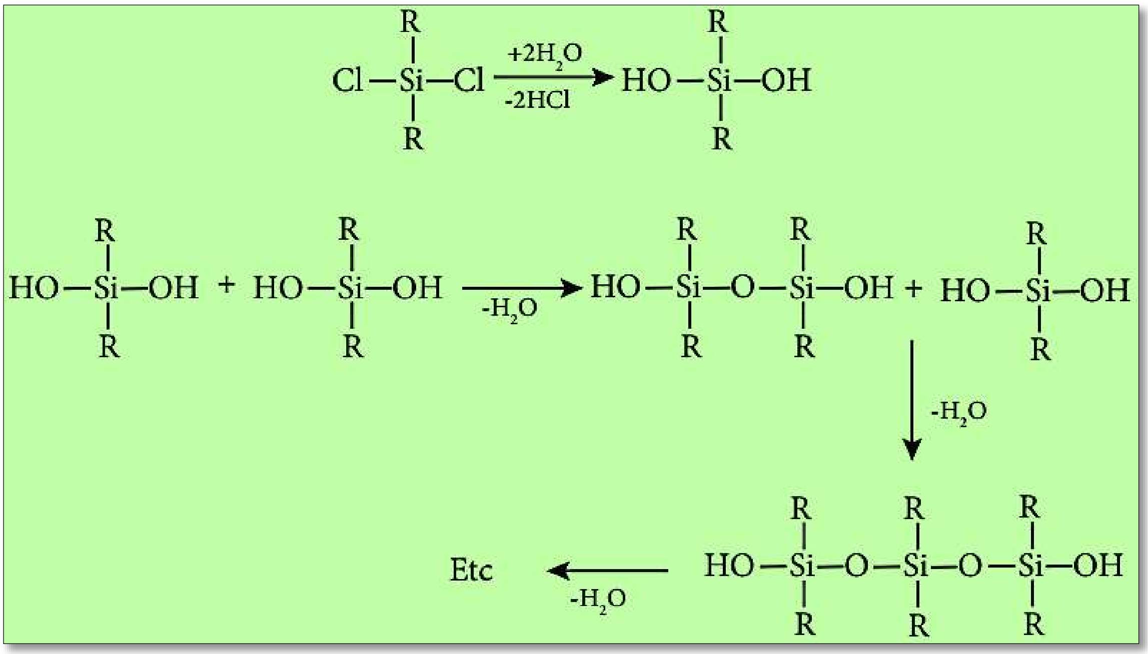
1. All silicones are water repellent because of their organic side groups.
2. They are thermal and electrical insulators.
3. They are chemically inert.
4. Lower silicones are oily liquids, whereas long chain silicones are waxy solids.
5. Viscosity of silicon oil doesn’t change with temperature, they don't thicken during winter.

27.**List the uses of silicones.**

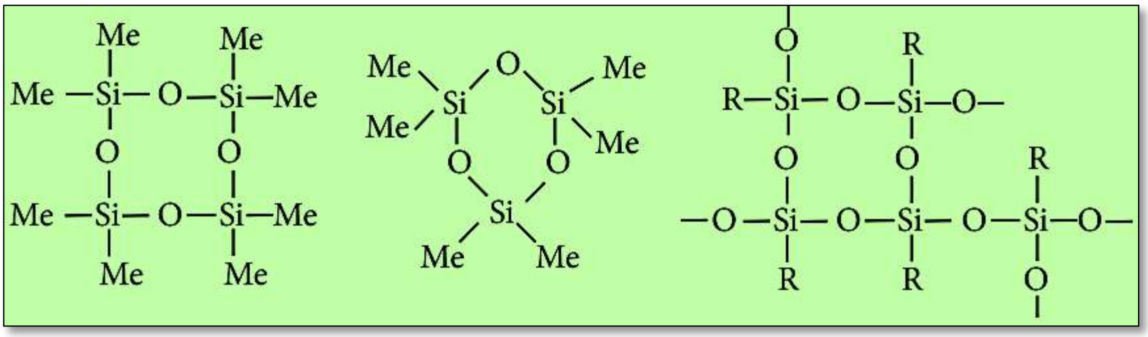
1. Silicones are used in vacuum pumps, high temperature oil baths etc...
2. They are used for making water proofing clothes.
3. They are used as insulting material in electrical motor and other appliances
4. They are mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.

28.How are silicones prepared?

- The hydrolysis of R_2SiCl_2 yields to a straight chain polymer which grown from both the sides.



- The hydrolysis of monoalkylchlorosilanes $RSiCl_3$ yields to a very complex cross linked polymer.
- Linear silicones can be converted into cyclic or ring silicones when water molecules is removed from the terminal –OH groups.



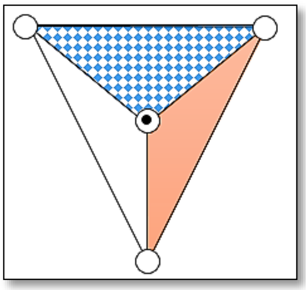
29.Explain the Types of Silicates with one example each.

Ortho silicates (Neso silicates):

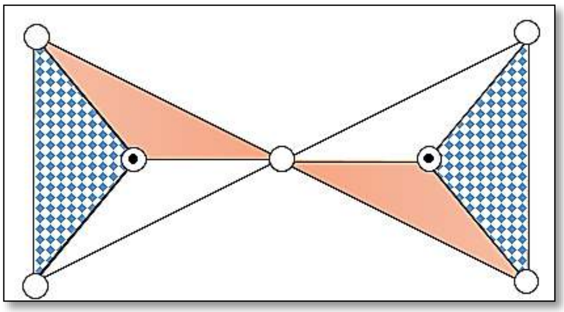
Silicates which contain discrete $[SiO_4]^{4-}$ tetrahedral units are called ortho silicates or neso silicates. Examples:

Phenacite - Be_2SiO_4

Olivine $-(Fe/Mg)_2SiO_4$

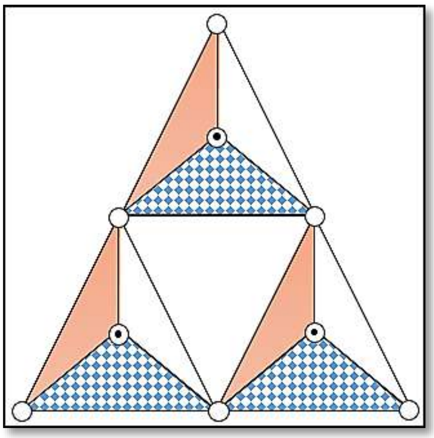


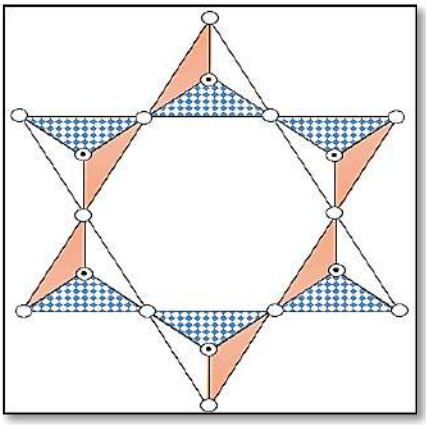
Pyro silicate (or) Soro silicates):



Silicates which contain $[Si_2O_7]^{6-}$ ions are called pyro silicates (or) Soro silicates. They are formed by joining two $[SiO_4]^{4-}$ tetrahedral units by sharing one oxygen atom at one corner. Example : Tortveitite – $Sc_2Si_2O_7$

Cyclic silicates (or Ring silicates)





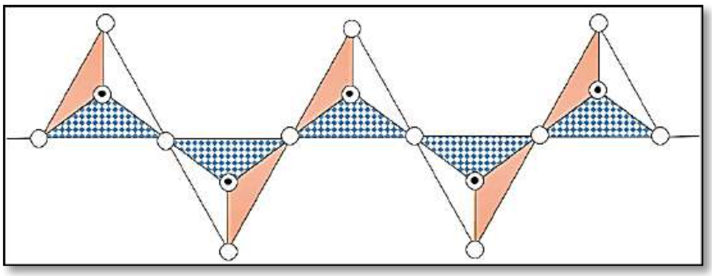
Silicates which contain $(SiO_3)_n^{2n-}$ ions are called cyclic silicates. They are formed by linking three or more $[SiO_4]^{4-}$ tetrahedral units cyclically. In cyclic silicates, each silicate unit shares two of its oxygen atoms with other units.

