SURFACE CHEMISTRY

BASIC CONCEPTS

The branch of the Chemistry which deals with the study of surface phenomena is called SURFACE CHEMISTRY.

POINTS TO BE REMEMBERED: ---

1. **Adsorption**: - The accumulation of molecules species at the surface rather in the bulk of a solid or liquid is termed adsorption.

2. **Desorption:-**Removal of adsorbate from the surface of adsorbent is known as desorption.

3. **Sorption:-**When adsorption and absorption both takes place simultaneously.

4. Type of adsorption: - On the basis of interaction between adsorption and absorption, adsorbate are of two types:

(i) **Physical adsorption/physisorption: -** When weak vanderwaal interaction involve between adsorbate and adsorbent.
(ii) **Chemical adsorption/chemisorption**:-When chemical bonds form between adsorbate and adsorbent.
5. **Adsorption isotherm**:-The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.

6. **Application of adsorption**:-

(a) Removal of colouring matter from solution using animal charcoal.
(b) Chromatographic analysis is based on adsorption.

7. **Freundlich adsorption isotherm**:-It is a graph which shows relationship between the quality of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.
x/m=kp1/n
8 .Factors affecting adsorption:-

(i) **Surface area**: - Adsorption increases with increases of surface area of adsorbent.
(ii) **Nature of adsorbate**:- Easily liquefiable gases are readily adsorbed.
(iii) **Temperature**:- Low temperature is favorable for physical adsorption and High temperature for chemisortion.
(iv) **Pressure: -** Pressure increases, adsorption increases.
9. CATALYSIS:-Substances which alter the rate of chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction are known as catalyst and the phenomenon is known as catalysis.

10. PROMOTERS AND POISONS

Promoters are substance that enhance the activity of catalyst while poisons decrease the activity of catalyst.

$$N_2 + 3H_2 \rightarrow 2NH_3\ (g)$$

Fe =catalyst, Mo= promoter

11. Homogenous catalyst– when reactants and catalyst are in same phase.

e.g. $2\ SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3(g)$

12. Heterogeneous catalyst– the catalytic process in which the reactants and catalyst are in different phase.

$$\text{e.g. } SO_2 + O_2 \rightarrow 2SO_3\ (g)$$

13. Adsorption theory of Heterogeneous catalysis– It explains the mechanism of heterogeneous catalyst.

The mechanism involves 5 steps:-

a. Diffusion of reactants to the surface of catalyst.

b. Adsorption of reactant molecules on the surface of catalyst.

c. Chemical reaction on the catalyst surface through formation of an intermediate.

d. Desorption of reaction product from the catalyst surface.

e. Diffusion of reaction product away from the catalyst surface.

14. IMPORTANT FEATURES OF SOLID CATALYST

Activity- The activity of a catalyst depend on the strength of chemisorption.

Catalytic activity increases from group 5 to group 11 elements of the periodic table.

Pt

$$2H_2 + O_2 \rightarrow 2H_2O$$

Selectivity– The selectivity of a catalyst is its ability to direct a reaction to yield a particular product.

1. $$CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$$

2. $$CO + H_2 \xrightarrow{Cu} HCHO$$

15. SHAPE SELECTIVE CATALYSIS

The catalytic reaction that depends upon the pure substance of the catalyst and the size of reactant and product molecules is called shape selective catalysis.

e.g. Zeolites are good shape selective catalyst.

16. ENZYME CATALYSIS

Enzymes are protein molecules of high molecular mass which catalyse the biochemical reaction.

e.g. Inversion of cane sugar by invertase enzyme.

17. Characteristic of enzyme catalysis –

a. Enzymes are specific to substrate.

b. Enzymes are highly active under optimum temperature.

c. Enzymes are specific to pH.e.g. Pepsin act in acidic medium

d. Enzymes are inhabited by the presence of certain substance.

Mechanism of enzyme catalysis –

1. Binding of enzyme to substrate to form an activated complex.

$E + S \rightarrow ES^*$

2. Decomposition of activated complex to form product.

$ES \rightarrow E + P$

18. Colloid-a colloid is a heterogeneous system in which one substance is dispersed(dispersed phase)in another substance called dispersion medium and size of dispersed phase is from 1nm-1000 nm.

19. TYPES OF COLLOIDS

(1) On the basis of nature of interaction between dispersed phase and dispersion medium.

(a) Lyophobic colloid-solvent , hating colloid, these colloids can not be prepared by simply mixing of dispersed phase into dispersion medium.

e.g. metallic sols.

(b) Lyophillic colloid-solvent loving these colloids can be prepared by simply mixing of dispersion phase into dispersion medium.

e.g. Starch sol.

(2) On the basis of types of particles of the dispersed phase

(a) Multimolecular colloid-on dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in colloidal range. The species thus formed are called Multimolecular colloids.

e.g. Sulphur sol.

(b) Macromolecular colloids -macromolecules are suitable solvent from solution in which size of the particles are in range of colloidal range.

e.g. starch sol.

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(c) Associated colloids (micelles)-some substances in law concentration behaves as normal strong electrolyte but at higher concentration exhibit colloidal behavior due to formation of aggregates. The aggregated particles are called micelles and also known as associated colloids.

(3) Kraft temperature- Temp. above which formation of micelles takes places.

(4) Critical micelle concentration (cmc) - concentration above which micelle formation takes place is known as cmc.

(5) PREPERATION OF COLLOIDS

(a) Chemical methods- By double decomposition, oxidation reaction or hydrolysis

OXIDATION

e.g. $SO_2 + 2H_2S \rightarrow 3S\,(SOL) + 2H_2O$

HYDROLYSIS

e.g. $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$

(sol)

(b) Bredig's arc method- For preparation of metallic sol. It involves dispersion as well as condensation.

(c) Peptization- Process of converting a precipitate into colloidal sol. By shaking it with dispersion medium in the presence of a small amount of electrolyte.

