DAY TWENTY FIVE

General Principles and Processes of Isolation of Elements

Learning & Revision for the Day

- Minerals and Ores
- Principles and Methods of Extraction
- Steps involved in Extraction of Metals
- Thermodynamics of Metallurgy
- Occurrence and Principles of Extraction of Some Important Metals

.Earth crust is the source of many metals in which aluminium is the most abundant metal of earth crust and iron comes second. The percentage of different elements in earth crust is O-49%, Si-26%, Al-7.5%, Fe-4.2%, Ca-3.2%, Na-2.4%, K-2.3%, Mg-2.3%, H-1%.

Metals occur in two forms in nature :

(i) In native state (ii) In combined state.

Minerals and Ores

The substance (or compound) in the form of which metal is found in nature is called a mineral and the mineral from which extraction of metal is beneficial and cheap is called an ore. Thus, all ores are minerals but all minerals are not ores.

Depending upon the nature of associated group or atom, ores are of following types.

(i) **Oxide ores**, e.g. Haematite (Fe_2O_3), zincite (ZnO) etc.

(ii) **Sulphide ores**, e.g. Galena (PbS), cinnabar (HgS), argentite (Ag_2S), ruby silver ($Ag_2S \cdot Sb_2S_3$).

(iii) **Carbonate ores**, e.g. Magnesite ($MgCO_3$), siderite ($FeCO_3$) etc.

(iv) **Sulphate ores,** e.g. Gypsum ($CaSO_4 \cdot 2H_2O$), Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) etc.

(v) **Silicate ores**, e.g. Willemite (Zn_2SiO_4), feldspar ($NaAlSi_3O_8$).

(vi) **Nitrate ores**, are rare because all nitrates are water soluble and at higher temperature, they decompose into oxides or metal.

NOTE **Gangue** or **Matrix** are the impurities associated with the ore.

Principles and Methods of Extraction

The extraction of a metal from its ores is known as **metallurgy**.

Metallurgical processes may be divided into three different processes:

(i) **Pyrometallurgical process** involves extraction of metals at very high temperature, e.g. Cu, Fe, Zn, Sn, Pb, Ni, Cr, Hg are extracted by pyrometallurgical process.

(ii) **Hydrometallurgical process** involves the extraction of metal by the use of their aqueous solution

e.g. Ag and Au are extracted by this process.

In hydrometallurgy, metals like Fe cannot be used because it is not easy to remove excess iron from precious metal such as Ag, Au; while excess zinc can easily be removed, as it is volatile.

(iii) **Electrometallurgical process** involves extraction of sodium, potassium, lithium, calcium, magnesium and aluminium from their molten salt solutions through electrolytic method.

Steps Involved in the Extraction of Metals

Main steps involved in a metallurgical process are concentration, oxidation, reduction and refining.

1. Concentration of Ores

Removal of unwanted materials from the ores is known as **concentration of ores** or **ore dressing**.

Some of the important procedures are described below

- **Hydraulic washing** (Levigation) involves an upward stream of running water to wash the powdered ore. The oxides ores of iron (Fe_3O_4 and Fe_2O_3) are concentrated by this method.
- **Magnetic separation** is based on differences in magnetic properties of the ore components.
- **Electrostatic separation** involves electrically charged surfaces to separate metallic particles from non-metallic particles of ore.
- **Froth Floatation method** is used for the concentration of sulphide ores where a suspension of the powdered ore is made with water and collectors and froth stabilisers are added to it.

NOTE
- Collectors (e.g. pine oil, fatty acids, xanthates etc.) enhance non-wettability of the mineral particles and froth stabilisers (e.g. cresols, aniline) stabilise the froth.
- Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants'. e.g. In case of an ore containing ZnS and PbS, the depressant used is NaCN.

- **Leaching** is often used if the ore is soluble in some solvent (i.e. acids, bases or other chemicals) but not the impurities. e.g.

(i) **Leaching of alumina from bauxite** (Baeyer process)

$$Al_2O_3(s) + 2NaOH\ (aq) + 3H_2O\ (l) \xrightarrow{473-523\,K} \underset{\text{Sodium meta aluminate}}{2\ Na\ [Al(OH)_4](aq)}$$

$$SiO_2(s) + 2NaOH\ (aq) \xrightarrow{473-523\,K} \underset{\text{Sodium silicate}}{Na_2SiO_3}\ (aq) + H_2O$$

The resulting solution is filtered, cooled and pH is adjusted with CO_2, causing precipitation of aluminium hydroxide to Al_2O_3, xH_2O.

$$2Na\ [Al(OH)_4](aq) + 2CO_2(g) \longrightarrow Al_2O_3 \cdot xH_2O\ (s)\downarrow + 2NaHCO_3(aq)$$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3.

$$Al_2O_3 \cdot xH_2O(s) \xrightarrow{1470\,K} Al_2O_3(s) + x.H_2O(g)$$

(ii) **In the metallurgy of silver and gold**

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

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

2. Oxidation of Ores

The following steps are considered under the conversion of concentrated ore to oxide.

- **Calcination** is the strong heating of ore in absence of air.