Example: Beryl $-[Be_3Al_2(SiO_3)_6]$

Inosilicates :

Silicates which contain 'n' number of silicate units liked by sharing two or more oxygen atoms are called Inosilicates. They are further classified as chain silicates and double chain silicates.

a. Chain silicates – Pyroxenes:

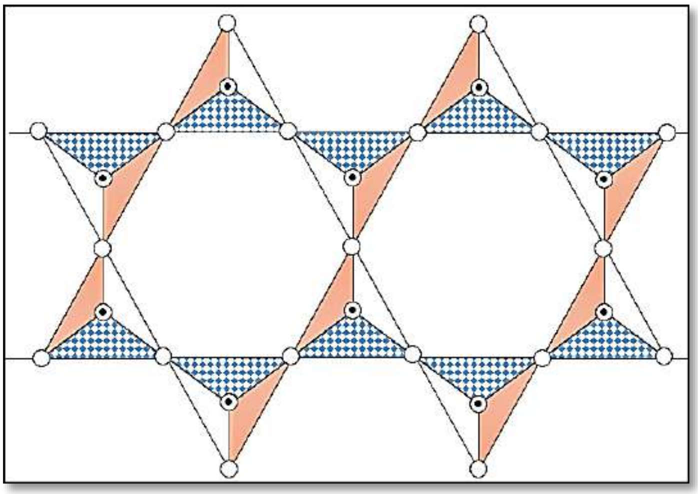


These silicates contain $(SiO_3)_n^{2n-}$ ions. They are formed by linking ‘n’ number of $[SiO_4]^{4-}$ tetrahedral units linearly.

Each silicate unit shares two of its oxygen atoms with other units.

Example: Spodumene – $LiAl(SiO_3)_2$.

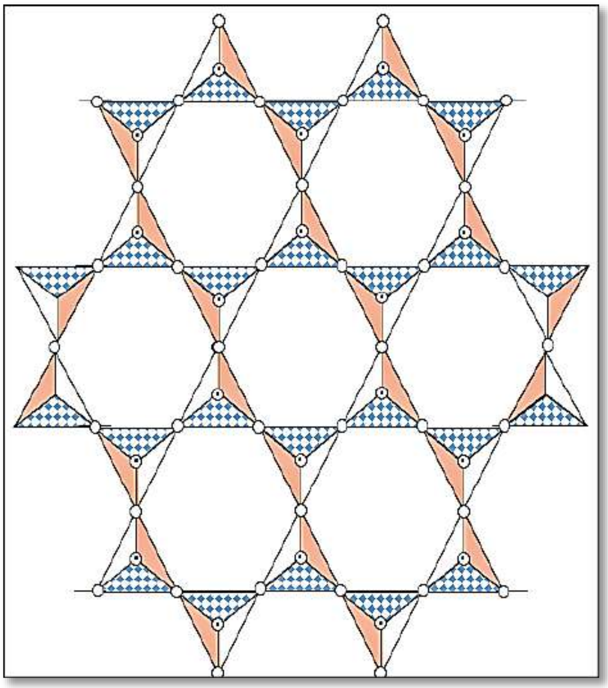
b. Double chain silicates – Amphiboles



These silicates contains $[Si_4O_{11}]_n^{6n-}$ ions. In these silicates there are two different types of tetrahedra. (i) Those sharing 3 vertices (ii) Those sharing only 2 vertices.

Examples: Asbestos

c. Sheet or Phyllo silicates



Silicates which contain $(Si_2O_5)_n^{2n-}$ ions are called sheet or Phyllo silicates. In these, Each $[SiO_4]^{4-}$ tetrahedron unit shares three oxygen atoms with others and thus by forming two-dimensional sheets.

Example: Talc, Mica etc...

d. Three dimensional silicates (or tecto silicates):

Silicates in which all the oxygen atoms of $[SiO_4]^{4-}$ tetrahedra are shared with other tetrahedra to form three-dimensional network are called three dimensional or tecto silicates. They have general formula $[SiO_2]_n$ .Example: Quartz.

30. Write a note on zeolites.

- ♣ Zeolites are 3D crystalline solids with general formula $NaO.Al_2O_3.x(SiO_2).yH_2O$ $(x = 2 \text{ to } 10;\ y = 2 \text{ to } 6)$. They are hydrated sodium alumino silicates.
- ♣ Zeolites have a 3D structure looks like a honeycomb, which contains interconnected tunnels and cages.
- ♣ Zeolites have pores in which the Na^+ & H_2O are loosely held. Water molecules moves freely in and out of these pores but the zeolite framework remains rigid.
- ♣ Zeolites have uniform pore sizes. Hence, they can act as a molecular sieve. Zeolites are used to remove permanent hardness of water.

UNIT-4 TRANSITION AND INNER TRANSITION ELEMENTS

1. **What are transition metals? Give four examples.**

   An element whose atom or its cation has an incomplete d sub shell is called a transition metal. Examples: Sc, Cu, Fe, Zn, Ag, Au..

2. **Write the electronic configurations of Chromium and Copper.**

   Electronic configurations of Cr and Cu are

   $_{24}Cr - [Ar]3d^5 4s^1$.

   $_{29}Cu - [Ar]3d^{10} 4s^1$

   Chromium gets extra stability due to half- filled electronic configuration.
   Copper gets extra stability due to fully- filled electronic configuration.

3. **Which metal in the 3d series exhibits +1 oxidation state most frequently and why?**

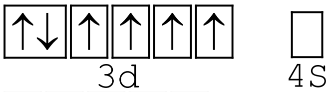
   Copper most frequently exhibit +1 oxidation state, because Cu^+ ion is stabilized by fully filled $3d^{10}$ configuration.

4. **Why transition elements show variable oxidation states?**
   - They have more number of electrons in (n-1)d and ns orbitals.
   - The energy difference between them (n-1)d and ns orbitals is very small.

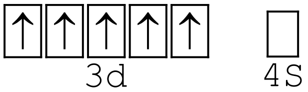
5. **Why iron is more stable in +3 oxidation state than in +2 and the reverse is true for Manganese?**

   electronic configuration

   $Fe^{2+} - 3d^6 4s^0$



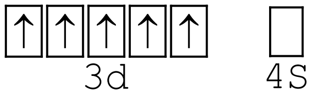
   $Fe^{3+} - 3d^5 4s^0$



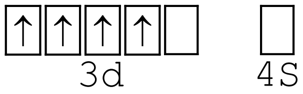
   Fe^{3+} ion is more stable than Fe^{2+} ion. Fe^{3+} ion can gain extra stability due to its half- filled electronic configuration

   electronic configuration

   $Mn^{2+} - 3d^5 4s^0$



   $Mn^{3+} - 3d^4 4s^0$



   Mn^{2+} ion is more stable than Mn^{3+} ion. Mn^{2+} ion can gain extra stability due to its half- filled electronic configuration

6. **Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?**
   - ➢ $Cr^{2+}(d^4)$ Readily loses one electron and changed into $Cr^{3+}(d^3)$ ion having half-filled t_{2g} level. Thus Cr^{2+} ion is a strong reducing agent.
   - ➢ $Mn^{3+}(d^4)$ Readily accepts one electron and changed into $Mn^{2+}(d^5)$ ion having half-filled d^5 configuration. Thus Mn^{3+} ion is a strong oxidising agent.

7. **Calculate the number of unpaired electrons in Ti^{3+}, Mn^{2+} and calculate the spin only magnetic moment.**

   electronic configuration of Ti : $3d^2\ 4s^2$

   electronic configuration of Ti^{3+} : $3d^1\ 4s^0$

   Ti^{3+} ion consists of only one unpaired electron. Its spin only magnetic moment is

   $\mu=\sqrt{1(1+2)}=\sqrt{3}=1.73\mu_B$

   electronic configuration of Mn : $3d^5\ 4s^2$

   electronic configuration of Mn^{2+} : $3d^5\ 4s^0$

   Mn^{2+} ion consists of five unpaired electron. Its spin only magnetic moment is

   $\mu=\sqrt{5(5+2)}=\sqrt{35}=5.916\mu_B$

8. **What are diamagnetic substances?**
   - ❖ Materials with no elementary magnetic dipoles are diamagnetic. A species with all electrons paired exhibit diamagnetism.
   - ❖ Diamagnetic materials are repelled by the magnetic field.