(6)PURIFICATION OF COLLIODAL SOLUTION :-
(a) Dialysis-it is a process of removing a dissolved substance from a colloidal solution by membrane.
(b)Electro dialysis-when dialysis is carried out with an electric field applied around the membrane.
(c) Ultra filtration- Use of special filters which are permeable to all ionic substances except colloidal particles.
(7)PROPERTIES OF COLLOIDAL SOLUTION:-
(1) They show colligative properties
(2) Brownian movement-zig-zag motion of colloidal particles
(3) Tyndall effect-scattering of light by colloidal particles by which path of beam becomes clearly visible. This effect is known as tyndall effect.
1. Charge on colloidal particles – Colloidal particles carry an electric charge and nature of charge is same on all particles.
2. Electrophoresis - Movement of Colloidal particles towards opposite electrode in presence of external electric field.
3. Coagulation – The process of setting of colloidal particles is called coagulation of the sol.
4. Hardy Sehulze Law – Coagulating value of a coagulating ion is directly proportional to the charge on the ion.
Eg: $Na^{+} < Ca^{++} < Al^{3+}$ for negatively charged sol.
$Cl^{-} < CO_3^{2-} < PO_4^{3-} < [Fe(CN)_6]^{4-}$ for positive sol.
5. Emulsion – Liquid – liquid colloidal system is known as Emulsion.
There are two types of Emulsion**.**
a) O/W type - Oil dispersed in water. Eg: milk, vanishing cream.
b) W/O type – Water dispersed in oil. Eg: Butter & Cream.
6. Emulsifying Agent – The substance which stabilizes emulsion**.**

VERY SHORT ANSWER QUESTIONS

1.What is electrophoresis due to?

It is due to either positive or negative charge on colloidal particles.

2. What is Tyndall effect due to?

It is due to scattering of light by colloidal particles.

3. Mention two ways by which lyophillic colloids can be coagulated.

(i) By adding an electrolyte (ii) By adding a suitable solvent

4. What is the cause of Brownian movement in a colloidal solution?

Brownian movement is due to the unbalanced bombardment of dispersed phase particles with the molecules of the dispersion medium of a colloidal solution.

5.

Arrangethe solutions: True solution, colloidalsolution, suspension in decreasing order of their particles size?

Suspension > colloidal > true solution.

6.What is an emulsion? What are the different types of emulsions?

Emulsions are colloidal solutions in which both dispersed phase and dispersion medium are liquids. Emulsions are of two different types:- (i) oil in water type ex.milk (ii) water in oil type ex. butter

7. What is meant by shape selective catalysis?

A catalyst whose catalytic action depends on its pore structure and molecular size of reactants and products is known as shape selective catalysts and the catalytic action is called shape selective catalysis. For example- zeolites

8. Define electrophoresis.

The phenomenon of movement of colloidal particles towards oppositely charged electrodes under the influence of applied electric field is called electrophoresis.

9. Define peptization.

The process of conversion of a freshly prepared precipitate into a colloidal solution by adding suitable electrolyte is called peptization.

10.What is coagulation or flocculation?

The conversion of colloidal solution into precipitate by the addition of suitable electrolyte is called coagulation.

11.Out of physisorption and chemisorption, which has a higher enthalpy of adsorption?

Chemisorption

12.What is especially observed when a beam of light is passed through a colloidal solution?

Tyndall effect

SHORT ANSWER QUESTIONS

1.What are the differences between physisorption and chemisorption?

Physical adsorption	**Chemical Adsorption**
1. It arises because of Van der waals' forces	1. It is caused by chemical bond formation
2. It is not specific	2. It is specific
3. It is reversible	3. It is irreversible
4. Enthalpy of adsorption is low (20-40 K J mol^{-1})	4. Enthalpy of adsorption is high (80-240 K J mol^{-1})
5. Low temperature is favorable , it decreases with increase in temperature	5. High temperature is favorable , it first increase with increase in temperature and then decreases
6. No appreciable activation energy is needed	6. High appreciable activation energy is needed
7. Multimolecular layers are formed	7. Monomolecular layers are formed

2. Explain what is observed when

(i) An electrolyte, NaCl is added to hydrated ferric oxide sol .

(ii) Electric current is passed through a colloidal sol .

(iii)When a beam of light is passed through a colloidal solution .

Ans: (i)The positively charged colloidal particles of $Fe(OH)_3$ get coagulated by the oppositely charged Cl^- ions provided by NaCl.

(ii) On passing direct current , colloidal particles move towards the oppositely charged electrode where they lose their charge and get coagulated .

(iii) Scattering of light by the colloidal particles takes place and the path of light becomes visible .

3.Differentiate between lyophillic and lyophobic colloids.

Lyophillic colloids	Lyophobic colloids
These are easily formed by simple mixing of dispersed phase with dispersion medium	These are formed by some special methods
Particles of colloids are not visible even under an ultra microscope	Particles of colloids are easily visible under an ultra microscope
These are stable	These are unstable

4.What is the principle involved in Dialysis?

Ans.Dialysis is based on the principle that impurities can pass through parchment membrane while colloidal particles cannot.

5.What are micelles? Give an example.

Ans. Micelles are associated colloids which behave as normal strong electrolytes at low concentration but behave as colloidal particles at higher concentrations. For example:- soap molecules when dissolved in water gives sodium and stearate ions. The stearate ions associate to form ionic micelles of colloidal size.

$C_{17}H_{35}COONa \longleftrightarrow C_{17}H_{35}COO^- + Na^+$

6. Differentiate between multimolecular, macromolecular and associated colloids.

Multimolecular colloids	Macromolecular colloids	Associated colloids
a)They consist of aggregates of atoms or molecules which generally have diameter less than 1nm. b)Theyareusually lyophobic	a)Theyconsistof particles having colloidal dimensions between 1nm to 1000nm b)They are hydrophilic.	a)Act as normal strong electrolyte at lower concentration and behave as colloidal solution at higher concentration. b)They have both lyophobic &lyophilic character

7. Explain the following terms giving suitable example in each case:

(i) Gel (ii) homogeneous catalysis (iii) Sol

Ans. (i) A gel is a colloidal solution in which dispersed phase is a liquid and dispersion medium is a solid. ex- jellies

(ii) When the reactants, products and catalyst are in the same physical states the catalysis is called homogeneous catalysis.

