DAY NINETEEN

General Principles and Processes of Isolation of Metals

Learning & Revision for the Day

- Occurrence of Elements in Nature
- Minerals and Ores
- Metallurgy
- Extraction of Metals
- Thermodynamics and Electrochemical Principles of Metallurgy
- Refining of Crude Metal
- Occurrence and Extraction of Some Important Metals

About 118 elements are known till today. Among them, few elements occur in free state while others in combined form. Some general principles are adopted for extraction and isolation of an element from its combined form.

Occurrence of Elements in Nature

- Earth crust is the source of many elements. 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 and (ii) in combined state.

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where, $0 < x < 1$]
	Kaolinite (a form of clay)	$[Al_2(OH)_4Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

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.**

The impurities associated with the ore are called **gangue** or **matrix**.

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).

(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 ($NaAlSi_3O_8$).

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

Metallurgy

Extraction of a metal from its ores is known as metallurgy. Metallurgy of a metal includes several metallurgical operations depending upon the nature of metal, its ore and impurities.

All metallurgical processes may be divided into three processes:

1. **Pyrometallurgical Process** It involves extraction of metals at very high temperature. Cu, Fe, Zn, Sn, Pb, Ni, Cr, Hg are extracted by pyrometallurgical process.
2. **Hydrometallurgical Process** It involves extraction of metal by the use of their aqueous solution. Ag and Au are extracted by this process.

NOTE 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 be easily removed as it is volatile.

3. **Electrometallurgical Process** Sodium, potassium, lithium, calcium, magnesium and aluminium are extracted from their molten salt solutions through electrolytic method.

Extraction of Metals

Various steps/processes involved in the extraction of a metal are as follows:

1. Concentration of Ores

It is the method that involves removal of unwanted materials from the ores. This method is also known as **ore dressing.**

Various methods adopted for the ore dressing are as follows:

(i) **Hydraulic Washing** (Levigation) It is based on the differences in gravities of the ore and gangue particles.

- In this process, an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.
- The oxide ores of iron (Fe_3O_4 and Fe_2O_3) are concentrated by this method.

(ii) **Magnetic-Separation Method** It is based on differences in magnetic properties of the minerals. If either the ore or the gangue is capable of being attracted by a magnetic field, then this process is used.

In electrostatic separation, electrically charged surfaces are used to separate metallic particles from non-metallic particles of ore.

(iii) **Froth-Floatation Method** It is used for the concentration of sulphide ores. In this process, a suspension of the powdered ore is made with water. To it, collectors and froth stabilisers are added.

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.

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

(a) **Leaching of Alumina From Bauxite** (Baeyer's process)

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

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

The resulting solution is filtered, cooled and pH is adjusted by neutralisation with CO_2 which causes precipitation of aluminium hydroxide.

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

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

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

(b) **In the Metallurgy of Silver and Gold** The respective metal is leached with dilute solution of NaCN or KCN in the presence of air (from O_2).

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

(where, M = Ag or Au))

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

2. Extraction of Crude Metal from Concentrated Ore

It involves two major steps, i.e. conversion of concentrated ore to oxide and reduction of the oxide to metal.

In conversion of concentrated ore to oxide following steps are considered:

(i) **Calcination** Strong heating of ore in absence of air. e.g.

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

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

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

Usually **carbonates and hydroxides are converted** into oxides by this method. Volatile impurities of S, As and P are removed as their volatile oxides.

(ii) **Roasting** Strong heating of ore in presence of air. e.g.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

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.

- **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.**

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

NOTE
- 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 $ZnSO_4$.
- 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.
- **Misch metal** is used as a reducing agent for extraction of pure vanadium. Hydrogen is used as a reducing agent in extraction of pure tungsten and vanadium.

Thermodynamics and Electrochemical Principles 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 made.

Gibbs equation,

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

where, ΔH = enthalpy change, ΔG = Gibbs free energy,
T = temperature, ΔS = entropy change

$$\Delta G° = -2.303\, RT \log K$$

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 still be made to occur by coupling it with another reaction having large negative ΔG. Such coupling is easily understood through **Ellingham diagram**. This diagram help us in predicting the feasibility of thermal reduction of an ore.
- Ellingham diagram plots Gibbs free energy change (ΔG) values for formation of oxides against temperature.
- From Ellingham diagram, it is evident that metals which have more negative $\Delta_f G°$ of their oxides can reduce those metal oxides for which $\Delta_f G°$ is less negative.
- Reduction can also be done by using Al, H_2 etc. By using Al, oxides of Cr, Fe and Mn can be reduced. A mixture of Fe_2O_3 and Al is called **thermite mixture**.
- Highly electropositive metals like Na, K, Al are reduced by the electrolysis of their fused salts.