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

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

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

- **Roasting** is the strong heating of ore in presence of air.

e.g. $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

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

The sulphide ores of copper are heated in reverberatory furnace. If the ore contains iron, it is mixed with silica before heating. Iron oxide slags off as iron silicate and copper is produced in the form of copper matte which contains Cu_2S and FeS.

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

SO_2 produced is utilised for manufacturing H_2SO_4.

In chloridising roasting, the ore containing As, S or Sb as impurity is heated with common salt in presence of silver ores.

In sulphating roasting, sulphide ores are oxidised into sulphate, e.g. ZnS is oxidised to $ZnSO_4$.

3. Reduction of Oxide to Metal

- Reduction of the metal oxide to metal takes place when heated with **reducing agents** such as C (coke,) or CO or even another metal. The process is known as **smelting.**

$$M_xO_y + yC \longrightarrow xM + yCO$$

- Some metals like Fe dissolve the reducing agent used (carbon) in their extraction. This can be removed by heating the impure metal with more of the ore.

- Electrolytic reduction involves reduction of highly electropositive metals like Na, K, Al which are reduced by the electrolysis of their fused salts. e.g.

$$\underset{\text{Fused}}{NaCl} \rightleftharpoons Na^+ + Cl^-$$

$$Na^+ + e^- \longrightarrow Na \qquad \text{(at cathode)}$$

$$Cl^- \longrightarrow Cl + e^- \qquad \text{(at anode)}$$

$$\downarrow \text{ACl}$$

$$Cl_2$$

- Reduction can also be done by using Al, H_2 etc. By Al, oxides of Cr, Fe and Mn are reduced. A mixture of Fe_2O_3 and Al is called **thermite mixture.**

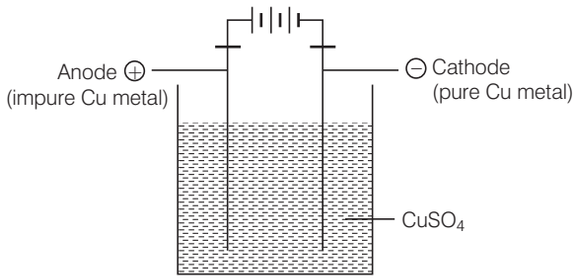
4. Refining

The metal obtained from the above processes is not 100% pure, hence called **crude metal.** From the impure metal, the metal of high purity is obtained by refining.

Several techniques are used in refining depending upon the differences in properties of the metal.

These are as follows :

- **Distillation** is very useful for low boiling point metals like zinc, cadmium and mercury. The impure metal is evaporated to obtain the pure metal as distillate.
- **Liquation** is useful for low melting point metals like tin, bismuth and lead, can be made to flow on a sloping surface of a reverberatory furnance and heated above their melting point. In this way it is separated from higher melting impurities.
- **Electrolytic Refining** (Electrolysis) Various elements such as Cu, Au, Ag, Pb, Zn and Al can be purified by this method.



Electrolytic refining of $CuSO_4$ (*aq.*)

Anode, $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Cathode, $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

- **Zone Refining** It is based on the principle that the impurities are more soluble in the melt form than in the solid state of the metal. This method is very useful for producing semiconductors and other metals of very high purity, e.g. germanium, silicon, boron, gallium and indium.
- **Vapour Phase Refining** In this method, the metal is converted into its volatile compound and then decomposed to give pure metal.

Some examples are as follows:

(i) **Mond process** for refining nickel

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

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

(ii) **van-Arkel method** for zirconium, titanium, vanadium or thorium

$$Zr + 2I_2 \longrightarrow ZrI_4 \text{ (volatile)}$$

$$ZrI_4 \xrightarrow{1800\ K} Zr + 2\,I_2$$

- **Chromatographic method** is based on the principle that different components of a mixture are adsorbed differently on an adsorbent.

Thermodynamics of Metallurgy

- To understand the variation of temperature requirement for thermal reactions and suitable reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are used.

  Gibbs equation is given as :

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

  where, ΔH = enthalpy change, ΔG = Gibbs free energy,

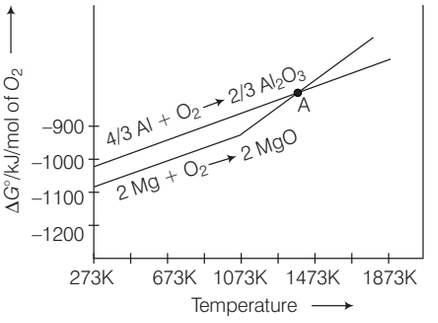
  T = temperature,

  ΔS = entropy change

$$\Delta G^\circ = -2.303\,RT \log K,$$

  K = equilibrium constant

- If ΔG = – ve, process is spontaneous, ΔG = + ve, process is non-spontaneous, ΔG = zero, process is at equilibrium.
- A reaction with positive ΔG can be made (–ve) by coupling it with another reaction having large negative ΔG. Such coupling is easily understood through **Ellingham diagram** as given below.



- From Ellingham diagram, it is evident that metals which have more negative $\Delta_f G^\circ$ values of their oxides can reduce those metal oxides for which $\Delta_f G^\circ$ is less negative.