$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$

(iii) A sol is a colloidal solution in which dispersed phase is a solid and dispersion medium is a liquid.

8.What do you mean by activity and selectivity of catalysts ?

Ans : Activity of catalyst : The ability of a catalyst to increase the rate of a reaction is called its activity .For exp . a mixture of H_2 and O_2 does not react at all, however in presence of Pt catalyst the mixture reacts explosively .

$$2H_2 + O_2 \xrightarrow{(Pt)} 2H_2O$$

Selectivity of a catalyst : The ability of a catalyst to direct a reaction to yield a particular product is called the activity of a catalyst .

eg.$CH_3CH_2OH \xrightarrow{Cu\ (s)} CH_3CHO + H_2$

(dehydrogenation reaction takes place in presence of Cu catalyst at 573 K .)

$CH_3CH_2OH \xrightarrow{Al_2O_3(s)} CH_2{=}CH_2 + H_2O$

(dehydration reaction takes place in presence of Al_2O_3 catalyst.)

9.Explain the mechanism of enzyme catalysis.

1) binding of enzyme to substrate to form an activated complex.

$E + S \dashrightarrow ES^*$

2) Decomposition of the activated complex to form the product.

$ES^* \dashrightarrow E + P$

10.

Name the fixed layer and the diffused layer

(1) when $AgNO_3$ is added to KI

(2) When KI is added to $AgNO_3$

In the first case, AgI is formed and it adsorps I^-. AgI/I^- fixed layer and K^+ is diffused layer

When KI is added to $AgNO_3$, AgI/Ag+ is the fixed layer NO_3^- is the diffused layer.

11.

How are deltas formed?

River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets sea water, the electrolytes present in sea water coagulates the colloidal solution of clay resulting in formation of deltas.

12. State Hardy Schulze Law.

Ans. Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

Eg: $Na^{+} < Ca^{++} < Al^{3+}$ for negatively charged sol.

$Cl^{-} < CO3^{2-} < PO_4^{3-} < [Fe(CN)_6]^{4-}$ for positive sol.

13. What is meant by critical temperature of gas?

(Ans) Critical temperature is the minimum temperature above which a gas cannot be liquefied howsoever high the pressure may be applied.

14. Give the expression for Fruendlich adsorption isotherm.

(Ans) $x/m = kp^{1/n}$

15. What do x and m represent in the expression $x/m=kp^{1/n}$?

(Ans) 'm' is the mass of the adsorbent and 'x' is the number of moles of the adsorbate when the dynamic equilibrium has been achieved between the free gas and the adsorbed gas.

16.Why is heterogeneous catalysis also known as surface catalysis?

(Ans) In heterogeneous catalysis the reaction always starts at the surface of the catalyst. So, it is also known as surface catalysis.

17. What is a hydrosol?

(Ans) A colloid in which the dispersion medium is water is known as hydrosol.

18. Define Brownian movement?

(Ans) Brownian movement can be defined as continuous zig- zag movement of the colloidal particles in a colloidal sol.

19. Why is Brownian movement important?

(Ans) Brownian movement opposes the force of gravity and does not allow the colloidal particles to settle down, thus making the colloidal solution stable.

20. Differentiate between adsorption and absorption**.**

(Ans) **Adsorption**	**Absorption**
a)it occurs only at surface	a) it is a bulk phenomenon
b)concentration on the surface is more than in the bulk	b) concentration is same through out the material

21. What is the effect of temperature on adsorption?

(Ans) Adsorption processes, being exothermic, decreases with increase in temperature.

22. When a finely powdered active carbon is stirred into a solution of a dye, the intensity of color in solution decreases. Why?

(Ans) The intensity of color in the solution decreases because the dye gets adsorbed on the surface of carbon.

23**.** Why do finely divided substances have larger adsorption power?

(Ans) Finely divided substances have large surface area for adsorption and hence have larger adsorption power.

24. What are zeolites?

(Ans) Zeolites are aluminosilicates i.e. three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms.

25.Why are zeolites called shape selective catalysts?

(Ans) Zeolites are called shape selective catalysts because their catalytic action depends upon the size and shape of the reactant and the product molecules as well as on their own pores and cavities.

26. A small amount of silica gel and that of anhydrous $CaCl_2$ are placed separately in two corners of a vessel containing water vapours. What phenomena will occur in the two corners?

(Ans) Adsorption would occur where silica gel is kept in the vessel where as absorption will occur in the corner where $CaCl_2$ is placed.

27. Name the substance catalysed by Zymase.

(Ans) Glucose--$\xrightarrow{\text{Zymase}}$-> ethyl alcohol.

28.How can colloidal solution of ferric hydroxide be prepared by peptization?

(Ans) A colloidal sol. of ferric hydroxide can be prepared by adding small quantity of ferric chloride solution to freshly prepared precipitate of ferric hydroxide.

29.What happens to a gold sol. when gelatin is added to it?

(Ans) Gold sol. which is lyophobic starts behaving like lyophilic sol.

30. Write down the relation between pressure of the gas and the amount of it adsorbed**?**

(Ans) $x/m = K P^{1/n}$

31. Which adsorption may be a multilayered formation phenomenon**?**

(Ans) Physisorption

32. Which is irreversible and why**? Physisorption or chemisorption.**

(Ans) chemisorption.Because of the formation of chemical bond.

33. Name the promoter used in Haber's process**?**

(Ans) Molybdenum.