Refining of Crude Metal

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 :

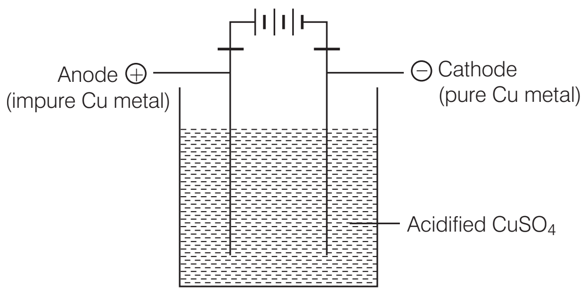
(i) **Distillation** This method is very useful for low boiling metals like zinc, cadmium and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

(ii) **Liquation** This method, involves low melting metals like tin, bismuth and lead that can be made to flow on a sloping surface of a reverberatory furnace and heated above their melting point. In this way, it is separated from higher melting impurities.

(iii) **Electrolytic Refining** (Electrolysis) Various elements such as Cu, Au, Ag, Pb, Zn and Al can be purified by this method. Here, crude metal is made anode whereas the thin sheet of pure metal is made cathode.

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

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



Electro refining

(iv) **Zone-Refining** This method 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 semiconductors and other metals of very high purity, e.g. germanium, silicon, boron, gallium and indium.

(v) **Vapour Phase Refining** This method, involves the conversion of metal into its volatile compound. It is then decomposed to give pure metal.

e.g.

- **Mond process** for refining nickel.

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

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

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

$$\underset{\text{(Impure)}}{Zr + 2I_2} \longrightarrow \underset{\text{(Volatile)}}{ZrI_4}$$

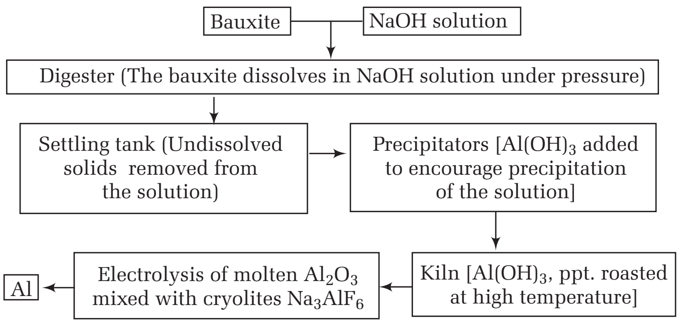
$$ZrI_4 \xrightarrow{1800\ K} \underset{\text{(Pure)}}{Zr} + 2I_2$$

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

Occurrence and Extraction of Some Important Metals

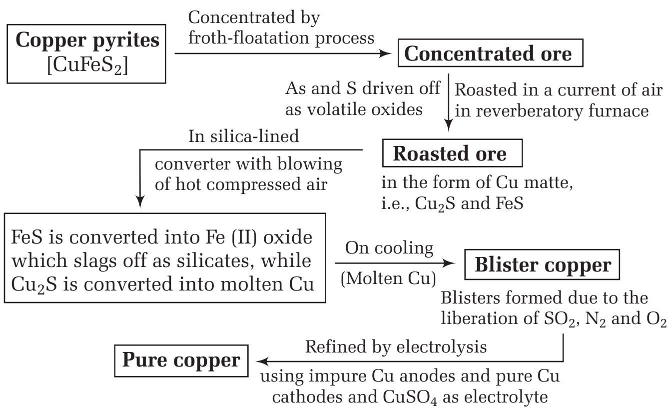
1. Aluminium

Its chief ore is **bauxite** ($Al_2O_3 \cdot 2H_2O$). The outline of its extraction from its ore is shown below:



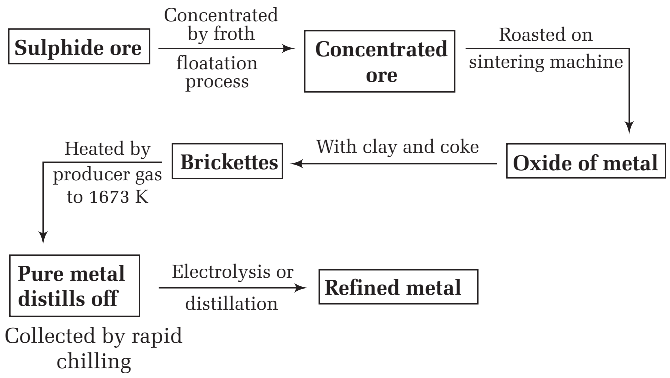
2. Copper

It does not occur abundantly in nature. Its chief ore are **copper pyrites** ($CuFeS_2$), **malachite** ($CuCO_3 \cdot Cu(OH)_2$), **cuperite** (Cu_2O), **copper glance** (Cu_2S). The outline of its extraction from its ore looks like