9. **What are paramagnetic substances?**
   - ❖ Materials which possess magnetic dipoles are paramagnetic. In the absence of external magnetic field, the dipoles are randomly arranged and shows no net magnetism.
   - ❖ But in the presence of magnetic field, the dipoles are aligned parallel to the direction of the applied field and are attracted by an external magnetic field.

10. **What are ferromagnetic substances?**
    - Ferromagnetic materials have domain structure and in each domain the magnetic dipoles are arranged. The spin dipoles of the adjacent domains are randomly oriented.
    - Some transition elements or ions with unpaired d electrons show ferromagnetism.

11.What are the essential conditions for the formation of alloys?

According to Hume-Rothery rule to form substitute alloy

a. The difference between the atomic radii of solvent and solute is less than 15%.
b. Both solvent and solute must have the same crystal structure and valency
c. The electro negativity difference must be close to zero.

12.What are interstitial compounds?

A compound that is formed when small atoms like hydrogen, boron, carbon or nitrogen are trapped in the interstitial hole in a metal lattice is called an interstitial compound.

13.List the properties of interstitial compounds?

- They are hard and show electrical and thermal conductivity.
- They have high melting points higher than those of pure metals.
- Transition metal hydrides are used as powerful reducing agents.
- Metallic carbides are chemically inert.

14.Why do transition elements form more number of complexes?

Transition elements have a tendency to form coordination complexes with ligands. Reasons for complex formation are

1. Small size
2. High positive charge density.
3. Availability of low energy vacant orbitals to accept an electron pairs.

15.Transition metals show high melting points why?

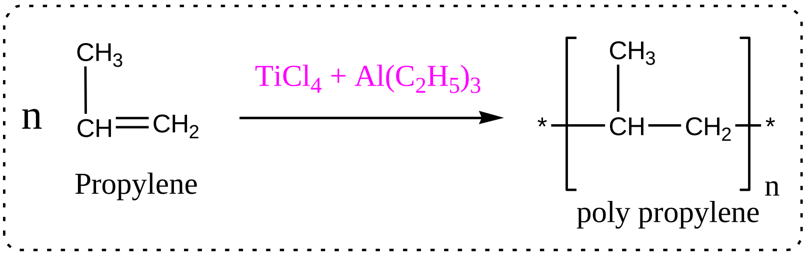
Transition metals show high melting points because they have plenty of unpaired electrons available for metallic bonding. As number of unpaired electrons available for metallic bonding increases, its melting point also increases.

16.Transition metals and their compounds act as good catalysts. Why?

- Transition metal has energetically available d orbitals that can accept electrons from reactant molecule.
- Metal can form bond with reactant molecule using its d electrons.
- The variable oxidation states of transition metals.

17.What is Zeigler- Natta catalyst? Mention its use.

A mixture of TiCl4 and Trialkyl aluminium is called a Zeigler natta catalyst, it is used for polymerization.



18.How is Potassium dichromate prepared from chromate ore?

$$\underset{\text{Chromite ore}}{4FeCr_2O_4}+8Na_2CO_3+7O_2 \xrightarrow{900 - 1000^0C} \underset{\text{Sodium chromate (yellow) soluble}}{8Na_2CrO_4}+\underset{\text{Iron oxide insoluble}}{2Fe_2O_3}+8CO_2\uparrow$$

$$\underset{\text{sodium chromate (yellow)}}{2Na_2CrO_4}+H_2SO_4 \longrightarrow \underset{\text{sodium dichromate (orange red)}}{Na_2Cr_2O_7}+Na_2SO_4+H_2O$$

$$\underset{\text{sodium dichromate (orange red)}}{Na_2Cr_2O_7}+2KCl \longrightarrow \underset{\text{potassium dichromate (orange red)}}{K_2Cr_2O_7}+2NaCl$$

19.Discuss the action of heat on potassium di chromate crystals

$$\underset{\text{potassium dichromate}}{4K_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{potassium chromate}}{4K_2CrO_4}+\underset{\text{chromium(III) oxide}}{2Cr_2O_3}+3O_2$$

20.What is Chromyl chloride test?

When potassium dichromate is heated with any chloride salt in the presence of Conc H_2SO_4, orange red vapours of chromyl chloride (CrO_2Cl_2) is evolved.

$$K_2Cr_2O_7+4NaCl+6H_2SO_4 \longrightarrow \underset{\text{Chromyl chloride}}{2CrO_2Cl_2}+2KHSO_4+4NaHSO_4+3H_2O$$

21.List the uses of potassium dichromate.

1. $K_2Cr_2O_7$ It is used as a strong oxidizing agent.
2. It is used in dyeing and printing.
3. It used in leather tanneries for chrome tanning.
4. It is used in quantitative analysis for the estimation of iron compound and iodides.

22.Discuss the action of heat on potassium permanganate crystals.

$$2KMnO_4 \longrightarrow 2K_2MnO_4+MnO_2+O_2$$

23.What is Bayer's reagent? Mention its uses.

Cold dilute alkaline $KMnO_4$ is known as Bayer's reagent. It is used to oxidise alkenes into diols. For example, ethylene can be converted into ethylene glycol.

24.Discuss the oxidising nature of potassium permanganate in acid medium.

In the presence of dilute sulphuric acid, potassium permanganate acts as a very strong oxidising agent. Permanganate ions is converted into Mn^{2+} ion.

$$MnO_4^-+8H^++5e^- \longrightarrow Mn^{2+}+4H_2O$$

It oxidises iodide ions into iodine

$$2MnO_4^-+16H^++10I^- \longrightarrow 2Mn^{2+}+5I_2+8H_2O$$

25.List the uses of potassium permanganate.

1. $KMnO_4$ is used as a strong oxidizing agent.
2. It is used for the treatment of various skin and fungal infections of the foot.
3. It used in water treatment industries to remove Iron and H_2S from well water.
4. It is used as a Bayer's reagent for detecting unsaturation in an organic compound.
5. It is used in quantitative analysis for the estimation of ferrous salts, oxalates, hydrogen peroxide and iodides.

26.What are Lanthanoids? Give three examples.

The fourteen elements from Cerium ($_{58}Ce$) to Lutetium ($_{71}Lu$) following Lanthanum ($_{57}La$) are called Lanthanoids. Examples: Ce, Gd, Lu

27.Out of $Lu(OH)_3$ and $La(OH)_3$ which is more basic and why?

Because of Lanthanoid contraction, while moving from La^{3+} to Lu^{3+}, the size of Ln^{3+} ions decreases, the ionic character of $Ln-OH$ bond decreases, covalent character increases. Thus $La(OH)_3$ is the most basic, $Lu(OH)_3$ is least basic.

28.What are actinides? Give three examples.

The fourteen elements from Thorium ($_{90}Th$) to Lawrencium ($_{103}Lr$) following Actinium ($_{89}Ac$) are called Actinoids. Examples: Th, U, Pu

29.Why europium (II) is more stable than Cerium (II)?

Eu^{2+} ion is more stable because of its half-filled $\left(4f^7\right)$configuration. Whereas Ce^{2+} ion contains $\left(4f^2\right)$configuration which is unstable.

30.Write the electronic configuration of Ce^{4+}.

Elctronic configuration of Ce is $[Xe]4f^2 5d^0 6s^2$

Elctronic configuration of Ce^{4+} is $[Xe]4f^0 5d^0 6s^0$

31.What is lanthanide contraction? What are the effects of lanthanide contraction?

As we move across from Ce to Lu in 4f series, there is a gradual decrease in atomic and ionic radii of Lanthanoids with increase of atomic number. This decrease in ionic size is called Lanthanoid contraction.

Cause of Lanthanoid contraction:

a. As we move from one element to another in 4f series, the nuclear charge increases by one unit and an additional electron enters the same 4f sub shell.

b. 4f sub shell is diffused and the shielding effect of 4f electrons are relatively poor.

c. When nuclear charge increases, the valence shell is pulled slightly towards nucleus. As a result, the elective nuclear charge increases and the size of Ln^{3+} ions decreases.