34. How are micelles formed in soap solution?

(Ans) Soap is sodium salt of fatty acids (RCOONa) which when dissolved in water dissociates to give $RCOO^-$ and Na^+. The $RCOO^-$ consists of polar group COO^- which is hydrophilic and stays at the surface and the non polar group R which being hydrophobic stays away from the surface. At high concentrations $RCOO^-$ ions are pulled into the solution to form spherical aggregates with R pointing to the centre COO^- part remaining outward. This aggregate is known as ionic micelle.

35**.**How can lyophobic sols be prepared by mechanical disintegration?

(Ans) The coarse suspension of the substance is introduced in the colloid mill that consists of two metal discs close together rotating at a high speed in the opposite directions. Here the suspension particles are broken to the colloidal size.

36**.** Describe the mechanism of peptization?

(Ans) When electrolyte is added to the freshly precipitated substance, the particles of the precipitate preferentially absorb one particular type of ions of the electrolyte and get dispersed due to electrostatic repulsions giving particles of colloidal size and hence cause peptization.

37. Give any two reasons for the origin of electrical charge on the colloidal particles.

(Ans) The two reasons are:

i) Due to electron capture by sol particles during electro dispersion of metals, due to preferential adsorption of ions from solution

ii) Dissociation of colloidal sols.

38. How is the electrical charge of the colloidal particles responsible for the stability of colloidal sols?

(Ans) The electrical charges of the particles prevent them from coming together due to electrostatic repulsion. All the dispersed particles in a colloidal solution carry the same charge while the dispersion medium has equal and opposite charge.

39**.** What is demulsification? Name two demulsifiers.

(Ans) The process of separation of the constituent liquids of an emulsion is called demulsification. Demulsification can be done by centrifugation or boiling.

40. Why lyophilic colloids are called reversible sols while lyophobic sols are called irreversible sols?

(Ans) In the lyophilic colloids if the dispersed medium is separated from the dispersion medium the sol can be made again by simply remixing with the dispersion medium. So they are called reversible sols.

In lyophobic sols if small amount of electrolyte is added, the sols are readily precipitated and do not give back the colloid by simple addition of the dispersion medium. So they are called irreversible sols.

41. Describe the preparation of the following colloidal solution.
(a) Gold sol (b) Sulphur sol

(Ans) (**a) Preparation of Gold sol :-** By the reduction of very dilute solution of silver salts with a suitable reducing agent

$$2AuCl_3 + 3SnCl_2 \text{ ----------> } 2Au + 3SnCl_4$$

Gold sol

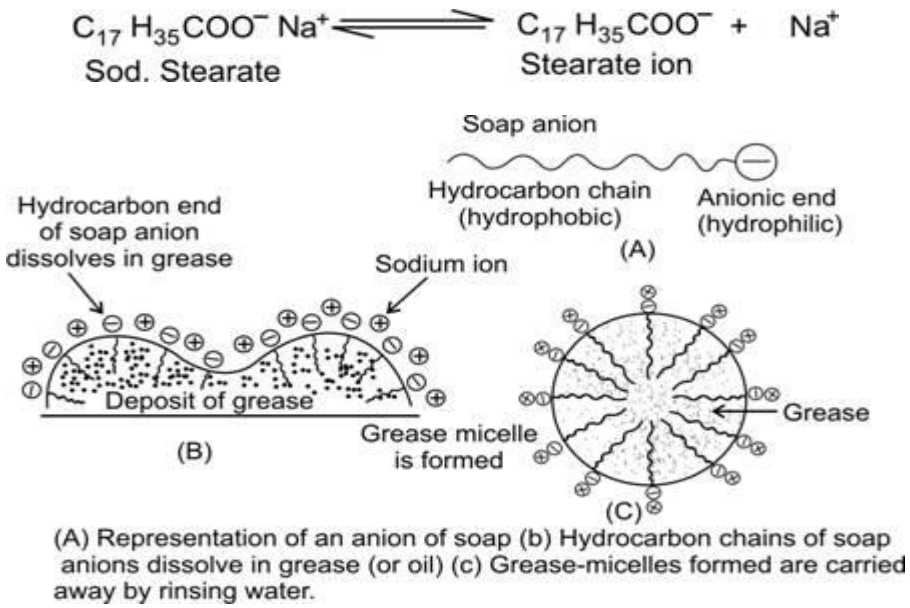
(b) Preparation of Sulphursol :- By the oxidation of H_2S in the presence of suitable oxidizing agent like nitric acid, bromine water, etc.

$$H_2S + Br_2 \text{ ----------> } S + 2HBr$$

$$H_2S + 2HNO_3 \text{ ----------> } 2H_2O + 2NO_2 + S$$

42. **"Action of soap is due to emulsification and micelle formation".Comment.**

(Ans) Yes, action of soap is due to emulsification and micelle formation. Soaps are sodium salt of higher fatty acids like sodium stearate, $C_{17}H_{35}COO^-Na^+$



(A) Representation of an anion of soap (b) Hydrocarbon chains of soap anions dissolve in grease (or oil) (c) Grease-micelles formed are carried away by rinsing water.

The anionic head of stearate ion ($-COO^-$) is hydrophobic in nature and has great affinity for water, while the hydrocarbon part ($C_{17}H_{35}^-$) is hydrophilic in nature and great affinity for oil, grease etc. When soap is used in water, the anions ($C_{17}H_{35}COO^-$) form micelle and due to emulsifications, encapsulate oil or grease inside. These micelle are removed by rinsing with water; while free dirt (from oil or grease) either settle down or are washed away by water. Thus the main function of a soap is to entrap oil or grease with the micelles through emulsification, thereby freeing dirt from grease and oil.

43. Why the sun looks red at the time of setting? Explain on the basis of colloidal properties.

(Ans) At the time of setting, the sun is at the horizon. The light emitted by the sun has to travel a longer distance through the atmosphere. As a result, blue part of the light is scattered away by the dust particles in the atmosphere. Hence, the red part is visible.

(Q.) Explain the reason for these:

(a) Sky looks blue in colour.

(b) Delta is formed at the meeting place of river and sea water.

(c) Blood coagulate on treatment with alum.