Occurrence and Principles of Extraction of Some Important Metals

Some of the important metals, their occurrence and extraction are given below:

Aluminium (Al)

- **Occur** as bauxite ($Al_2O_3 \cdot 2H_2O$), cryolite-(Na_3AlF_6)
- **Common method of extraction** involves electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6 (Hall and Heroult process).

Iron (Fe)

- **Occur** as haematite (Fe_2O_3), magnetite (Fe_3O_4) etc.
- **Common method of extraction** involves reduction of the oxide with CO and coke in blast furnace.
- The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (e.g. S, P, Si, Mn) and is known as **pig iron.**
- **Cast iron** is different from pig iron and is made by melting pig iron with scrap iron and coke, using hot air blast.
- Cast iron has slightly lower carbon content (about 3%) and is extremely hard and brittle.
- **Wrought iron or malleable iron** is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace, lined with haematite.

Copper (Cu)

- **Occur** as copper pyrites ($CuFeS_2$), copper glance (Cu_2S) etc.
- **Common method of extraction** involves roasting of sulphide partially and auto-reduction.

Zinc (Zn)

- **Occur** as zinc blende or sphalerite (ZnS), calamine ($ZnCO_3$), zincite (ZnO) etc.
- **Common method of extraction** Roasting followed by reduction with coke.
- The metal may be purified by fractional distillation.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 An example of halide ore is
(a) bauxite (b) cryolite (c) cinnabar (d) galena

2 Argentite is a mineral of
(a) gold (b) silver (c) copper (d) platinum

3 Important ore of zinc is
(a) calamine (b) cryolite (c) cassiterite (d) malachite

4 Which one of the following is a mineral of iron?
→ CBSE-AIPMT 2012
(a) Malachite (b) Cassiterite
(c) Pyrolusite (d) Magnetite

5 "Metals are usually not found as nitrates in their ores".
→ CBSE-AIPMT 2015
Out of the following two (*A* and *B*) reasons which is/are true for the above observation?
A. Metal nitrates are highly unstable.
B. Metal nitrates are highly soluble in water.
(a) *A* and *B* are true (b) *A* and *B* are false
(c) *A* is false but *B* is true (d) *A* is true but *B* is false

6 Which of the following are ores of copper?
1. Malachite 2. Corundum
3. Chalcopyrites 4. Cinnabar
Codes
(a) 1, 2 and 3 are correct (b) 1 and 2 are correct
(c) 2 and 4 are correct (d) 1 and 3 are correct

7 Sulphide ores are generally concentrated by
(a) hand picking (b) froth floatation process
(c) gravity separation (d) magnetic separation

8 The substance added in water in froth floatation process is
(a) pine oil (b) coconut oil
(c) soap powder (d) None of these

9 Cassiterite is concentrated by
(a) liquefaction (b) floatation
(c) electromagnetic separation (d) levigation

10 Bauxite ore is concentrated by
(a) froth floatation (b) electromagnetic separation
(c) chemical separation (d) hydraulic separation

11 The chief impurity present in red bauxite is
(a) SiO_2 (b) Fe_2O_3 (c) K_2SO_4 (d) NaF

12 Which of the following benefaction processes is used for the mineral, $Al_2O_3 \cdot 2H_2O$?
(a) Leaching (b) Froth floatation
(c) Liquation (d) Magnetic separation

13 Complex is formed in the extraction of
(a) Fe (b) Cu (c) Ag (d) Na

14 Reagent used to extract silver from Ag_2S is
(a) NaCN (b) NaCN in the presence of O_2
(c) NaCl (d) $AgNO_3$

15 In the equation,
$4M + 8CN^- + 2H_2O + O_2 \longrightarrow 4[M(CN)_2]^- + 4OH^-$
Identify the metal, *M*.
(a) Copper (b) Iron (c) Gold (d) Zinc

16 Which one of the following ores is concentrated by chemical leaching method?
(a) Galena (b) Copper pyrite
(c) Cinnabar (d) Argentite

17 Cyanide process is used in the extraction of
(a) Au (b) Cu (c) Ag (d) Both (a) and (c)

18 Extraction of gold and silver involves leaching with CN^- ion. Silver is later recovered by **→ NEET 2017**
(a) liquation (b) distillation
(c) zone refining (d) displacement with Zn

19 Which of the following reaction is an example of calcination process?
(a) $2Ag + 2HCl + [O] \longrightarrow 2AgCl + H_2O$
(b) $2Zn + O_2 \longrightarrow 2ZnO$
(c) $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
(d) $MgCO_3 \longrightarrow MgO + CO_2$

20 Heating of ore in the presence of air to remove sulphur impurities is called
(a) calcination (b) roasting
(c) smelting (d) None of these

21 The substance which is mixed with the ore for the removal of impurities is termed as
(a) slag (b) catalyst (c) gangue (d) flux

22 Roasting of sulphides gives the gas *X* as a by product. This is colourless gas with choking smell of burnt sulphur and caused great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas *X* is **→ NEET 2013**
(a) SO_2 (b) CO_2 (c) SO_3 (d) H_2S

23 General method for the extraction of metal from oxide ore is
(a) reduction by aluminium (b) reduction by hydrogen
(c) carbon reduction (d) electrolytic reduction