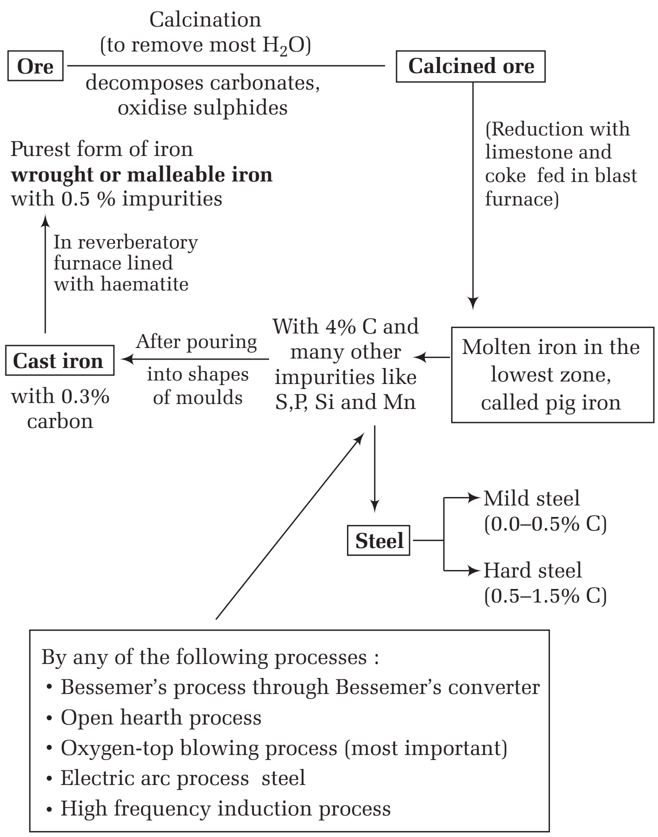
3. Zinc

Its chief ore is **zinc blende** (ZnS) and other ores are **calamine** ($ZnCO_3$), **zincite** (ZnO), **willemite** (Zn_2SiO_4) etc. The outline of its extraction looks like



4. Iron

Iron is the second most abundant metal after Al in the earth's crust. Its most important ores are **haematite** (Fe_2O_3), **magnetite** (Fe_3O_4), **siderite** ($FeCO_3$) and **iron pyrites** (FeS_2). The outline of its extraction from its ore looks like



DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Among the following statement, the incorrect one is
(a) calamine and siderite are carbonates
(b) argentite and cuprite are oxides
(c) zinc blende and pyrites are sulphides
(d) malachite and azurite are ores of copper

2 Which ore contains both iron and copper?
(a) Cuprite (b) Chalcocite
(c) Chalcopyrite (d) Malachite

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

4 Which one of the following ores is best concentrated by froth floatation method? → JEE Main 2016
(a) Siderite (b) Galena
(c) Malachite (d) Magnetite

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

6 In the process of extraction of gold,

$$\text{Roasted gold ore} + CN^- + H_2O \xrightarrow{O_2} [X] + OH^-$$
$$[X] + Zn \longrightarrow [Y] + Au$$

Identify the complexes $[X]$ and $[Y]$.
(a) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_4]^{2-}$
(b) $X = [Au(CN)_4]^{3-}$, $Y = [Zn(CN)_4]^{2-}$
(c) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_6]^{4-}$
(d) $X = [Au(CN)_4]^-$, $Y = [Zn(CN)_4]^{2-}$

7 Extraction of gold and silver involves leaching the metal with CN^- ion. The metal is recovered by
(a) displacement of metal by some other metal from the complex ion
(b) roasting of metal complex
(c) calcination followed by roasting
(d) thermal decomposition of metal complex

8 The process of converting hydrated alumina into anhydrous alumina is called
(a) roasting
(b) smelting
(c) dressing
(d) calcination

9 Calcination is the process in which → Online JEE (Main) 2013
(a) removal of water takes place
(b) decomposition of carbonates takes place
(c) oxidation of sulphides takes place
(d) All of the above

10 Which one of the following reactions is an example of auto-reduction?
(a) $Fe_3O_4 + 4C \longrightarrow 3Fe + 4CO_2$
(b) $Cu_2O + C \longrightarrow 2Cu + CO$
(c) $Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$
(d) $Cu_2O + \frac{1}{2}Cu_2S \longrightarrow 3Cu + \frac{1}{2}SO_2$

11 The methods chiefly used for the extraction of lead and tin from their ores are respectively
(a) self reduction and carbon reduction
(b) self reduction and electrolytic reduction
(c) carbon reduction and self reduction
(d) cyanide process and carbon reduction