(Ans) (a) Sky looks blue in colour because colloidal particles suspended in environment scatter the light and blue light is scattered maximum.

(b) The charged colloidal particles of river water is neutralized by ions present in sea water. So coagulation takes place.

(c) The charged colloidal particles present in blood are neutralized by ions of alum.

Value based questions

1.Sohan Lal is a brick kiln owner who owns three brick kilns in Amritsar. Punjab Pollution Control Board has warned Sohan Lal to do something about the black smoke coming out of his chimneys or he will not be allowed to run his brick kilns. Sohan Lal is worried and does not know what to do.

(a) As a student of chemistry what would you suggest to Sohan Lal to control the black smoke coming out of chimneys of his brick kilns?
(b) What are the values associated with the above decision?
Ans.(i) Smoke is a dispersion of negatively charged colloidal particles of carbon in air and can be made free of these colloidal particles by passing it through a Cottrell precipitator installed in the chimney. It consists of two metal discs charged to a high potential. The carbon particles get discharged and precipitate while gases come out of the chimneys.
(ii) Values associated – concern towards keeping the environment healthy
2. A house wife while working in the kitchen got a cut on her finger which started bleeding. Her daughter Reena, immediately applied ferric chloride on the cut and the bleeding stopped.
(i) Why did the bleeding stop?
(ii) What is the value associated behind the act of Reena?
Ans.(i) Blood is a negatively charged colloid. Fe^{3+} ions of $FeCl_3$ neutralise the charge on the colloidal particles of blood. This leads to coagulation of blood
(ii) Concern towards parents

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

BASIC CONCEPTS

Minerals -Naturally occurring compounds of an element obtainable from the earth by

mining.

Ores -Minerals from which the element can be isolated economically.

'All ores are minerals, but all minerals are not ores'

Metallurgy - The process used for the isolation of metal from its ore.

Metallurgy involve the following major steps-

I. Concentration or Enrichment of ore

II. Isolation of Metal from the concentrated ore

III. Purification of the metal.

I. Concentration of the Ore

- Removal of Earthy impurities (sand, clay, soil…)
- Earthy impurities are known as Gangue
- Also known as Dressing Or Benefaction
- The ores are graded and powdered to reasonable size.
-

METHODS OF CONCENTRATION

- 1. Hydraulic Washing
- Used when there is difference in gravities between ore and gangue.
  - Powdered ore is washed in an upward stream of running water.
  - The lighter gangue particles are washed away and heavier ores are left behind.

2. Magnetic Separation

- Used when either the ore or the gangue are capable of being attracted by the magnetic field

3. Froth Floatation Process

- Used for removing Gangue from Sulphide ores.
- Principle behind this process is the preferential wetting of ore particle with oil and gangue by water.
- A suspension of powdered ore is made with water.
- To this Collectors(oil, fatty acids etc) and froth stabilisers(cresols, aniline etc) are added
- Minerals will be wet by oil while gangue by water
- When the mixture is agitated froth will be formed which will carry the ore particles
- It is possible to separate two Sulphide ores by using Depressants

Eg :-In ore containing ZnS and PbS , NaCN acts as a Depressant & selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

4. Leaching-A chemical method

- Used when the ore is soluble in some suitable solvent
  (i) eg.-Leaching of Alumina From Bauxite
- Bauxite usually contain SiO_2, Iron oxides, TiO_2 etc as impurities
- Powdered ore is digested with conc NaOH at 473-523K and 35-36 bar pressure
- Al $_2O_3$ and SiO_2 are leached out as Sodium aluminate and Sodium silicate

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$$

- The impurities are left behind
- The aluminate is neutralised by passing CO_2 so that hydrated aluminium oxide is precipitated(seeded with fresh Hydrated Al_20_3

$$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3\ (aq)$$

- The sodium silicate remains in the solution
- Hydrated alumina is Filtered, dried and heated to give pure Al $_2O_3$

$$Al_2O_3.xH_2O(s) \xrightarrow{1470\ K} Al_2O_3(s) + xH_2O(g)$$

(ii) eg. - Leaching of Silver and Gold

- Leached with a dilute solution of NaCN or KCN in presence of air
- The metal is obtained later by Displacement

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq) \quad (M = Ag \text{ or } Au)$$

$$2[M(CN)_2]^-(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s)$$

II. Extraction of The Crude Metal

- The metals are extracted from its ore by Reduction
- Oxide ores are easier to be reduced therefore sulphide ores and carbonate ores are first converted into oxides
- Therefore the extraction process consist of two processes
  - Conversion to oxide
  - reduction

Conversion to Oxides

1. Calcination - Heating in a limited supply of air or oxygen.
   - Usually carbonate ores are subjected to this process
   - Volatile matter escapes leaving behind the Oxide

$$Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3(s) + xH_2O(g)$$

$$ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

$$CaCO_3.MgCO_3(s) \xrightarrow{\Delta} CaO(s) + MgO(s) + 2CO_2(g)$$

2. Roasting - Heating in plenty of Air or oxygen at a temperature below the melting point.

Usually sulphide ores are subjected to this process.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

Gangue-The impurities present in the ore.

Flux -The substance added to remove the Gangue

Slag-The easily fusible substance formed by the combination of Gangue & Flux.

Gangue + Flux $\longrightarrow$ Slag

III. <u>Purification of the Metal</u>

1. Distillation- This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

2. Liquation -A low melting metal like tin can be made to flow on a sloping surface.

In this way it is separated from higher melting impurities.

3. Electrolytic Refining -

- The impure metal is made as anode.
- A strip of the same metal in pure form is used as cathode.
- A soluble salt of the same metal is used as electrolyte.
- The more basic metal remains in the solution and the less basic ones go to the anode mud.
- The reactions are:

  Anode: $M \rightarrow M^{n+} + ne–$

  Cathode: $M^{n+} + ne– \rightarrow M$

4. Zone Refining -

- Is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.
- This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

5. Vapour Phase Refining -The metal is converted into its volatile compound and collected. It is then decomposed to give pure metal.