Consequences of Lanthanoid contraction:

1. **Basicity differences**

   As we from Ce^{3+} to Lu^{3+}, the size of Ln3+ ions decreases, the ionic character of $Ln-OH$ bond decreases (covalent character increases) which results in the decrease in the basicity of $Ln(OH)_3$.

2. **Similarities among Lanthanoids:**

   In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed. Because of very small change in radii of Lanthanoids, their chemical properties are quite similar.

32.Compare lanthanides and actinides.

s.no	**Lanthanoids**	**Actinoids**
1	Differentiating electron enters in 4f orbital	Differentiating electron enters in 5f orbital
2	Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3	They show less tendency to form complexes	They show greater tendency to form complexes
4	Most of the Lanthanoids are colourless	Most of the Actinoids are coloured.
5	They do not form Oxo cations	They do form Oxo cations.
6	Besides +3 oxidation states Lanthanoids show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states Actinoids show higher oxidation states such as +4,+5, +6 and +7.

6. SOLID STATE

1. **What are the general characteristics of solids?**
    - Solids are rigid and incompressible.
    - Solids have definite volume and shape.
    - Solids have strong cohesive (attractive) forces.
    - Solids have short inter atomic, ionic or molecular distances.
    - Constituents have fixed positions and oscillate only about their mean position.
2. **What are crystalline and amorphous solids?**

    Crystalline solids:

    Solids in which its constituents have an orderly arrangement over a long range are called crystals.

    Amorphous solids:

    Solids in which its constituents its constituents are randomly arranged are called amorphous solids.
3. **What are Isotropy and anisotropy?**
    - ♣ Isotropy means uniformity in all directions. In solid state, it means having identical values of physical properties in all directions.
    - ♣ Anisotropy is the property which depends on the direction of measurement.
    - ♣ Crystalline solids are anisotropic and they show different values of physical properties when measured along different directions.
    - ♣ Amorphous solids are isotropic and they show similar properties irrespective of the direction of measurement.
4. **Differentiate crystalline solids and amorphous solids.**

S.no	Crystalline solids	Amorphous solids
1	Orderly arrangement of constituents over a long range.	Random arrangement of constituents.
2	They have definite shape.	They have Irregular shape.
3	They are anisotropic in nature	They are isotropic in nature.
4	They are true solids	They are pseudo solids (or) super cooled liquids
5	They have sharp melting points.	Gradually soften over a range of temperature and so can be moulded.
6	Examples: NaCl , diamond etc.,	Examples: Rubber , plastics, glass etc

5. **Give the characteristics of ionic crystals.**
   - ❖ In ionic crystal cations and anions are bound together by strong electrostatic attractive forces.
   - ❖ Ionic crystals possess definite crystal structure and they are very hard.
   - ❖ Ionic solids have high melting points.
   - ❖ They do not conduct electricity in solid state, because the ions are not free to move.
   - ❖ They do conduct electricity in molten state (or) when dissolved in water because, the ions are free to move.
6. **Give the characteristics of covalent solids.**
   - ➢ In covalent solids, the constituent atoms are connected by covalent bonds forming a three dimensional network.
   - ➢ They are very hard, and have high melting point.
   - ➢ They are usually poor thermal and electrical conductors.
   - ➢ Examples: Diamond, silicon carbide etc.
7. **Give the characteristics of molecular solids.**
   - ♣ The constituents of molecular solids are neutral molecules.
   - ♣ These molecules are held together by weak van der Waals forces.
   - ♣ Molecular solids are soft and they do not conduct electricity.
8. **Explain the types of molecular solids.**
   - **a) Non-polar molecular solids:**

     Molecules are held together by weak dispersion forces or London forces. They have low melting points, and are liquids or gases at room temperature. Examples: naphthalene, Anthracene etc.,
   - **b) Polar molecular solids**

     Polar molecules are held together by relatively strong dipole-dipole interactions. They have higher melting points than the non-polar molecular solids**.** Examples : solid CO_2 , solid NH_3 etc.
   - **c) Hydrogen bonded molecular solids**

     Molecules are held together by hydrogen bonds. They are generally soft solids under room temperature. Examples: solid ice (H_2O), glucose, urea etc.,
9. **Give the characteristics of metallic solids?**
   - ❖ The lattice points are occupied by positive metal ions and a cloud of electrons spread around the metal ions.
   - ❖ They are hard, and have high melting point.
   - ❖ They are excellent electrical and thermal conductors.
   - ❖ They possess bright lustre. Examples: Metals and metal alloys.

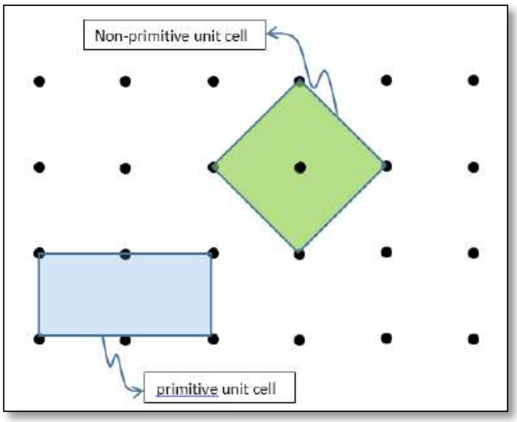
10. What is coordination number? What is the coordination number of atoms in a bcc structure?

The number of nearest neighbours that surrounding a particle in a crystal is called the coordination number of that particle. In bcc structure each atom is surrounded by 8 neighboring atoms. Hence its coordination number is 8.

11. Why ionic crystals are hard and brittle?

- The ionic crystals are hard, because the ions are held together by the strong electrostatic forces of attraction.
- When pressure is applied repulsive forces arises between similar charged ions. This repulsion will shatter the crystal lattice of the ionic compound.

12. What are Primitive and non-primitive unit cell?



- A unit cell in which only the corner positions are occupied by constituents is called a primitive unit cell.
- A unit cell in which constituent particles present either at body centre or at face centres in addition to those at corners is called non-primitive unit cell.

13. Write the Bragg's equation? Explain the terms in it.

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

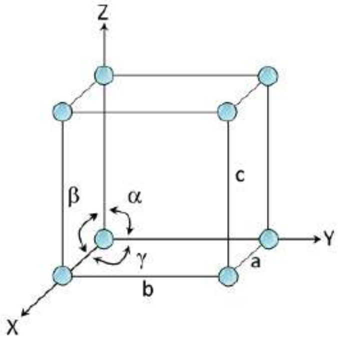
Where

λ the wavelength of X-ray

θ-The angle of diffraction and

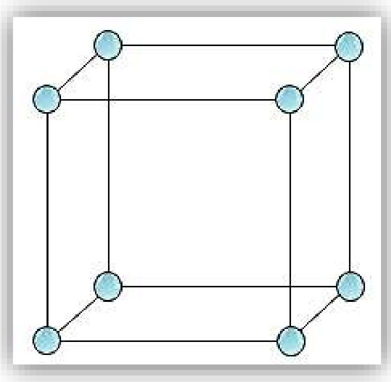
d- inter planar distance

14. Define unit cell.



The fundamental repeating structural unit of a crystalline solid is called a unit cell.

15.Calculate the number of atoms in a simple cubic (SC) unit cell.

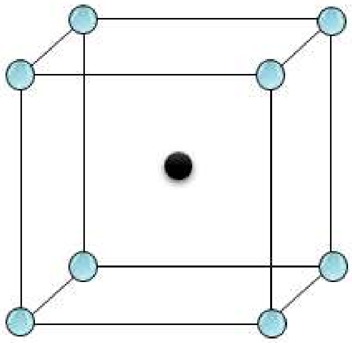


In SC unit cell, each corner is occupied by identical constitutes. Each corner atom is shared by 8 neighboring unit cells, so each corner atoms makes $\left(\frac{1}{8}\right)$contribution to the unit cell.

$$No\ of\ \ atoms\ in\ a\ \mathrm{SC}\ unit\ cell = \left(\frac{Nc}{8}\right)$$

$$= \left(\frac{8}{8}\right) = 1$$

16.Calculate the number of atoms in a body centred cubic (BCC) unit cell.