12 Which of the following metals is obtained by electrolytic reduction process?
(a) Fe (b) Cu (c) Ag (d) Al

13 Which of the following statements about the advantage of roasting of sulphide ore before reduction is not true?
(a) $\Delta_f G^\circ$ of the sulphide is greater than those of CS_2 and H_2S
(b) $\Delta_f G^\circ$ is negative for roasting of sulphide ore to oxide
(c) Roasting of sulphide to oxide is thermodynamically feasible
(d) Carbon and hydrogen are suitable reducing agents for metal sulphides

14 The value of $\Delta_f G^\circ$ for the formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1}. Is the reduction of Cr_2O_3 with Al is feasible reaction?
(a) The data is incomplete
(b) The reaction is feasible
(c) The reaction is not feasible
(d) The reaction may or may not be feasible

15 Use the relationship, $\Delta G^\circ = -nFE^\circ_{cell}$ to estimate the minimum voltage required to electrolyse Al_2O_3 in the Hall-Heroult process

$$\Delta_f G^\circ (Al_2O_3) = -1520 \text{ kJ mol}^{-1}$$
$$\Delta_f G^\circ (CO_2) = -394 \text{ kJ mol}^{-1}$$

(a) 0.8 V (b) 1.60 V (c) 2.8 V (d) 3.0 V

16 In Goldschmidt aluminothermic process which of the following reducing agent is used? → Online JEE (Main) 2013
(a) Calcium (b) Coke
(c) Al powder (d) Sodium

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

18 Zone-refining is based on the principle that

(a) impurities of low boiling metals can be separated by distillation
(b) impurities are more soluble in molten metal than in solid metal
(c) different components of a mixture are differently adsorbed on an adsorbent
(d) vapours of volatile compound can be decomposed into pure metal

19 Which method of purification is represented by the following equation?

$$Ti(s) + 2I_2(g) \xrightarrow{523\text{ K}}$$
$$TiI_4(g) \xrightarrow{1700\text{ K}} Ti(s) + 2I_2(g)$$

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

20 Which of the following does not represent correct method?

(a) $TiCl_2 + 2Mg \longrightarrow Ti + 2MgCl_2$: Kroll
(b) $Ni(CO)_2 \longrightarrow Ni + 4CO$: Mond
(c) $Ag_2CO_3 \longrightarrow 2Ag + CO_2 + \frac{1}{2}O_2$: van-Arkel
(d) $ZnI_4 \longrightarrow Zn + 2I_2$: van-Arkel

21 During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are

(a) Fe and Ni (b) Ag and Au
(c) Pb and Zn (d) Se and Ag

22 Refining of impure copper with zinc impurity is to be done by electrolysis using electrodes as

	Cathode	Anode
(a)	Pure copper	Pure zinc
(b)	Pure zinc	Pure copper
(c)	Pure copper	Impure copper
(d)	Pure zinc	Impure zinc

23 Which metal can't be obtained from electrolysis?

(a) Ca (b) Mg (c) Cr (d) Al

24 In the context of the Hall-Heroult process for the extraction of Al, which of the following statement is false?

➞ JEE Main 2015

(a) CO and CO_2 are produced in this process
(b) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity
(c) Al^{3+} is reduced at the cathode to form Al
(d) Na_3AlF_6 serves as the electrolyte

25 When copper ore is mixed with silica in a reverberatory furnace, copper matte is 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)

26 Extraction of zinc from zinc blende is achieved by

(a) electrolytic reduction
(b) roasting followed by reduction with carbon
(c) roasting followed by reduction with another metal
(d) roasting followed by self reduction

27 In blast furnace, maximum temperature is in

(a) zone of fusion
(b) zone of combustion
(c) zone of slag combustion
(d) zone of reduction

28 Which series of reactions correctly represents chemical relations related to iron and its compound?

➞ JEE Main 2014

(a) $Fe \xrightarrow{\text{Dil.}H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{Heat}} Fe$
(b) $Fe \xrightarrow{O_2,\text{Heat}} FeO \xrightarrow{\text{Dil.}H_2SO_4} FeSO_4 \xrightarrow{\text{Heat}} Fe$
(c) $Fe \xrightarrow{Cl_2,\text{Heat}} FeCl_3 \xrightarrow{\text{Heat, air}} FeCl_2 \xrightarrow{Zn} Fe$
(d) $Fe \xrightarrow{O_2,\text{Heat}} Fe_3O_4 \xrightarrow{CO,\ 600\ ^\circ C} FeO \xrightarrow{CO,\ 700\ ^\circ C} Fe$

29 Match the following and choose the correct options.

Column I	Column II
A. Blister Cu	1. Aluminium
B. Blast furnace	2. $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$
C. Reverberatory furnace	3. Iron
D. Hall-Heroult process	4. $FeO + SiO_2 \longrightarrow FeSiO_3$

Codes

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

Direction (Q. Nos. 30-33) *In the following questions assertion followed reason is given. Choose the correct answer out of the following choices.*

(a) Both A and R are true and R is correct explanation of A
(b) Both A and R are true but R is not correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

30 **Assertion** (A) Hydrometallurgy involves dissolving the ore in a suitable reagent followed by precipitation by a more electropositive metal.