The two requirements are:

1. The metal should form a volatile compound with an available reagent,
2. The volatile compound should be easily decomposable, so that the recovery is easy.

eg. -i. Mond Process for Refining Nickel

- Nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.
- $Ni + 4CO \xrightarrow{330 - 350\ K} Ni(CO)_4$
- It is decomposed at high temperature giving the pure metal.
- $Ni(CO)_4 \xrightarrow{450 - 470\ K} Ni + 4CO$

ii. Van Arkel Method for Refining Zirconium or Titanium

- Useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti.
- The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:

$$Zr + 2I_2 \rightarrow ZrI_4$$

- The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI_4 \rightarrow Zr + 2I_2$$

6. Chromatographic Method –

- Based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

SURE SHOT QUESTIONS

Q1. How is copper extracted from a low grade ore of it?

A1 It is extracted by hydrometallurgy. It is carried out in two steps-

- Leaching- low grade copper ores and scrapes are leached by using acid or bacteria.
- Reduction- The solution containing copper ions is treated with H2

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

Q2. What is the role of collectors in Froth Floatation process?

A2. Collectors like pine oil, fatty acids, xanthates enhance non wettability of mineral particles.

Q3. Copper matte is charged into a silica lined converter in extraction of copper. What is the role of silica lining here?

A3. Silica acts as a flux and combines with iron oxide present as gangue to form a fusible slag .

Q4. What is meant by the term ‘pyrometllurgy’**?**

A4. The process of reducing a metal oxide with coke or with any other reducing agent at high temperature is called pyrometallurgy.

Q6. Write the reactions involved in the following process

(i) Leaching of bauxite ore to prepare pure alumina

(ii) Refining of Zirconium by van Arkel method.

(iii) Recovery of gold after gold ore has been leached with NaCN solution.

A6. (i) $Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4](aq)$

$2Na[Al(OH)_4](aq) + CO_2 \longrightarrow Al_2O_3.x\ H_2O + 2NaHCO_3$

$Al_2O_3.x\ H_2O(s) \xrightarrow{1470K} Al_2O_3(s) + x\ H_2O\ (g)$

(ii) Van- Arkel Method: It is used to get ultra pure metals. Zr is purified by this process. Zr is heated in iodine vapours at about 870k to form volatile ZrI_4 which is heated over tungsten filament at 2075K to give pure Zr.

$$Zr(s) + 2I_2 \xrightarrow[870K]{heat} ZrI_4(s)$$

$$\text{Impure } ZrI_4(s) \xrightarrow{2075K\ [w]} Zr(pure) + 2I_2$$

(iii) Extraction of gold

$$4Au(s) + 8CN^-(aq) + 2H_2O + O_2 \longrightarrow 4[Au(CN)_2]^-(aq) + 4OH^-$$

$$2[Au(CN)_2]^- + Zn(s) \longrightarrow [Zn(CN)_4]^{2-}(aq) + 2Au$$

In this reaction zinc acts as reducing agent.

Q7. State the role of

(i) NaCN in froth floatation process

(ii) Calcium oxide in the extraction of iron

(iii) Graphite rods in the extraction of aluminium.

A7. (i) It prevents certain sulphides like ZnS to enter the froth in presence of PbS, therefore, helps in their separation. Sodium cyanide is used as depressant in separation of ZnS

from PbS.

(ii) It acts as flux.

(iii) Graphite rods act as anode in extraction of aluminium.

Q8. Describe the role of

(i) NaCN in the extraction of gold from gold ore

(ii) SiO2 in the extraction of copper from copper matte.

(iii) Iodine in the refining of zirconium

Write chemical equations for the involved reactions.

A8. (i) Extraction of gold:

NaCN forms a complex with gold ore which can be easily reduced

$$4Au(s) + 8NaCN\ (aq) + 2H_2O\ (l) + O_2(g) \longrightarrow 4Na[Au(CN)_2](aq) + 4NaOH(aq)$$

Or

$$4Au(s)\ 8CN^-(aq) + 2H_2O\ (l) + O_2\ (g) \longrightarrow 4[Au\ (CN)_2]^-\ (aq) + 4OH^-(aq)$$

$$2[Au(CN)_2]^-(aq) + Zn(s) \longrightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

In this reaction, zinc acts as reducing agent.

(ii) SiO_2 acts as flux, reacts with gangue FeO to remove it in form of slag(iron silicate)

$$FeO + SiO_2 \longrightarrow FeSiO_3(slag)$$

(iii) Iodine reacts with impure Zr to form a volatile compound ZrI_4 which on heating decomposes to give pure zirconium

$$Zr + 2I_2 \xrightarrow[870K]{\textbf{heat}} ZrI_4 \xrightarrow[2070K]{heat} Zr(pure) + 2I_2$$

Q9. Describe the role of the following:

(i) NaCN in the extraction of silver from a silver ore.

(ii) Iodine in the refining of titanium.

(iii) Cryolite in the metallurgy of aluminium

A.9 (i) dil. NaCN forms a complex with Ag_2S which on reduction with zinc gives silver

metal. Impurities remain unaffected and can be filtered off.

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)2] + Na_2S$$

$$2Na[Ag(CN)_2] + Zn \xrightarrow{Zn} Na_2[ZnCN)_4] + 2Ag$$

(ii) Iodine reacts with Titanium to form titanium iodide which on heating strongly gives pure titanium and iodine back.

$$Ti\ (pure) + 2I_2 \longrightarrow TiI_4$$

$$TiI_4 \xrightarrow{heat} Ti(pure) + 2I_2$$

(iii) Cryolite lowers the melting point of alumina and increases electrical conductivity. Fused Al_2O_3 is bad conductor of electricity. Therefore cryolite (Na_3AlF_6) is added to Purified Al_2O_3 which reduces the melting point of Al_2O_3 mixture up to around 1140K and also increases electrical conductance.