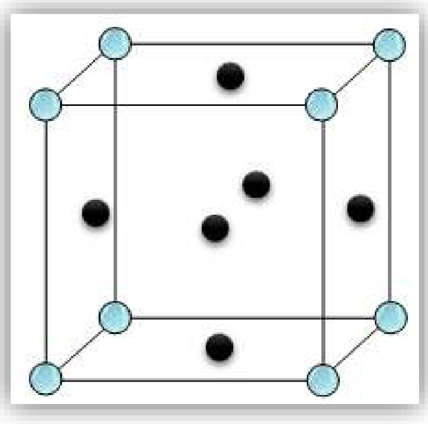


In a bcc unit cell, all the corners and a body center are occupied by identical constitutes. An atom present at the body centre belongs to only to a particular unit cell.

$$\text{No. of atoms in bcc unitcell} = \left(\frac{Nc}{8}\right) + \left(\frac{\mathrm{N_b}}{1}\right)$$

$$= \left(\frac{8}{8}\right) + \left(\frac{1}{1}\right) = 2$$

17.Calculate the number of atoms in a face centred cubic (FCC) unit cell.



In a fcc unit cell, all the corners and all the face centers are occupied by identical constitutes. Each face centered atom is shared by two unit cells and its share to the particular unit cell is $\left(\frac{1}{2}\right)$.

$$\therefore \text{No.of atoms in a fcc unitcell} = \left(\frac{\mathrm{Nc}}{8}\right) + \left(\frac{\mathrm{N_f}}{2}\right)$$

$$= \left(\frac{8}{8}\right) + \left(\frac{6}{2}\right) = 4$$

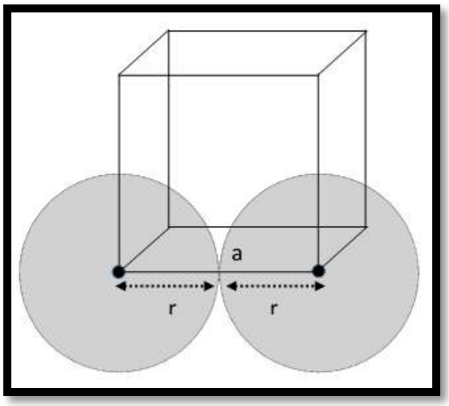
18.What is Radius ratio? In what way radius ratio value is helpful in finding crystal structure?

The ratio of radius of cation and the radius of anion is called a radius ratio. Radius ratio values are useful in determining the structure of an ionic crystal.

$$\text{Radius ratio} = \left(\frac{r_{C^+}}{r_{A^-}}\right)$$

19.Calculate the packing fraction in simple cubic crystal.

In SC unit cell, each corner is occupied by identical constitutes. They touch along the edges of the cube and do not touch diagonally. If the edge length of the unit cell is a.



$$\text{Volume of the unit cell} = a^3$$

$$a = 2r$$

$$r = \frac{a}{2}$$

∴ Volume of the sphere with radius 'r' is $V = \left(\frac{4}{3}\right)\pi r^3$

$$V = \left(\frac{4}{3}\right)\pi\left(\frac{a}{2}\right)^3$$

$$V = \left(\frac{\pi}{6}\right)a^3$$

In a simple cubic arrangement, number of spheres belongs to a unit cell is 1

∴ Total volume occupied by the spheres in SC unit cell $= 1 \times \left(\frac{\pi}{6}\right)a^3$

$$\text{Packing fraction} = \left(\frac{\begin{array}{c}\text{Total volume occupied by}\\ \text{spheres in a unit cell}\end{array}}{\text{Volume of the unit cell}}\right) \times 100$$

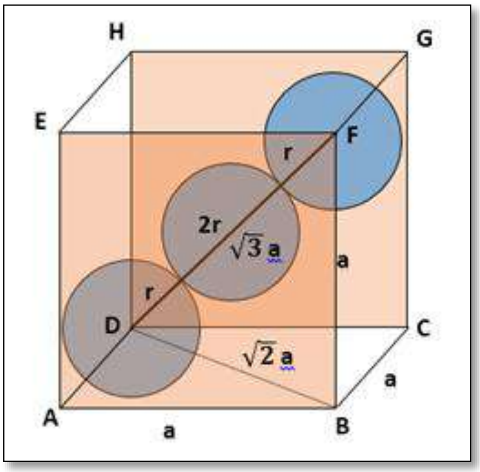
$$\text{Packing fraction} = \frac{\left(\frac{\pi a^3}{6}\right)}{\left(a^3\right)} \times 100$$

$$= \frac{100\ \pi}{6}$$

$$= 52.33\%$$

20. Calculate the percentage efficiency of packing in case of body centred cubic crystal.

In bcc arrangement, the spheres are touching along the leading diagonal of the cube.



Volume of the unit cell = a^3

Length of the cube diagonal DF = $\sqrt{3}$ a

If the radius of the sphere is r then

$4r = \sqrt{3}\,a$

$r = \frac{\sqrt{3}}{4}a$

$\therefore$ Volume of the sphere with radius 'r' is

$$V = \left(\frac{4}{3}\right)\pi r^3$$

$$V = \frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3$$

$$V = \frac{\sqrt{3}}{16}\pi a^3$$

In a bcc arrangement, number of spheres belongs to a unit cell is 2

Total volume occupied by the spheres in unit cell $= 2 \times \left(\frac{\sqrt{3}\,\pi a^3}{16}\right)$

$$= \frac{\sqrt{3}\,\pi a^3}{8}$$

$$\text{Packing fraction} = \left(\frac{\text{Total volume occupied by spheres in a unit cell}}{\text{Volume of the unit cell}}\right)\times 100$$

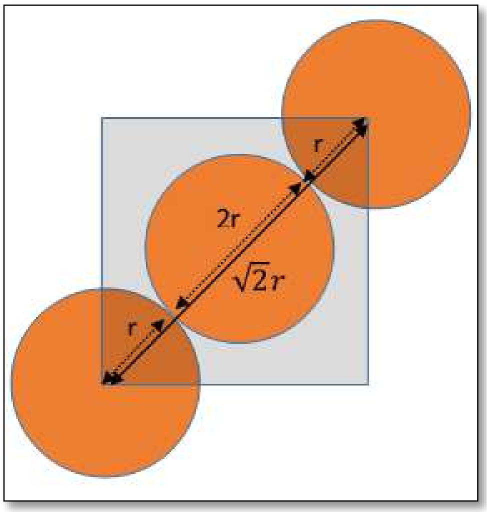
$$\text{Packing fraction} = \frac{\left(\frac{\sqrt{3}\,\pi a^3}{8}\right)}{\left(a^3\right)}\times 100$$

$$= \frac{\sqrt{3}\,\pi}{8}\times 100 = \frac{1.732 \times 3.14 \times 100}{8}$$

$$= 68\ \%$$

21.**Calculate the percentage efficiency of packing in fcc crystal.**

In fcc arrangement, the spheres are touching along the face diagonal.



Volume of the unit cell $= a^3$

Length of the face diagonal $= \sqrt{2}\ a$

If the radius of the sphere is r then

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

$$r = \frac{\sqrt{2}\ a}{4}$$

$\therefore$ Volume of the sphere with radius 'r' is

$$V = \left(\frac{4}{3}\right)\pi r^3$$

$$V = \frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}a\right)^3$$

$$V = \frac{\sqrt{2}}{24}\pi a^3$$

In a fcc arrangement, number of spheres belongs to a unit cell is 4

Total volume occupied by the spheres in a bcc unit cell $= 4 \times \left(\frac{\sqrt{2}\ \pi\ a^3}{24}\right)$

$$= \frac{\sqrt{2}\ \pi\ a^3}{6}$$

$$\text{Packing fraction} = \left(\frac{\begin{array}{c}\text{Total volume occupied by}\\ \text{spheres in a unit cell}\end{array}}{\text{Volume of the unit cell}}\right)\times 100$$

$$\text{Packing fraction} = \frac{\left(\frac{\sqrt{2}\ \pi\ a^3}{6}\right)}{\left(a^3\right)}\times 100$$

$$= \frac{\sqrt{2}\ \pi}{6}\times 100 = \frac{1.414 \times 3.14 \times 100}{6}$$

$$= 74\%$$

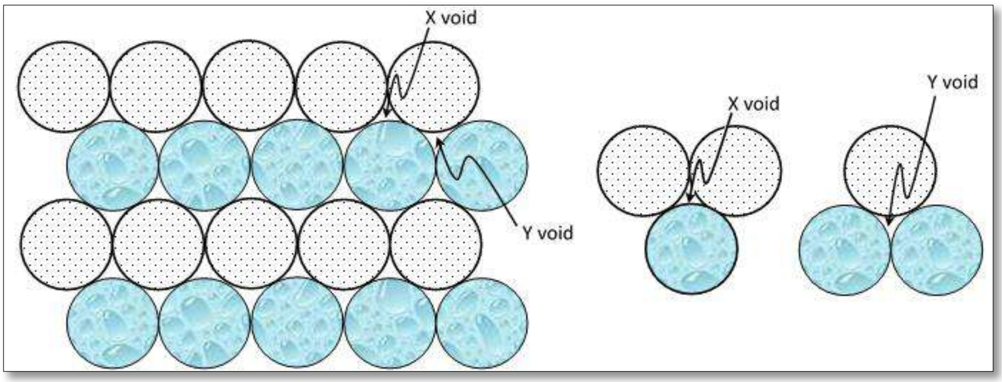
22.Explain about the hexagonal and face centered cubic arrangement.