Reason (R) Copper is extracted by hydrometallurgy.

31 **Assertion** (A) Nickel can be purified by Mond process.

Reason (R) $Ni(CO)_4$ is a volatile compound which decomposes at 460 K to give pure Ni.

32 **Assertion** (A) Zone refining method is very useful for producing semiconductors.

Reason (R) Semiconductors are of high purity.

33 **Assertion** (A) van-Arkel method is used to prepare ultra pure sample of some metals.

Reason (R) It involves reaction of CO with metals to form volatile carbonyls which decompose on heating to give pure metal.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 When 1.164 g of a certain metal sulphide was roasted in air, 0.972 g of the metal oxide was formed. If the oxidation number of the metal is +2, calculate the molar mass of the metal.

(a) 25.67 g (b) 31.56 g
(c) 47.35 g (d) 65 g

2 The major role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is

(a) that of a catalyst
(b) to make the fused mixture very conducting
(c) to lower the temperature of the melt
(d) to decrease the rate of oxidation of carbon at anode

3 From the Ellingham graph on carbon, which of the following statements is false?

(a) CO reduces Fe_2O_3 to Fe at temperature less than 983 K
(b) CO is less stable than CO_2 at temperature more than 983 K
(c) CO reduces Fe_2O_3 to Fe in the reduction zone of blast furnace.
(d) CO_2 is more stable than CO at temperature less than 983 K

4 In the electrolytic method for obtaining aluminium from purified bauxite, cryolite is added to

(a) minimise the heat loss due to radiation
(b) protect aluminium produced from oxygen
(c) dissolve bauxite and increases its conductivity
(d) lower the melting point of bauxite

5 Bauxite ore is made up of $Al_2O_3 + SiO_2 + TiO_2 + Fe_2O_3$. This ore is treated with conc. NaOH solution at 500 K and 35 bar pressure for few hours and filtered hot. In the filterate, the species present are

(a) $NaAl(OH)_4$ (b) $Na_2Ti(OH)_6$
(c) $Na[Al(OH)_4]$ and Na_2SiO_3 (d) Na_2SiO_3

6 Consider the following reactions:

$$Ag_2S + NaCN \longrightarrow (A)$$
$$(A) + Zn \longrightarrow (B)$$

(B) is a metal. Hence (A) and (B) are

(a) $[Na_2Zn(CN)_4]$, Zn (b) $Na[Ag(CN)_2]$, Ag
(c) $Na_2[Ag(CN)_4]$, Ag (d) $Na_3[Ag(CN)_4]$, Ag

7 When copper pyrites is roasted in excess of air, a mixture of CuO + FeO is formed. FeO is present as impurities. This can be removed as slag during reduction of CuO. The flux added to form slag is

(a) SiO_2, which is an acidic flux
(b) limestone, which is a basic flux
(c) SiO_2, which is a basic flux
(d) CaO, which is a basic flux

8 Free energies of formation ($\Delta_f G$) of MgO (s) and CO (g) at 1273 K and 2273 K are given below:

$\Delta_f G$ [MgO(s)] = –941 kJ / mol at 1273 K
$\Delta_f G$ [MgO(s)] = –314 kJ / mol at 2273 K
and $\Delta_r G = \Delta_f G$ (products) – $\Delta_f G$ (reactants)

$$\Delta_f G[CO(g)] - \Delta_f G[MgO(s)]$$
$$\Rightarrow (-439) - (-941) = +502 \text{ kJ mol}^{-1}$$
$$\Delta_f G[CO(g)] = -439 \text{ kJ/mol at 1273 K}$$
$$\Delta_f G[CO(g)] = -628 \text{ kJ/mol at 2273 K}$$

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for MgO(s).