Q10. What chemical principle is involved in choosing a reducing agent for getting the metal from its oxide ore? Consider the metal oxides Al_2O_3 and Fe_2O_3, and justify the choice of reducing agent in each case.

A10. The choice of reducing agent and temperature is decided with the help of Ellingham diagram and sign of $\Delta G^{\mathbf{0}}$. Al can reduce MgO at 2000K because at this temperature range the line for $\Delta_f G^o$(Mg, MgO) lies above the line $\Delta_f G^o$(Al, Al_2O_3).This indicates at this temperature Al_2O_3 is more stable than MgO and $\Delta_f G^o$for the reaction given below would be negative above 1665K.

$$2Al + 3MgO \longrightarrow Al_2O_3 + 3Mg$$

Below 1665K Mg can reduce Al_2O_3 to Al because $\Delta_f G^o$will be negative for the reaction given belo

$$3Mg + Al_2O_3 \longrightarrow 2Al + 3MgO$$

$$2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O2(g)$$

$$6CO\ (g) + 3O_2(g) \longrightarrow 6CO_2(g)$$

$$2Fe_2O_3(s) + 6CO(g) \longrightarrow 4Fe(s) + 6CO_2(g)$$

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

$\Delta_r G^0 = +1487 kJ\ mol^{-1}$

$\Delta_r G^0 = -1543.2 kJmol^{-1}$

$\Delta_r G = -56.2 kJ\ mol^{-1}$

$\Delta_r G^0 = -28.1 kJ\ mol^{-1}$

Since $\Delta_r G^0$ is negative at a particular temperature therefore CO is suitable reducing agent for $Fe2O_3$.The temperature at which reduction will take place can be calculated with the help of Ellingham diagram.

11. **Give the name and composition of ore chosen for extraction of aluminium.**

Ans: The ore chosen for the extraction of aluminium is bauxite and its composition is $Al_2O_3.xH_2O$.

12. **What is leaching?**

Ans: Leaching is the process of extracting a substance from a solid by dissolving it in a liquid. In metallurgy leaching is used for the ores that are soluble in a suitable solvent.

13. **Why cryolite&fluorospar added to alumina during electrolytic reduction?**

Ans: Cryolite and fluorospar are added to alumina during electrolytic reduction to reduce the melting point of alumina and to increase its conductivity

14. **Reduction with C for Cu_2O can be done at lower temp. than ZnO. Why?**

Ans: In the Ellingham diagram the curve for Cu_2O lies higher than ZnO i.e. for the reduction of Cu_2O with C the negative value of Gibbs energy can be reached at a lower temperature than ZnO.

15. **Although thermodynamically feasible in practice magnesium metal is not used for the reduction of alumina. Why?**

Ans: Magnesium can reduce alumina at the temperature above the intersection point of the curves for Al_2O_3 and MgO in the Gibbs Energy vs T plot (Ellingham diagram). But the temperature at which this is feasible is too high to be achieved economically and is also technologically difficult. So this reduction is not done.

16. **What is the significance of leaching in extraction of aluminium?**

Ans: In the extraction of aluminium leaching is used for the concentration of ore by removing the impurities i.e. silica, iron oxides and titatinium oxides.

17. **Define Metallurgy.**

Ans: Metallurgy is the process of extraction of metals from their ores that includes various steps.

18. **Why is hydraulic washing a type of gravity separation?**

Ans: The process of hydraulic washing is based on the differences in gravity of the ore and the gangue particles and so is known as gravity separation.

19. **What is the use of van Arkel method?**

Ans: Van Arkel method is used for removal of impurities like oxygen and nitrogen from the metals like zirconium and titanium.

20. **How is distillation used for metal refining?**

Ans: Distillation is used for the metals with boiling point lower then the impurities. So the metals can be evaporated and separately obtained as distillate.

21. **Why do the anodes used in the electrolytic cell for the reduction of alumina need to be replaced regularly?**

Ans: The oxygen liberated at the anode during the reduction of alumina, reacts with the carbon of the anode to form CO and CO burns away the anode and hence the anodes need to be replaced.

22. **What is the role of depressant in froth floatation process?**

Ans: In froth floatation process the depressant selectively prevents one of the ores from coming to the froth in a mixture of two ores hence enabling the separation of the other one with the froth.

23. **State the role of silica in the metallurgy of copper.**

Ans: Silica in the metallurgy of copper helps in removal of iron oxide as iron silicate (slag).

24. **What is the role of graphite rods in the electrometallurgy of aluminium?**

Ans: In the electrometallurgy of aluminium, graphite rods act as anodes in the electrolytic cell of reduction and are the site for release of oxygen

25. **Give an example when an element is extracted by oxidation.**

Ans: Extraction of chlorine from brine is based on oxidation.

26. **What will happen if aqueous solution of NaCl is subjected to electrolysis?**

Ans: If aqueous Solution of NaCl is subjected to electrolysis, Cl_2 will be obtained with NaOH and H_2 gas as the side products.

27. **What is refining of metals?**

Ans: Refining of metal is the process of purification of a metal extracted from its ore.

28. **What is vapour phase refining?**

Ans: Vapour phase refining is the method of metal refining by changing the metal into volatile compound that can be collected separately leaving behind the impurities and can be decomposed to give the pure metal.

29. **Give the principle underlying the process used for refining of gallium.**

Ans: The process used for the refining of gallium is **zone refining** and the principle underlying it is that the impurities are more soluble in the melt than in solid state of the metal.

30. **State the principle on which the chromatographic methods of metal refining are based?**

Ans: Chromatographic methods of metal refining are based on the principle that different components of a mixture are differently adsorbed on an adsorbent

31. **Which is the purest form of iron and what are its uses?**

Ans: The purest form of iron is **wrought** iron & is used in making anchors, wires, bolts etc.

32. **What are minerals and how are they different from ores?**

Ans: Minerals are the naturally occurring chemical substances in the earth's crust obtained by mining. Its different from ores, as ores are the minerals that are used for the extraction of metals profitably.