- **Formation of first layer:**

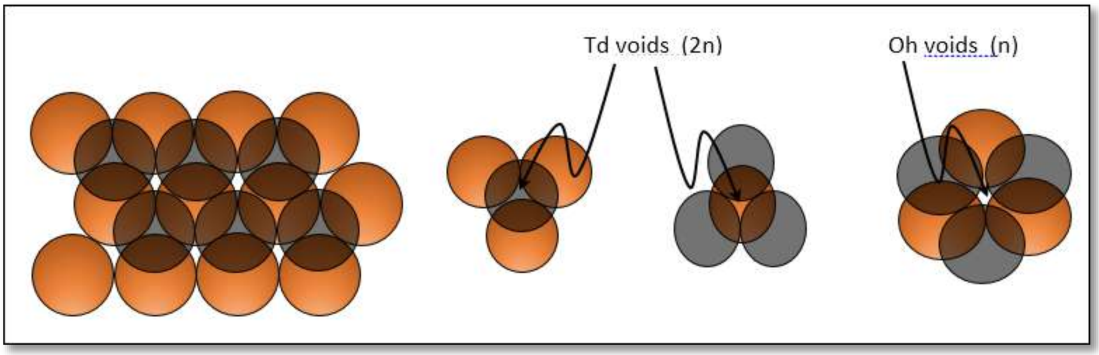
  In this arrangement, the first layer is formed by arranging the spheres as in the case of two dimensional ABAB arrangements i.e. the spheres of second row fit into the depression of first row. Now designate this first layer as 'a'.

- **Formation of second layer:**

  In the first layer (a) there are two types of voids (or holes) and they are designated as x and y.



The second layer (b) can be formed by placing the spheres either on the depression x (or) on y.



Wherever a sphere of second layer (b) is above the void (x) of the first layer (a), a tetrahedral void is formed. This constitutes four spheres – three in the lower (a) and one in the upper layer (b). When the centers of these four spheres are joined, a tetrahedron is formed.

At the same time, the voids (y) in the first layer (a) are partially covered by the spheres of second layer (b), now such a void in (a) is called a octahedral void. This constitutes six spheres – three in the lower layer (a) and three in the upper layer (b). When the centers of these six spheres are joined, an octahedron is formed.

Simultaneously new octahedral voids (or holes) are also created by three spheres in second layer (b) and one sphere of first layer (a)

- **Formation of third layer:**

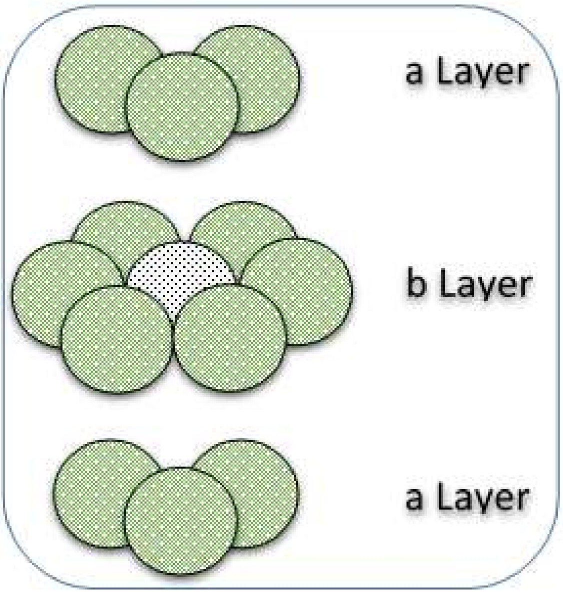
  The third layer of spheres can be formed in two ways to achieve closest packing

  (i) Hexagonal close packing : HCP structure – ababab.. Arrangement

  (ii) Cubic close packing : CCP structure – abcabc… Arrangement

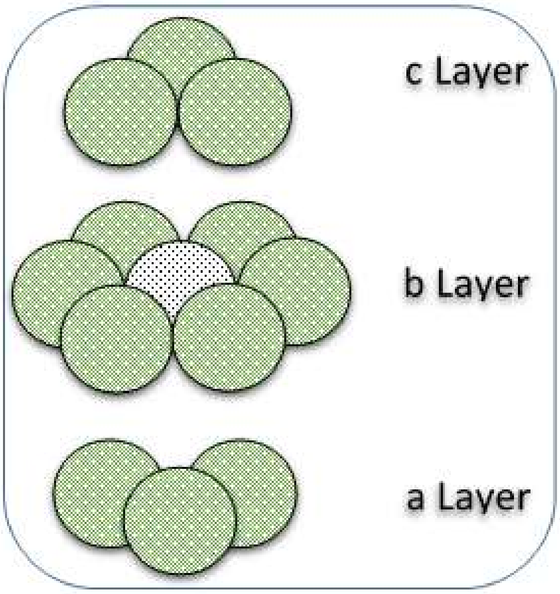
Hexagonal Close Packing (HCP)

If the third layer is placed over the second layer in such a way that all the spheres of the third layer fit in tetrahedral voids. In this case, the spheres of the third layer are exactly aligned with those of the first layer. This "aba'' arrangement is known as the hexagonal close packed (HCP) arrangement.



Cubic Close Packing (CCP)

If the third layer is placed over the second layer in such a way that all the spheres of the third layer fit in octahedral voids. This arrangement of the third layer is different from other two layers (a) and (b), and hence, it is designated (c). If the stacking of layers is continued in abcabcabc… pattern, then the arrangement is called cubic close packed (CCP) structure.



In both HCP and CCP arrangements, the coordination number of each sphere is 12. Six neighboring spheres in its own layer, three spheres in the layer above and three sphere in the layer below. This is the most efficient packing.

23.Distinguish between hexagonal close packing and cubic close packing.

(Find the answer above)

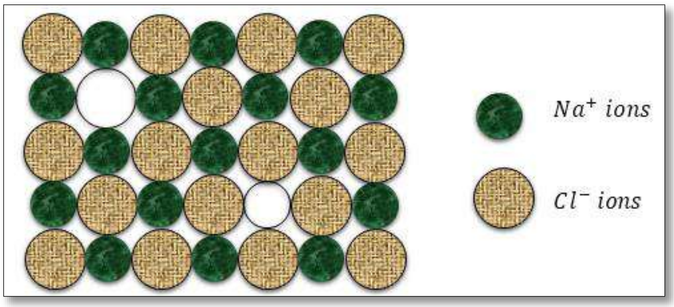
24. What are the importance of crystal defects?

Crystal defects affect the physical and chemical properties of the solid. For example, Doping leads to a crystal imperfection and it increases the electrical conductivity of a semiconductor such as silicon. The ability of magnetization and demagnetization of ferromagnetic material (Fe,Ni etc) depends on the presence of imperfections.