(a) 2273
(b) 1273
(c) Both (a) and (b)
(d) None of the above

9 In the extraction of nickel by Mond's process, the metal is obtained by

(a) electrochemical reduction
(b) thermal decomposition
(c) chemical reduction by aluminium
(d) reduction by carbon

10. In the Baeyer's process,

(a) Al_2O_3 goes into solution as soluble $Al(OH)_4^-$, while other basic oxides as TiO_2 and Fe_2O_3 remain insoluble.
(b) Al_2O_3 changes to AlN which in turn decomposed by H_2O
(c) Al_2O_3 changes to $Al_2(CO_3)_3$ which changes to $AlCl_3$
(d) None of the above is correct

11 In the metallurgy of sodium by electrolysis, excess of calcium chloride is mixed with sodium chloride to

(a) make the latter a good conductor
(b) make the latter soft
(c) generate more energy for the electrolytic cell
(d) assist liquefaction of the later much lower temperature

12 Froth-floatation process is used for the concentration of sulphide ore. Which of the following processes is correct?

(a) It is based on the difference in wettability of different minerals
(b) In this process sodium ethyl xanthate, $C_2H_5OCS_2Na$ is used as collector
(c) In this process NaCN is used as depressant in the mixture of ZnS and PbS when ZnS forms soluble complex and PbS forms froth
(d) All of the above

13 An impure metal is allowed to react with carbon monoxide at 50°C and the volatile gas thus, formed is collected and heated further to about 200°C. This process gives the metal of 99.99% purely. What is the metal?

(a) Fe (b) Cr
(c) Co (d) Ni

14 Of the following reduction processes,

I. $Fe_2O_3 + 3C(s) \longrightarrow Fe + 3CO$
II. $ZnO + C(s) \longrightarrow Zn + CO$
III. $Ca_3(PO_4)_2 + C(s) \longrightarrow P$
IV. $PbO + C(s) \longrightarrow Pb + CO$

Correct processes are

(a) All of these (b) All but III
(c) All but IV (d) Both II and IV

ANSWERS

SESSION 1

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

SESSION 2

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

Hints and Explanations

SESSION 1

1 Argentite (Ag_2S) is a sulphide ore and cuprite (Cu_2O) is an oxide ore.

2 Cuprite — Cu_2O
Chalcocite — Cu_2S
Chalcopyrite — $CuFeS_2$
Malachite — $Cu(OH)_2 \cdot CuCO_3$

3 Cassiterite is tin oxide (SnO_2) which is non-magnetic and contains wolframite, $FeWO_4$ (magnetic) impurities. These are separated by electromagnetic separation.

4 Galena (PbS) is sulphide ore, hence concentrated by froth-floatation process.

5 $Al_2O_3 \cdot 2H_2O$ (bauxite) is concentrated by leaching with NaOH, Al_2O_3 dissolves while other impurities remains undissolved.

6
$$\underset{\text{From gold ore}}{Au} + 4CN^- + H_2O + \frac{1}{2}O_2 \longrightarrow \underset{(X)}{2[Au(CN)_2]^-} + 2OH^-$$
$$\underset{(X)}{2[Au(CN)_2]^-} + Zn \longrightarrow \underset{(Y)}{[Zn(CN)_4]^{2-}} + 2Au$$

7
$$2[Ag(CN)_2]^- + Zn \longrightarrow 2Ag + [Zn(CN)_4]^{2-}$$
$$2[Au(CN)_2]^- + Zn \longrightarrow 2Au + [Zn(CN)_4]^{2-}$$
Thus, the metal is recovered by displacement of metal by some other metal from the complex ion.

8 In calcination, moisture or hydrated water is removed on heating.
$$Al_2O_3 \cdot 2H_2O \longrightarrow Al_2O_3 + 2H_2O\uparrow$$

9 Calcination is a thermal treatment in the presence of air to ores and other solid materials to bring about a thermal decomposition, phase transition or removal of volatile fractions.
$$M_2CO_3 \xrightarrow{\Delta} M_2O + CO_2$$

10 Among the given options, example of auto-reduction is
$$Cu_2O + \frac{1}{2}Cu_2S \longrightarrow 3Cu + \frac{1}{2}SO_2$$

11 The process in which the anions associated with the metal help in the reduction is called self-reduction. It is mainly used in case of sulphide ores and the process of extracting a metal by fusion of the oxide ore with carbon is known as carbon reduction.

12 Metals like Na, K, Mg, Ca, Al etc. are reduced by electrolytic reduction.

13 Both C and H_2 are not suitable for reducing sulphide ore because $\Delta_f G^\circ$ of metal sulphide is more than that of CS_2 and H_2S which will be formed as a result of reduction.