24 Chemical reduction is not suitable for converting
(a) zinc oxide into zinc (b) cupric sulphide into copper
(c) bauxite into aluminium (d) haematite into iron

25 The auto-reduction process is not used in the metallurgy of
(a) Hg (b) Cu (c) Pb (d) Fe

26 Electrometallurgical process is used to extract
(a) Na (b) Pb (c) Ag (d) Fe

27 Electrolytic refining is used to purity which of the following metals?
(a) Cu and Zn (b) Ge and Si (c) Zr and Ti (d) Zn and Hg

28 In zone refining method, the molten zone
(a) contains impurities
(b) contains purified metal only
(c) contains more impurity than the original metal
(d) moves to either side

29 Mond's process is used for
(a) Ni (b) Al (c) Fe (d) Cu

30 Which of the following pairs of metals is purified by van-Arkel method? **→ CBSE-AIPMT 2011**
(a) Zr and Ti (b) Ag and Au (c) Ni and Fe (d) Ga and Ni

31 Match items of Column I with the items of Column II and assign the correct code. **→ NEET 2016, Phase I**

	Column I		Column II
A.	Cyanide process	1.	Ultrapure Ge
B.	Froth floatation process	2.	Dressing of ZnS
C.	Electrolytic reduction	3.	Extraction of Al
D.	Zone refining	4.	Extraction of Au
		5.	Purification of Ni

Codes

	A	B	C	D
(a)	2	3	1	5
(c)	3	4	5	1

	A	B	C	D
(b)	1	2	3	4
(d)	4	2	3	1

32 Ellingham diagram represents
(a) change of ΔG with temperature
(b) change of ΔH with temperature
(c) change of ΔG with pressure
(d) change of $(\Delta G - T\Delta S)$ with temperature

33 Considering Ellingham diagram, which of the following metals can be used to reduce alumina? **→ NEET 2018**
(a) Mg (b) Zn (c) Fe (d) Cu

34 Carbon can reduce ferric oxide to iron at a temperature above 983 K because
(a) carbon monoxide formed is thermodynamically less stable than ferric oxide
(b) carbon has a higher affinity towards oxygen than iron
(c) free energy change for the formation of carbon dioxide is less negative than that for ferric oxide
(d) iron has a higher affinity towards oxygen than carbon

35 Aluminium is extracted from alumina (Al_2O_3) by electrolysis of a molten mixture of **→ CBSE-AIPMT 2012**
(a) $Al_2O_3 + HF + NaAlF_4$
(b) $Al_2O_3 + CaF_2 + NaAlF_4$
(c) $Al_2O_3 + Na_3AlF_6 + CaF_2$
(d) $Al_2O_3 + KF + Na_3AlF_6$

36 In the metallurgy of aluminium …
(a) Al^{3+} is oxidised to Al(*s*)
(b) graphite anode is oxidised to carbon monoxide and carbon dioxide
(c) oxidation state of oxygen changes in the reaction at anode
(d) oxidation state of oxygen changes in the overall reaction involved in the process

37 The temperature of the slag zone in the metallurgy of iron using blast furnace is
(a) 1500-600°C (b) 400-700°C
(c) 800-1000°C (d) 1200-1500°C

38 Bessemer convertor is used for the preparation of
(a) copper
(b) wrought iron
(c) pig iron
(d) both (a) and (b)

39 Which of the following elements is present as the impurity to the maximum extent in the pig iron? ➞ **CBSE-AIPMT 2011**
(a) Carbon (b) Silicon
(c) Phosphorus (d) None of these

40 In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with ➞ **CBSE-AIPMT 2015**
(a) copper (I) sulphide (Cu_2S)
(b) sulphur dioxide (SO_2)
(c) iron sulphide (FeS)
(d) carbon monoxide (CO)

41 Heating mixture of Cu_2O and Cu_2S will give
(a) Cu_2SO_3 (b) $CuO + CuS$
(c) $Cu + SO_3$ (d) $Cu + SO_2$

42 In the electrolytic refining of zinc
(a) graphite is at the anode
(b) the impure metal is at the cathode
(c) the metal ion gets reduced at the anode
(d) acidified zinc sulphate is the electrolyte

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Which one of the following statements is false?
(a) During roasting, moisture is removed from the ore
(b) The ore is free from almost all non-metallic impurities
(c) Calcination of ore is carried out in the absence of any blast of air
(d) The concentrated zinc blende is subjected to calcination during its extraction by pyrometallurgy

2 The final step for the extraction of copper from copper pyrite in Bessemer converter involves the reaction
(a) $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$
(b) $4Cu_2O + FeS \longrightarrow 8Cu + FeSO_4$
(c) $2Cu_2O + FeS \longrightarrow 4Cu + Fe + SO_2$
(d) $Cu_2S + 2FeO \longrightarrow 2Cu + 2Fe + SO_2$