33. **Name one ore each for iron & copper & give their chemical compositions.**

Ans: The ore of iron is hematite- Fe_2O_3 and the ore for copper is copper pyrites- $CuFeS_2$.

34. **What is the purpose of adding collectors and froth stabilisers during froth floatation? Give an example for each.**

Ans: During froth floatation process collectors like pine oil and fatty acids are added to enhance non wettability of the mineral particles and the froth stabilisers like cresol and aniline stabilise the froth.

35. **How can the ores ZnS and PbS be separated from a mixture using froth floatation process?**

Ans: During the froth floatation process a depressant like NaCN is added to the tank. The depressant selectively prevents ZnS from coming to the froth but allows PbS to come to the froth and hence helps the separation of PbS with the froth.

36. **Give the equations involved in the concentration of bauxite ore.**

Ans: i) $Al_2O_{3(s)} + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]_{(aq)}$

ii) $2Na[Al(OH)_4]_{(aq)} + CO_{2(g)} \longrightarrow Al_2O_3.xH_2O_{(s)} + 2NaHCO_3$

iii) $Al_2O_3.xH_2O_{(s)} \longrightarrow Al_2O_{3(s)} + xH_2O$

37. **Give one reaction each for roasting and Calcination.**

Ans: Calcination: $ZnCO_3 \longrightarrow ZnO(s) + CO_2$

Roasting: $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

38. **Why is coke preferred over CO for reducing FeO?**

Ans: According to Ellingham diagram the point of intersection of the curves of C, CO and Fe, FeO lies at temperature lower than that of the point of intersection of CO,CO_2 and Fe, FeO curves. This means the reduction of FeO will occur at much lower temperature with C than with CO. So C is preferred to CO for reduction.

39. **How is cast iron different from pig iron?**

Ans: Pig iron has 4% carbon and can be easily cast into verity of shapes. Whereas cast iron has lower carbon content and is extremely hard and brittle.

40. **Give the reactions that occur after the copper matte have been fed into silica lined converter.**

Ans: $2FeS+3O_2 \longrightarrow 2FeO + 3O_2$

$FeO + SiO_2 \longrightarrow FeSiO_3$

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

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

41. **Give the reactions taking place at the anode and the cathode during the electrolytic reduction of alumina.**

Ans: Anode: $C(s) + O^{2-}(melt) \longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}(melt) \longrightarrow CO_2(g) + 4e^-$

Cathode: $Al^{3+}(melt) + 3e^- \longrightarrow Al(l)$

42. **Explain the process of magnetic separation for concentration of ores.**

Ans: In magnetic separation ore is carried over a conveyer belt which passes over a magnetic roller. If either the ore or the gangue is capable of being attracted by the magnetic field then it will collect near the roller and the particles showing non magneticbehaviour will be collected away from the roller.

43. **Differentiate between roasting and Calcination.**

Ans: Calcination:

i) it involves heating of the ore in the absence of air

ii) it is generally used for carbonate ores

Calcination: $ZnCO_3 \longrightarrow ZnO(s) + CO_2$

Roasting:

i) it involves the heating of the ore in the presence of air

ii) it is generally used for sulphide ores

Roasting: $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

44. **Give the reactions involved in the reduction of iron oxide to give iron in a blast furnace.**

Ans: The reactions are as follows:

$C + O_2 \longrightarrow CO_2$

$CaCO_3 \longrightarrow CaO + CO_2$

$CO_2 + C \longrightarrow CO$

$3Fe_2O_3 + CO \longrightarrow Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$

$FeO + CO \longrightarrow Fe + CO_2$

$FeO + C \longrightarrow Fe + CO$

$CaO + SiO_2 \longrightarrow CaSiO_3$

45. **How is copper extracted from low grade ores and scraps?**

Ans: For extraction of copper from low grade ores and scraps the ore is first leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scarp iron or H_2 and Cu is obtained.

$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$

$Cu^{2+} + Fe \longrightarrow Cu(s) + Fe^{2+}$

46. **How is gold extracted from its ore?**

Ans: Extraction of gold involves leaching the metal with CN- giving metal complex.

$$4Au + 8CN^-(aq) + 2H_2O + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

the metal is later recovered by displacement method with zinc acting as reducing agent.

$$2[Au(CN)_2]^-(aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^- (aq)$$

47. **Describe the method used for refining copper metal.**

Ans: Copper metal is refined by using electrolytic method with impure copper metal as anode and the pure copper metal strip as cathode. The electrolyte is acidified copper sulphate solution. Copper dissolves from the anode into the electrolyte and get reduced and deposited on the cathode as pure metal.

Anode: $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

Impurities deposit as anode mud.

48. **How is nickel refined?**

Ans: Nickel is refined by Mond's process which is based upon vapour phase refining.

In this process nickel is heated in stream of carbon monoxide giving a volatile complex, leaving the impurities behind. The complex is further subjected to higher temperature so that it gets decomposed to giving pure metal.

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

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

49. **Describe briefly column chromatography.**

Ans: Column chromatography is the method of chromatographic refining of metals available in minute quantities and the impurities are not chemically very much different from the element. In this process the column of Al_2O_3 is prepared in glass tube that forms the stationary phase and the solution of the components to be separated are taken as solution that forms the mobile phase. The components would separate out based on their different solubilities in the mobile phase and the stationary phase.

50. **What criterion is followed for the selection of the stationary phase in chromatography?**

Ans: Stationary phase is the immobile and immiscible phase in chromatographic method. Stationary phase is chosen such that the components to be separated have different solubilities in the mobile phase and the stationary phase.

51. **How is zinc extracted from zinc blende?** (

Ans: Zinc blende is ZnS. For the extraction of zinc from zinc blende, the ore is first concentrated by the method of froth floatation. The concentrated ore is then roasted by heating the ore in the presence of oxygen to give ZnO releasing SO_2. The ZnS is further reduced using coke at temperature of 673k giving zinc metal.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

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