25. What are point defects?

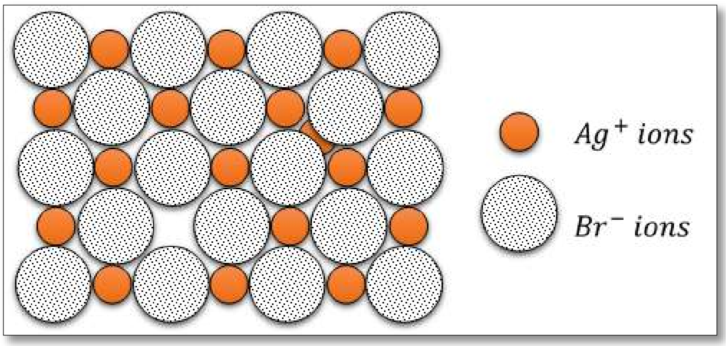
Deviation from ideal arrangement around a point or an atom in a crystalline substance is called as Point defect. Examples : Schottky defect , Frenkel defect, metal excess defect, metal deficiency defect etc.

26. Explain Schottky defect.



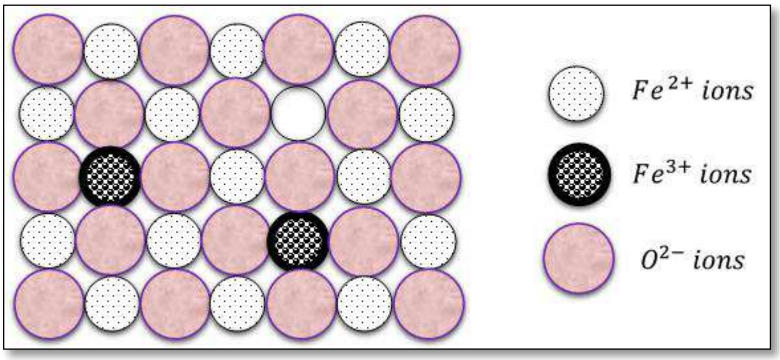
- ♥ Schottky defect arises due to the missing of equal number of cations and anions.
- ♥ This defect is shown by the crystals in which the cation and anion are of almost of similar size. Example: NaCl.
- ♥ This defect does not affect the stoichiometry of the crystal but it lowers the density of a crystal.

27. Write a note on Frenkel defect.



- ♣ Frenkel defect arises due to the dislocation of ions from their lattice points to interstitial position.This defect is shown by the crystals in which cation and anion differ in their sizes. Example AgBr.
- ♣ In AgBr, small Ag^+ ion leaves its normal site and occupies an interstitial position.
- ♣ This defect does not affect the density of the crystal.

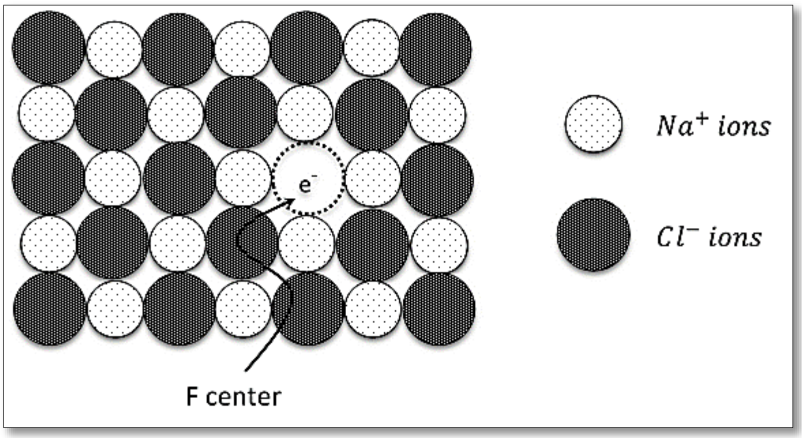
28.Explain metal deficiency defect with an example.



- This defect arises due to the presence of less number of cations than the anions.
- This defect is observed in a crystal in which, the cations have variable oxidation states. Example : FeO and FeS.
- In FeO crystal, some of the Fe^{2+} ions are missing from the crystal lattice. To maintain the electrical neutrality, twice the number of other Fe^{2+} ions in the crystal is oxidized to Fe^{3+} ions.

29.Explain metal excess defect with an example.

- It arises due to the presence of excess of metal ions as compared to anions.
- The electrical neutrality of the crystal can be maintained by the presence of anionic vacancies equal to the excess metal ions (or) by the presence of extra cation and electron present in interstitial position. Examples: NaCl, KCl



30.What are F centers? (or) What happens when sodium chloride crystal is heated in the presence of sodium vapour?

When NaCl crystals are heated in the presence of sodium vapour, (Na^+) ions are formed and are deposited on the surface of the crystal. Chloride ions (Cl^-) diffuse to the surface from the lattice point and combines with (Na^+) ion. The electron lost by the sodium atoms diffuse into the crystal lattice and occupies the vacancy created by the $\left(\mathrm{Cl}^-\right)$ ions. Such anionic vacancies occupied by unpaired electrons are called F centers. They impart yellow colour to NaCl crystal.

31.ZnO crystal is yellow when hot and white when cold. Account

- ZnO is colourless at room temperature. When it is heated, it becomes yellow in colour.
- On heating, it loses oxygen and thereby forming free Zn^{2+} ions.
- The excess Zn^{2+} ions move to interstitial sites and the electrons also occupy the interstitial positions.

32.Write a short note on Impurity defect.

≈ A general method of introducing defects in ionic solids is by adding impurity ions.

≈ If the impurity ions are in different valance state from that of host, vacancies are created in the crystal lattice of the host.

≈ For example, addition of $CdCl_2$ to silver chloride yields solid solutions where the divalent cation Cd^{2+} occupies the position of Ag^+. This will disturb the electrical neutrality of the crystal. In order to maintain the same, proportional number of Ag^+ ions leaves the lattice.

≈ This produces a cation vacancy in the lattice, such crystal defects are called impurity defects.

UNIT-7 CHEMICAL KINETICS

Two and three mark questions:

1. **What are average and instantaneous rate of a chemical reaction?**
   - **Average rate:**

     The change in concentration of a reactant (or product) of a chemical reaction in a given interval of time is called as an average rate.

     $$\text{Average Rate} = \frac{-\Delta[A]}{\Delta t}$$

   - **Instantaneous rate:**

     The change in concentration of a reactant or product of a chemical reaction at a given instant is called an instantaneous rate.

     $$\text{Instantaneous Rate} = \frac{-d[A]}{dt}$$

2. **Differentiate between rate and rate constant of a reaction.**

s.no	Rate of a reaction	Rate constant of a reaction
1	It represents the speed in which the reactants are converted into products at any instant.	It is a proportional constant
2	It is measured as decrease in the conc. of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants in unity
3	It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

3. **Define rate constant.**

   Rate constant of a reaction is defined as “Rate of the reaction, when the concentration of each of the reactants in unity”.

4. **Define order.**

   It is the sum of the powers of concentration terms involved in the experimentally determined rate law.

5. **Define molecularity.**

   It is the total number of reactant species that are involved in an elementary step is called molecularity of that particular step.

6. **Give the differences between order and molecularity of a reaction.**

s.no	Order of a reaction	Molecularity of a reaction
1	It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant species that are involved in an elementary step.
2	It can be zero (or) fractional (or) integer	It always a whole number, cannot be zero or fractional.
3	It is assigned for an overall reaction.	It is assigned for each elementary step of mechanism.

7. **Give any three examples for the first order reaction.**

1 Decomposition of dinitrogen pentoxide

$$N_2O_5 \longrightarrow 2NO_2 + 1/2O_2$$

2 Decomposition of **Thionylchloride**

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

3 Decomposition of the **Hydrogen peroxide** in aqueous solution

$$H_2O_2 \longrightarrow H_2O + 1/2O_2$$

4 Isomerisation of cyclopropane to propene.

8. **What are pseudo first order reactions? Give an example.**

"In a second order reaction, when one of the reactants concentration is in excess of the other then the reaction follows a first order kinetics, such reactions are called Pseudo first order reactions." Example: Acid hydrolysis of an ester.

9. **Give any three examples for the zero order reaction.**

1	**Photochemical reaction between H_2 and I_2** $H_2 + Cl_2 \xrightarrow{light} 2HCl$
2	Decomposition of N_2O on hot platinum surface $N_2O \rightleftharpoons N_2 + 1/2\ O_2$
3	Iodination of acetone in acid medium is zero order with respect to iodine. $CH_3COCH_3 + I_2 \xrightarrow{H^+} ICH_2COCH_3 + HI$ $Rate = k\ [CH_3COCH_3]\ [H^+]$

10. What are zero order reactions?

A reaction in which the rate is independent of the concentration of the reactant over a wide range of concentrations is called as zero order reactions.