3 In aluminium extraction by the Baeyer's process, alumina is extracted from bauxite by sodium hydroxide at high temperature and pressures.
$Al_2O_3(s) + 2OH^-(aq) \longrightarrow 2Al_2O_2^-(aq) + H_2O(l)$
Solid impurities such as Fe_2O_3 and SiO_2 are removed and then $Al(OH)_4^-$ is reprecipitated.
$$2Al(OH)_4^- \longrightarrow Al_2O_3 \cdot 3H_2O(s) + 2OH^-(aq)$$
In the industrial world
(a) carbon dioxide is added to precipitate the alumina
(b) temperature and pressure are dropped and the supersaturated solution seeded
(c) Both (a) and (b) are practised
(d) the water is evaporated

4 Consider the following reaction at 1000°C
(A) $Zn(s) + \frac{1}{2}O_2(g) \longrightarrow ZnO(s);\ \Delta G° = -360\ kJ\ mol^{-1};$
(B) $C\ (graphite) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta G° = -460\ kJ\ mol^{-1};$
Choose the correct statement at 1000°C.
(a) Zinc can be oxidised by carbon monoxide
(b) Zinc oxide can be reduced by graphite
(c) Both statements (a) and (b) are true
(d) Both statements (a) and (b) are false

5 Carbon can reduce ferric oxide to iron at a temperature above 983 K because
(a) carbon monoxide formed is thermodynamically less stable than ferric oxide
(b) carbon has a higher affinity towards oxygen than iron
(c) free energy change for the formation of carbon dioxide is less negative than that for ferric oxide
(d) iron has a higher affinity towards oxygen than carbon

6 Brine is electrolysed by using inert electrodes. The reaction at anode is
(a) $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-,\ E^\circ_{cell} = 1.36\ V$
(b) $2H_2O(l) \longrightarrow O_2(g) + 4H^+ + 4e^-;\ E^\circ_{cell} = 1.23\ V$
(c) $Na^+(aq) + e^- \longrightarrow Na(s);\ E^\circ_{cell} = 2.71\ V$
(d) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2O(g);\ E^\circ_{cell} = 0.00\ V$

7 In order to refine blister copper, it is melted in a furnace and is stirred with green logs of wood. The purpose is
(a) to expel dissolved gases in blister copper
(b) to bring the impurities to surface and oxidise them
(c) to increase the carbon content of copper
(d) to reduce the metallic oxide impurities with hydrocarbon gases, released from the wood

8 Which of the following process involves smelting?
(a) $Al_2O_3 \cdot 2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O$
(b) $Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO$
(c) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$
(d) $2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$

9 What should be the considerations during the extraction of metals by electrochemical method?

(a) Reactivity ot metal obtained
(b) Selectivity of metal obtained
(c) Suitability of electrodes
(d) Both (a) and (c)

10 Sulphide ores of metals are usually concentrated by froth floatation process. Which one of the following sulphide ores offers an exception and is concentrated by chemical leaching?

(a) Argentite (b) Galena
(c) Copper pyrite (d) Sphalerite

11 Which process of purifications is represented by the following scheme?

$$\underset{\text{Impure}}{Ti} + 2I_2 \xrightarrow{250^\circ C} TiI_4 \xrightarrow{1400^\circ C} \underset{\text{Pure}}{Ti} + 2I$$

(a) Cupellation (b) Poling
(c) Zone refining (d) van-Arkel process

12 The minimum voltage required to electrolyse alumina in the Hall-Heroult process is

(Given, $\Delta°_f(Al_2O_3) = -1520$ kJ mol^{-1};
$\Delta G_f(CO_2) = -394$ kJ mol^{-1};

(a) 1575 V (b) 1.60 V (c) 1.12 V (d) – 2.62 V

13 When copper ore is mixed with silica, in a reverberatory furnace copper matte produced. The copper matte contains

(a) sulphides of copper (II) and iron (II)
(b) sulphides of copper (II) and iron (III)
(c) sulphides of copper (I) and iron (II)
(d) sulphides of copper (I) and iron (III)

14 Identify the reactions that take place during the smelting process of copper extraction.

I. $Cu_2O + FeS \longrightarrow Cu_2S + FeO$
II. $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2 \uparrow$
III. $FeO + SiO_2 \longrightarrow FeSiO_3$
IV. $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2 \uparrow$

Codes

(a) I, II and III are correct (b) I and II are correct
(c) II, III and IV are correct (d) III and IV are correct

15 Pyrometallurgical method as used for the extraction of copper

(a) involves concentration of ores by heating
(b) involves concentration by leaching the sulphide ore with dil. H_2SO_4
(c) involves concentration of the sulphide ore by Froth floatation process
(d) involves calcination, roasting, smelting and refining

16 When the sample of Cu with Zn impurity is to be purified by electrolysis, the appropriate electrodes are

	Cathode	**Anode**
(a)	Pure Zn	Pure Cu
(b)	Impure sample	Pure Cu
(c)	Impure Zn	Impure sample
(d)	Pure copper	Impure sample

17 Match the metals in Column I and their ores in Column II and choose the correct option from the codes given below.

	Column I		**Column II**
A.	Aluminium	1	Bauxite
B.	Copper	2	Pitch blende
C.	Potassium	3	Pyrites
D.	Radium	4	Sylvine