14.
$$\frac{4}{3}Cr\,(s) + O_2(g) \longrightarrow \frac{2}{3}Cr_2O_3(s);$$
$$\Delta_f G^\circ = -540\,kJ\,mol^{-1} \quad ...(i)$$
$$\frac{4}{3}Al\,(s) + O_2(g) \longrightarrow \frac{2}{3}Al_2O_3(s);$$
$$\Delta_f G^\circ = -827\,kJ\,mol^{-1} \quad ...(ii)$$
Subtracting Eq. (ii) from Eq. (i)
$$\frac{2}{3}Cr_2O_3\,(s) + \frac{4}{3}Al\,(s) \longrightarrow \frac{2}{3}Al_2O_3(s) + \frac{4}{3}Cr\,(s),$$
$$\Delta_f G^\circ = -287\,kJ$$

Since, $\Delta G°$ comes out to be negative, the reaction is feasible.

15 $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$

$\Delta_f G° = 3\Delta G°(CO_2) - 2\Delta G°(Al_2O_3)$

$= 3 \times (-394) - 2 \times (-1520)$

$= 1858 kJ = 1858 \times 10^3 J$

$\therefore \ nFE° = 1858 \times 10^3$ (n = 12 electrons)

$$\therefore \quad E° = \frac{1858 \times 10^3}{12 \times 96500} = 1.60 \text{ V}$$

16 In Goldschmidt aluminothermic process, oxides of Cr, Fe etc., are treated with Al powder which reduces these oxides into crude metal. Thus, Al acts as reducing agent here.

$$Fe_2O_3 + \underset{\text{Reducing agent}}{2Al} \longrightarrow Al_2O_3 + 2Fe$$

17 Electrolytic refining is used to purify Cu and Zn.

18 Zone-refining is based upon the principle of fractional crystallisation. It is based on the fact that impurities are more soluble in the melt than in the pure metals.

19 van-Arkel process is based on the thermal decomposition of a volatile compound like an iodide, which is first formed by direct combination of metal to be purified and iodine. Metal formed is in purest form. Titanium and zirconium are purified by this method.

20 van-Arkel process is used for Zr or Ti, not for Ag.

21 During electrolysis, noble metals (inert metals) like Ag, Au and Pt are not affected and separate as anode mud from the impure anode.

22 In electrolytic refining of copper, impure copper acts as anode while pure copper acts as cathode. The impurities of iron, nickel, zinc and cobalt present in blister copper being more electropositive pass into solution as soluble sulphates.

23 Cr is less electropositive and can be obtained by the reduction of its oxide by aluminium.

24 (a) In Hall-Heroult process for extraction of Al, carbon anode is oxidised to CO and CO_2.

(b) When Al_2O_3 is mixed with CaF_2, it lowers the melting point of the mixture and brings conductivity.

(c) Al^{3+} is reduced at cathode to get Al.

(d) Here, Al_2O_3 is an electrolyte undergoing the redox process. Na_3AlF_6 although is an electrolyte but serves as a solvent, not electrolyte.

25 Copper matte consists of Cu_2S and FeS.

26 Extraction of Zn from ZnS is done by roasting ZnS and then treated with coke for reduction.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2 \uparrow$$

$$ZnO + C \xrightarrow{\Delta} Zn + CO \uparrow$$

27 In blast furnace, zone of combustion (1500-1600C°) has maximum temperature.

28 The correct reaction are as follows:

(a) $Fe + \text{dil. } H_2SO_4 \longrightarrow FeSO_4 + H_2$

$H_2SO_4 + 2FeSO_4 + \frac{1}{4}O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O$

$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3(s) + 3SO_3 \uparrow$

(b) $Fe \xrightarrow[\Delta]{O_2} FeO$

[It could also be Fe_2O_3 or Fe_3O_4]

$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$

$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

(c) $Fe \xrightarrow[Cl_2]{\Delta} FeCl_3 \xrightarrow[\text{Air}]{\Delta}$ No reaction

[It cannot give $FeCl_2$]

(d) $Fe \xrightarrow[\Delta]{O_2} Fe_3O_4 \xrightarrow[600° C]{CO} FeO \xrightarrow[700° C]{CO} Fe$

This is correct reaction.

29 A $\longrightarrow$ 2, B $\longrightarrow$ 3, C $\longrightarrow$ 4, D $\longrightarrow$ 1

30 Hydrometallurgy is used for the extraction of low grade copper, while pyrometallurgy is used for the extraction of bulk quantities of copper.

31 Nickel can be purified by Mond's process.

$$\underset{\text{Impure}}{Ni} + 4CO \xrightarrow{350-350\text{ K}} Ni(CO)_4 \xrightarrow{450-470\text{ K}} \underset{\text{Pure}}{Ni} + 4CO$$

32 **Correct explanation** In the zone refining method, the melt is allowed to crystallise. Since, impurities are more soluble in the melt than in the pure state of the metal therefore, semiconductor metals are obtained after repeated crystallisation.

33 van-Arkel method involve the use of I_2 to form volatile iodide of metals which on decomposition gives pure metal.