11. Define half-life of a reaction. Show that for a first order reaction half-life is independent of initial concentration.

The half-life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For any first order reaction

$$k=\frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$\text{when} \quad t=t_{1/2} \quad ; \quad [A]=\left(\frac{[A_0]}{2}\right)$$

$$k=\left(\frac{2.303}{t_{1/2}}\right)\log\frac{[A_0]}{\left(\frac{[A_0]}{2}\right)}$$

$$k=\frac{2.303}{t_{1/2}}\log 2$$

$$k=\frac{2.303 \times 0.3010}{t_{1/2}}$$

$$t_{1/2}=\frac{0.6932}{k}$$

Half-life period is independent on the initial concentration and it is a constant.

12. Derive an equation for the half-life period of a zero order reaction.

The rate constant for a zero order reaction is given by

$$k = \frac{[A_0]-[A]}{t} \qquad \text{when } t=t_{1/2} \quad ; \quad [A]=\left(\frac{[A_0]}{2}\right)$$

$$k = \frac{[A_0] - \left(\frac{[A_0]}{2}\right)}{t_{1/2}}$$

$$k = \frac{[A_0]}{2t_{1/2}}$$

$$t_{1/2} = \frac{[A_0]}{2k}$$

13. Write Arrhenius equation and explains the terms involved.

$$k = A\, e^{-\left(\frac{E_a}{RT}\right)}$$

A - Frequency factor; R - gas constant;

E_a - Activation Energy; T -Temperature (in K)

14.List the factors affecting reaction rate.

The rate of a reaction is affected by the following factors.

- Nature and state of the reactant
- Concentration of the reactant
- Surface area of the reactant
- Temperature of the system
- Presence of a catalyst

15.How do nature of the reactant influence rate of reaction?

- ♥ The net energy involved in a reaction depends on the nature of the reactant and hence the rates are different for different reactants.
- ♥ The oxidation of oxalate ion by $KMnO_4$ is relatively slow compared to the reaction between $KMnO_4$ and Fe^{2+} ion. In fact heating is required for the reaction between $KMnO_4$ and Oxalate ion and is carried out at around 60^0C.

16.**How do physical state of the reactant influence rate of reaction?**

- ❖ The physical state of the reactant influences the rate of reaction.
- ❖ Gas phase reactions are faster as compared to the solid or liquid reactants.
- ❖ Reaction of sodium metal with iodine vapours is faster than the reaction between solid sodium and solid iodine.

17.**How do surface area of the reactant influence the rate of reaction?**

- In heterogeneous reactions, the surface areas of the solid reactants play an important role in deciding the rate.For a given mass of a reactant, when the particle size decreases surface area increases.
- Increase in surface area of reactant leads to, more collisions per litre per second, and hence rate of reaction is increased.
- For example, powdered calcium carbonate reacts much faster with dilute HCl than with the same mass of $CaCO_3$ as marble

18.Explain the effect of catalyst on reaction rate.

- A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
- In the presence of a catalyst, the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of reaction.

19.How do concentrations of the reactant influence the rate of reaction?

- The rate of a reaction increases with increase of concentration of the reactants.
- According to collision theory of reaction rates, the rate of a reaction depends upon the number of collisions between the reacting molecules.
- Higher the concentration, greater is the possibility for collision and hence the rate.

20.**Derive integrated rate law for a first order reaction.**

$$A \longrightarrow \text{product}$$

$$\text{Rate} = k\,[A]^1 \text{ \~\~\~\~\~\~\~\~ } \{1\}$$

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

$$\frac{-d[A]}{[A]} = kdt$$

When time changes from $(t=0) \Rightarrow (t=t)$

Concentration changes from $[A_0] \Rightarrow [A]$

on Integrating the above equation within these limits

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k\int_0^t dt$$

$$\left[-\ln[A]\right]_{[A_0]}^{[A]} = k\left[t\right]_0^t$$

$$-\ln[A] - \left(-\ln[A_0]\right) = k\,(t-0)$$

$$-\ln[A] + \ln[A_0] = kt$$

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt \text{ \~\~\~\~\~\~\~\~ } \{2\}$$

$$2.303\log\left(\frac{[A_0]}{[A]}\right) = kt$$

$$k = \frac{2.303}{t}\log\left(\frac{[A_0]}{[A]}\right) \text{ \~\~\~\~\~\~\~\~ } \{3\}$$

21.Describe the graphical representation of first order reaction.

For a first order reaction

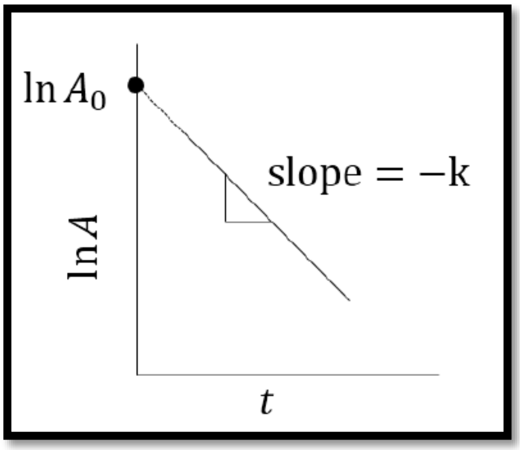
$$\ln\left(\frac{[A_0]}{[A]}\right) = kt$$

The above Equation can be written in the form $y = mx + c$ as below

$$\ln[A_0] - \ln[A] = kt$$

$$\ln[A] = -kt + \ln[A_0]$$

$$y = mx + c$$



A plot of $(\ln[A])$ against (t) mat be drawn. A straight line with negative slope of is obtained. From this, the rate constant is calculated.

22.Derive integrated rate law for a zero order reaction.

$$A \longrightarrow \text{product}$$

$$\text{Rate} = k[A]^0 \sim\sim\sim\sim\sim\sim\sim\sim \{1\}$$

$$\frac{-d[A]}{dt} = k \qquad (\therefore [A]^0 = 1)$$

$$-d[A] = k\,dt$$

When time changes from $(t = 0) \Rightarrow (t = t)$

Concentration changes from $[A_0] \Rightarrow [A]$

On integrating the above equation within these limits

$$-\int_{[A_0]}^{[A]} d[A] = k\int_0^t dt$$

$$-([A])_{[A_0]}^{[A]} = k(t)_0^t$$

$$-[A] - (-[A_0]) = k(t-0)$$

$$[A_0] - [A] = kt \sim\sim\sim\sim\sim\sim\sim\sim \{2\}$$

$$k = \frac{[A_0]-[A]}{t} \sim\sim\sim\sim\sim\sim\sim\sim \{3\}$$

23.Explain briefly the collision theory of bimolecular reactions.

- Chemical reactions occur as a result of collisions between the reacting molecules.
- The reaction between A_2 & B_2 proceeds through collisions between them.

  $A_2(g) + B_2(g) \longrightarrow 2AB(g)$
- The rate would be proportional to the number of collisions per second. The number of collisions is directly proportional to the concentration of both A_2 & B_2.

  $\text{Rate} \propto \text{number of collisions } L^{-1}s^{-1} (\text{collision rate})$

  $\text{Collision rate} \propto [A_2][B_2]$

  $\text{Collision rate} = Z[A_2][B_2]$ Where, Z is a constant.
- All collisions are not effective. In order to react, the colliding molecules must possess a minimum energy called activation energy (E_a).
- The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.
- Fraction of effective collisions (f) is given by the following expression

  $f = e^{-\left(\frac{E_a}{RT}\right)}$
- This fraction of collisions is further reduced due to orientation factor i.e., even if the reactant collide with sufficient energy, they will not react unless the orientation of the reactants is suitable for the formation of the transition state.
- The fraction of effective collisions (f) having proper orientation is given by the steric factor p.

  $\text{Rate} = p \times f \times \text{collision rate}$

  $\text{Rate} = p \times e^{-\left(\frac{E_a}{RT}\right)} \times Z[A_2][B_2] \sim\sim\sim\sim\sim\sim \{1\}$

  $\text{Rate} = k[A_2][B_2] \sim\sim\sim\sim\sim\sim \{2\}$
- On comparing equation $\{1\}$ and $\{2\}$

  $k = pZe^{-\left(\frac{E_a}{RT}\right)}$