Codes

	A	B	C	D		A	B	C	D
(a)	1	3	4	3	(b)	1	4	3	2
(c)	4	5	2	1	(d)	1	3	4	2

18 Match the following and choose the correct option from the codes given below.

	Column I		**Column II**
A.	Feldspar	1	$[Ag_3SbS_3]$
B.	Asbestos	2	$Al_2O_3 \cdot H_2O$
C.	Pyragyrite	3	$KAlSi_3O_8$
D.	Diaspore	4	$CaMg_3(SiO_3)_4$

Codes

	A	B	C	D		A	B	C	D
(a)	4	2	3	1	(b)	3	4	1	2
(c)	1	2	3	4	(d)	2	3	4	1

ANSWERS

SESSION 1

1 (b)	**2** (b)	**3** (a)	**4** (d)	**5** (c)	**6** (d)	**7** (b)	**8** (a)	**9** (c)	**10** (c)
11 (b)	**12** (a)	**13** (c)	**14** (b)	**15** (c)	**16** (d)	**17** (d)	**18** (d)	**19** (d)	**20** (b)
21 (d)	**22** (a)	**23** (c)	**24** (c)	**25** (d)	**26** (a)	**27** (a)	**28** (c)	**29** (a)	**30** (a)
31 (d)	**32** (a)	**33** (a)	**34** (b)	**35** (c)	**36** (b)	**37** (c)	**38** (a)	**39** (a)	**40** (a)
41 (d)	**42** (d)								

SESSION 2

1 (d)	**2** (a)	**3** (c)	**4** (b)	**5** (b)	**6** (a)	**7** (d)	**8** (b)	**9** (d)	**10** (d)
11 (d)	**12** (b)	**13** (c)	**14** (a)	**15** (d)	**16** (d)	**17** (d)	**18** (b)		

Hints and Explanations

SESSION 1

1 Cryolite (Na_3AlF_6) is an halide ore.

2 Argentite or silver glance (Ag_2S) is an ore of silver.

3 Calamine — $ZnCO_3$,

4

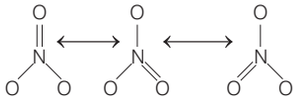
	Mineral	Chemical composition
d.	Magnetite	Fe_3O_4

Thus, magnetite is a mineral of iron.

5 Metals are usually not found as nitrates in their ores, because metals nitrates are highly soluble in water.

The nitrate anion has three equivalent oxygen surrounding a nitrogen atom.

This tends to spread the single negative charge and make it easier for water (using hydrogen bonds) to separate the ions in solution



6

	Ore	Chemical formula
1.	Malachite	$CuCO_3 \cdot Cu(OH)_2$
2.	Corundum	Al_2O_3
3.	Chalcopyrites	$CuFeS_2$
4.	Cinnabar	HgS

7 Froth floatation is based on the fact that the surface of sulphide ores is preferentially wetted by oil while that of gangue is wetted by water.

8 Pine oil is a foaming agent. Now another substance collecter such as potassium ethyl xanthate or amyl xanthate are also added.

9 Cassiterite (SnO_2) or tin stone an ore of tin being non-magnetic can be separated from magnetic impurities like Fe and Mn from electromagnetic separation method.

10 In chemical separation or leaching process, powdered ore (e.g. bauxite) is treated with a suitable reagent which can dissolve the ore but not the impurities.

11 The main impurity found in red bauxite is that of ferrite (Fe_2O_3) while silica is the chief impurity in white bauxite.

12 $Al_2O_3 \cdot 2H_2O$ (bauxite) is concentrated by leaching with $NaOH \cdot Al_2O_3$ dissolved leaving other impurities undissolved.

13 Ag is extracted by the process of leaching as follows :

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

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

14 The reaction is based on the fact that silver and its compounds form soluble complex with NaCN. This reaction is reversible and accumulation of Na_2S must be prevented. A free excess of air (O_2) is continuously passed through the solution which oxidises Na_2S to Na_2SO_4 and $Na_2S_2O_3$.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

$$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$$

Silver is recovered from solution by precipitating with zinc.

$$2Na[Ag(CN)_2] + 4NaOH + Zn \longrightarrow Na_2ZnO_2 + 4NaCN + 2H_2O + 2Ag$$

15 Least reactive metals like silver (Ag) and gold (Au) are obtained by cyanide process. In this process, the impure metal is treated with NaCN (solution) and air is passed. Metal is converted into soluble complex as

$$4Au + 8CN^- + 2H_2O + O_2 \longrightarrow \underset{\text{Soluble}}{4[Au(CN)_2]^-} + 4OH^-$$

From this soluble complex, metal is displaced by using more electropositive metal like Zn.

$$2.[Au(CN)_2]^- + Zn \rightarrow \underset{\text{Soluble}}{[Zn(CN)_4]^{2-}} + \underset{\text{ppt.}}{2Au\downarrow}$$

16 Gold and silver ores are concentrated by leaching. In this method the ore is treated with a suitable reagent in which ore is soluble but impurities do not. Thus, impurities are removed by filtration.

Among galena (PbS), copper pyrites ($CuFeS_2$), cinnabar (HgS), argentite (Ag_2S) and copper glance (Cu_2S), argentite being silver ore is concentrated by chemical leaching method as :

$$\underset{\text{Argentite}}{Ag_2S} + 4NaCN \longrightarrow \underset{\text{Soluble}}{2Na[Ag(CN)_2]} + \underset{\text{Insoluble}}{Na_2S}$$

17 Cyanide process is used in the extraction of both silver and gold because these form soluble complex salts with CN^- ion due to presence of lone pair of electron on nitrogen atom.