SESSION 2

1 Formula of sulphide is MS because oxidation number of metal ion being +2.

$$\underset{\substack{(M+32)\\1.164}}{MS} + \frac{3}{2}O_2 \longrightarrow \underset{\substack{(M+16)\\0.972}}{MO} + SO_2$$

$$\frac{M + 32}{1.164} = \frac{M + 16}{0.972}$$

or $\quad M = 65$ g

2 The major role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite is to lower the temperature of the melt.

3 The stability of carbon oxides is decided with the help of Ellingham diagram.

When carbon changes to CO_2, entropy (ΔS) is very small and ΔG hardly shows any change with increasing temperature but when carbon changes to CO, ΔS is positive and ΔG becomes more negative with increasing temperature. Below 983 K. temperature, formation of CO_2 is favoured whereas, above this temperature, formation of CO is preferred, CO is more stable than CO_2 at more than 983 K temperature.

4 Cryolite (Na_3AlF_6) is added to alumina (purified bauxite, i.e. Al_2O_3) for its electrolysis to decrease its melting point and also increase its conductivity.

5 The principal ore of aluminium is bauxite, ($Al_2O_3 \cdot 2H_2O$) usually contains SiO_2, iron oxides, titanium oxide (TiO_2) as impurities. Concentration of ore is carried out by treating the powdered ore with a concentrated solution of NaOH at 473-523 K and 35-36 bar pressure. Al_2O_3 is leached out as sodium aluminate and SiO_2 as sodium silicate leaving the impurities behind.

$$Al_2O_3 \cdot 2H_2O + 2NaOH + H_2O \longrightarrow \underset{\text{Sodium aluminate}}{2Na[Al(OH)_4]}$$

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O$$

Hence, the solution obtained after filtration contains sodium aluminate and sodium silicate.

6 $Ag_2S + NaCN \longrightarrow \underset{(A)}{Na[Ag(CN)_2]}$

$\underset{(A)}{Na[Ag(CN)_2]} + Zn \longrightarrow Na[Zn(CN)_2] + \underset{(B)}{Ag}$

7 The compounds which combine with impurities present in ore (at high temperature) and remove them as a fusible substance (slag), are known as flux. When basic impurities like FeO are present, an acidic flux like SiO_2 is used and *vice-versa*.

$$\underset{\text{Basic impurity}}{FeO} + \underset{\text{Acidic flux}}{SiO_2} \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

Thus, during reduction of CuO, SiO_2 being an acidic flux is added to remove FeO as $FeSiO_3$.

8 At 1273 K,

(i) $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$;

$\Delta_f G = -941 \text{ kJ mol}^{-1}$

(ii) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$;

$\Delta_f G = -439 \text{ kJ mol}^{-1}$

The redox equation for the reduction of MgO to Mg by C can be obtained by subtracting Eq (i) from Eq (ii). Thus,

$MgO(s) + C(s) \longrightarrow Mg(s) + CO(g)$,

$\Delta_f G = +502 \text{ kJ mol}^{-1}$

Since, $\Delta_r G$ of the above reduction reaction is +ve, the reduction of MgO by C is not feasible at 1273 K.

At 2273 K,

(iii) $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$;

$\Delta_f G = -314 \text{ kJ mol}^{-1}$

(iv) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$;

$\Delta_f G = -628 \text{ kJ mol}^{-1}$

Subtracting Eq. (iii) from Eq (iv), the redox equation is

$MgO(s) + C(s) \longrightarrow Mg(s) + CO(g)$;

$\Delta_r G = \Delta_f G \text{ (products)} - \Delta_f G \text{(reactants)}$

$= \Delta_f G[CO(g)] - \Delta_f G[MgO(s)]$

$= (-628) - (-314) = -314 \text{ kJ mol}^{-1}$

Since, $\Delta_r G$ for the above reaction is –ve, the reduction of MgO by carbon at 2273 K is feasible.

9 $\underset{\text{Impure}}{Ni} + 4CO \longrightarrow Ni(CO)_4$

$$Ni(CO)_4 \xrightarrow[\text{Thermal decomposition}]{\Delta} \underset{\text{Pure}}{Ni} + 4CO$$

(Mond's process)

10 In the Baeyer's process, Al_2O_3 goes into the solution as soluble $Al(OH_4)^-$, while that of basic oxides as TiO_2 and Fe_2O_3 remain insoluble.

11 In the metallurgy of sodium by electrolysis, excess of calcium chloride is mixed with NaCl to assist liquefaction of the later at much lower temperature.

12 All the given statements are correct.

13 Ni is the impure metal that react with CO at 50°C and the volatile gas formed is collected and heated to about 200°C.

14 All chemical processes are correct. In these reactions, metal oxide involves heating it with C (acts as reducing agent).