18 Extraction of gold and silver involves leaching with CN^- ion. Silver is later recovered by distillation with Zn.

In general,

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

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

M = Ag or Au

This method is known as **Mac-Arthur Forest** cyanide process.

19 The process of conversion of a concentrated ore into its oxide by heating in absence or in limited supply of air is called calcination. It is usually done for hydroxide and carbonate ores.

Thus, $MgCO_3 \xrightarrow{\Delta} MgO + CO_2$ is an example of calcination process.

20 Roasting is the process of heating of ore in excess supply of air below its melting point. During roasting volatile impurities are removed in this process impurities like sulphur, phosphorus, arsenic are removed as oxides. The ore is oxidised to form metal oxide or sulphate.

$$PbS + 3O_2 \longrightarrow 2PbO + SO_2\uparrow$$

21 Flux is added during smelting. It combines with infusible gangue present in the ore to form a fusible mass known as slag.

$$\text{Flux} + \text{Gangue} \longrightarrow \text{Slag}$$

22 SO_2 gas is obtained when any sulphide ore is roasted.

$$2M_2S + 3O_2 \xrightarrow{\Delta} 2M_2O + 2SO_2$$

This gas exhibits all the characteristics that are given in the question.

23 Carbon reduction method is employed for the extraction of metal from its oxide

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

24 Al is a strong reducing agent. It has stronger affinity with oxygen than carbon therefore chemical reduction is not suitable for converting bauxite into aluminium.

25 $2HgO + HgS \longrightarrow 3Hg + SO_2$

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

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

$PbS + 2PbO \longrightarrow 3Pb + SO_2$

26 Because Na is very reactive and cannot be extracted by means of reduction by C, CO etc. so extracted by electrolysis.

27 Electrolytic refining is used to purify several metals such as Cu, Zn, Ag, Au, Pb, Al etc.

28 Zone refining process is based upon the fact that impurities are more soluble in melt than in the original metal. Hence, molten zone contains more impurities than the original metal.

29 Mond's process is used for purification of nickel by converting it to volatile nickel carbonyl.

$$\underset{\text{Impure}}{Ni} + 4CO \xrightarrow{80^\circ C} Ni(CO)_4 \xrightarrow{180^\circ C} \underset{\text{pure}}{Ni} + 4CO$$

30 Zr and Ti are purified by van-Arkel method.

31 A – 4, B – 2, C – 3, D – 1

Cyanide process It is a metallurgical technique for extracting Au (gold) from low grade ore by converting the Au to a water-soluble coordination complex.

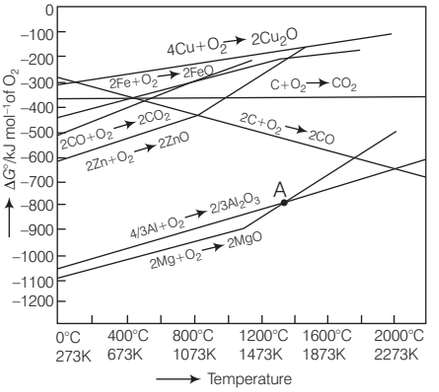
Froth floatation process This process is used for dressing of sulphide ore, i.e. ZnS.

Electrolytic reduction This process is used for extraction of Al which is carried out in a steel tank lined inside with graphite. Here, graphite serves as cathode. The electrolyte consists of alumina dissolved in fused cryolite (Na_3AlF_6) and fluorspar (CaF_2).

Zone refining This process is used for ultra pure Ge element. An ingot of Ge is first purified by zone refining. Then a small amount of antimony is placed in the molten zone which is passed through the pure Ge with the proper choice of rate of heating and other variables.

32 Ellingham diagram explain thermodynamics of a metallurgical process by plotting graph between change in free energy (ΔG) and temperature.

33 According to Ellingham diagram, the temperature at which two lines intersect shows that the metal will reduce the oxide of other metals which lie above it in ellingham diagram.



In other words, that metal oxide having more negative value of $\Delta G°_f$ can reduce the oxide having less negative $\Delta G°_f$. As, Mg has more $-\Delta G°$ value than alumina, so it will be in lower part of Ellingham diagram. Hence, Mg will be used to reduce alumina.

34 Above 983 K, free energy change for the formation of CO_2 is more negative than that for ferric oxide. Thus, above this temperature, carbon has a higher affinity towards oxygen than iron.

35 Alumina (Al_2O_3) is a bad conductor of electricity and has very high melting point, so before subjecting to electrolysis, it is mixed with fluorspar (CaF_2) and cryolite (Na_3AlF_6), which lower its melting point and make it more conducting.

36 In the metallurgy of aluminium (Al), graphite anode is oxidised to carbon monoxide (CO) and carbon dioxide (CO_2).

37 Slag formation zone is the central zone in the blast furnace where the temperature varies from 800 –1000°C. Here, limestone decomposes into CaO and CO_2.

$$CaCO_3 \xrightarrow{1000^\circ C} CaO + CO_2$$

CaO acts as a flux as it combines with silica present as an impurity (gangue) to form a fusible slag of $CaSiO_3$.

$$\underset{\text{Gangue}}{CaO + SiO_2} \xrightarrow{1000^\circ C} \underset{\text{Slag}}{CaSiO_3}$$

38 In Bessemer converter copper sulphide is partially oxidised to cuprous oxide which further reacts with remaining copper sulphide to form copper and sulphur dioxide.

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

39 Pig iron contains about 4% carbon (major impurity) and other impurities (S, P, Si, Mn) in trace amounts.

40 In the extraction of copper from its sulphide ore, when ore is subjected to roasting, some of it is oxidised to Cu_2O which reacts with the remaining Cu_2S (sulphide ore) to give copper metal.

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

In this process Cu_2S behaves as reducing agent.

41 Following reaction takes place during bessemerisation.

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

42 In the electrolytic refining of zinc, anode is made up of impure zinc while a strip of pure zinc acts as cathode. An acidified solution of zinc sulphate acts as electrolyte. When electricity is passed, following reactions occur

At cathode $Zn^{2+} + 2e^- \longrightarrow \underset{\text{Pure}}{Zn}$

At anode $\underset{\text{Impure}}{Zn} \longrightarrow Zn^{2+} + 2e^-$

SESSION 2

1 Zinc blende is heated in a regular supply of air in a furnance at a temperature below the melting point of the metal (roasting).

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

2 In Bessemer converter copper sulphide is partially oxidised to cuprous oxide which further reacts with remaining copper sulphide to form copper and sulphur dioxide.

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

3 Both the methods [(a) and (b)] are applicable to obtain pure alumina (Al_2O_3).

4 At 1000°C, zinc oxide can be reduced by graphite. $ZnO + C \longrightarrow Zn + CO$

5 Above 983 K, free energy change for the formation of CO_2 is more negative than that for ferric oxide. Thus, above this temperature, carbon has a higher affinity towards oxygen than iron.

6 Although, oxidation potential of Cl^- ion is higher than that of H_2O, but due to overvoltage of O_2 (i.e. water needs greater voltage for oxidation to O_2 as it is a kinetically a slow process) and needed higher potential than for the oxidation of Cl^- ions to Cl_2. 1.36 V

7 $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$3Cu_2O + CH_4 \longrightarrow 6Cu + 2H_2O$

From green logs of wood + CO

8 When concentrated ore is mixed with coke and flux and heated in the presence of air at high temperature, impurities get removed. This process is called smelting. Actually, it is a reduction process, in which oxide is reduced to metal. Therefore, following process will involve smelting.

$$Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO$$

9 (a) Reactivity of metal produced.

(c) Suitability of electrodes.

10 Galena (PbS), copper pyrite ($CuFeS_2$) and argentite (Ag_2S) are concentrated by froth floatation process but sphalerite (ZnS) is concentrated by chemical leaching.

11 $\underset{\text{Impure}}{Ti} + 2I_2 \xrightarrow{250^\circ C} TiI_4 \xrightarrow{1400^\circ C} \underset{\text{Pure}}{Ti} + I_2$

This process of purification is represented by van-Arkel process.

12 In Hall-Heroult process, the following reactions occur

$3C + 2Al_2O_3 \longrightarrow 4Al + 3CO_2$

$4Al^{3+} + 12e^- \longrightarrow 4Al$

$\therefore \Delta G^\circ = 3\Delta G^\circ_f(CO_2) - 2\Delta G^\circ_f(Al_2O_3)$

$= 3(-394) - 2(-1520) = 1858\ kJ$

$\because \Delta G^\circ = -nFE^\circ_{cell}$

$\therefore \quad -E^\circ_{cell} = \dfrac{1858 \times 1000}{12 \times 96500} = 1.60\ V$

13 Matte consists of $Cu_2S + FeS$, i.e. option (c) is correct.

14 The reaction,

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2 \uparrow$

occurs during roasting of pyrites ore. Roasting is the process of heating concentrated ore in the stream of air to convert it into oxide.

15 Pyrometallurgical process involves heat treatment to concentrated or dressed ores. It includes calcination, roasting, smelting and refining.

16 **At anode,**

$$\underset{\text{(impure)}}{Cu} \longrightarrow Cu^{2+} + 2e^-$$

At cathode, $Cu^{2+} \xrightarrow{2e^-} \underset{\text{(Pure)}}{Cu}$

17

	Metal	Ore
A.	Aluminium	Bauxite ($Al_2O_3 \cdot 2H_2O$)
B.	Copper	Pyrites ($CuFeS_2$)
C.	Potassium	Sylvine (KCl)
D.	Radium	Pitch blende

18 A. Feldspar orthosilicates is ($KAlSi_3O_8$).
It is used in the manufacture of porcelain.

B. Asbestos is $\{CaMg_3(SiO_3)_4\}$.
It is used for fireproof sheets, clothes etc.

C. Pyragyrite is (ruby silver) (Ag_3SbS_3).
It is an ore of silver.

D. Diaspore is ($Al_2O_3 \cdot H_2O$).
It is an ore of aluminium.