CHAPTER 15

General Principles and Processes of Isolation of Elements

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. Casseterite is ore of..... *(1980)*
2. In the thermite process ..... is used as reducing agent. *(1980)*
3. In the basic Bessemer process for the manufacture of steel the lining of the converter is made of..... . The slag formed consists of ..... *(1980)*
4. In extractive metallurgy of zinc partial fusion of ZnO with coke is called ..... and reduction of the ore to the molten metal is called ..... .
(smelting, calcining, roasting, sintering) *(1988 - 1 Mark)*

C MCQs with One Correct Answer

1. Copper can be extracted from *(1978)*
   (a) Kupfernical
   (b) Dolomite
   (c) Malachite
   (d) Galena
2. In the alumino-thermite process, aluminium acts as *(1983 - 1 Mark)*
   (a) an oxidizing agent
   (b) a flux
   (c) a reducing agent
   (d) a solder
3. The chemical composition of 'slag' formed during the smelting process in the extraction of copper is *(2001S)*
   (a) $Cu_2O + FeS$
   (b) $FeSiO_3$
   (c) $CuFeS_2$
   (d) $Cu_2S + FeO$
4. Which of the following process is used in the extractive metallurgy of magnesium? *(2002S)*
   (a) fused salt electrolysis
   (b) self reduction
   (c) aqueous solution electrolysis
   (d) thermite reduction
5. Which ore contains both iron and copper? *(2005S)*
   (a) Cuprite
   (b) Chalcocite
   (c) Chalcopyrite
   (d) Malachite
6. Extraction of zinc from zinc blende is achieved by
   (a) electrolytic reduction *(2007)*
   (b) roasting followed by reduction with carbon
   (c) roasting followed by reduction with another metal
   (d) roasting followed by self-reduction
7. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are *(2011)*
   (a) II, III in haematite and III in magnetite
   (b) II, III in haematite and II in magnetite
   (c) II in haematite and II, III in magnetite
   (d) III in haematite and II, III in magnetite
8. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are
   (a) O_2 and CO respectively *(2012)*
   (b) O_2 and Zn dust respectively
   (c) HNO_3 and Zn dust respectively
   (d) HNO_3 and CO respectively
9. Sulfide ores are common for the metals *(JEE Adv. 2013)*
   (a) Ag, Cu and Pb
   (b) Ag, Mg and Pb
   (c) Ag, Cu and Sn
   (d) Al, Cu and Pb

D MCQs with One or More Than One Correct

1. Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are :
   (a) Ag (b) Mg *(1990 - 1 Mark)*
   (c) Cu (d) Al
   (e) Cr.

2. Extraction of metal from the ore **cassiterite** involves *(2011)*
   (a) carbon reduction of an oxide ore
   (b) self-reduction of a sulphide ore
   (c) removal of copper impurity
   (d) removal of iron impurity

3. The carbon-based reduction method is **NOT** used for the extraction of *(JEE Adv. 2013)*
   (a) Tin from SnO_2
   (b) Iron from Fe_2O_3
   (c) Aluminium from Al_2O_3
   (d) Magnesium from $MgCO_3.CaCO_3$

4. Upon heating with Cu_2S, the reagent(s) that give copper metal is/are *(JEE Adv. 2014)*
   (a) $CuFeS_2$
   (b) CuO
   (c) Cu_2O
   (d) $CuSO_4$

5. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is(are) *(JEE Adv. 2015)*
   (a) Impure Cu strip is used as cathode
   (b) Acidified aqueous $CuSO_4$ is used as electrolyte
   (c) Pure Cu deposits at cathode
   (d) Impurities settle as anode-mud

6. Extraction of copper from copper pyrite ($CuFeS_2$) involves *(JEE Adv. 2016)*
   (a) crushing followed by concentration of the ore by froth-flotation
   (b) removal of iron as slag
   (c) self-reduction step to produce 'blister copper' following evolution of SO_2
   (d) refining of 'blister copper' by carbon reduction

E Subjective Problems

1. (a) Write the chemical equations involved in the extraction of lead from galena by self reduction process.
   (b) Match the following extraction processes with the appropriate metals listed below :

(i)	Silver	(A)	Fused salt electrolysis
(ii)	Calcium	(B)	Carbon reduction
(iii)	Zinc	(C)	Carbon monoxide reduction
(iv)	Iron	(D)	Amalgamation
(v)	Copper	(E)	Self reduction *(1979)*

2. Write the matching pairs: *(1980)*

Bleaching agent	Aluminium
Smelling salt	Carbon
Cryolite	Tin
Bell metal	Ammonium carbonate
Fluorspar	Ammonium phosphate
Fertilizer	Calcium
Anthracite	Chlorine

Examples :

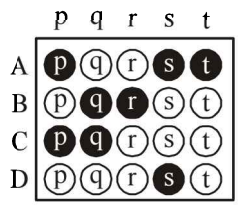
Bleaching agent
Chlorine
Smelling salt
Ammonium carbonate

3. Give reasons for the following :
   (*i*) Metals can be recovered from their ores by chemical methods. *(1984 - 1 Mark)*
   (*ii*) High purity metals can be obtained by zone refining method. *(1984 - 1 Mark)*
   (*iii*) Why is chalcocite roasted and not calcinated during recovery of copper? *(1987 - 1 Mark)*

4. Give the equations for the recovery of lead from Galena by air reduction. *(1987 - 1 Mark)*

F Match the Following

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :
If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.



1. Match the extraction processes listed in **Column I** with metals listed in **Column II** : *(2006 - 6M)*

Column I	*Column II*
(A) Self reduction	(p) Lead
(B) Carbon reduction	(q) Silver
(C) Complex formation and displacement by metal	(r) Copper
(D) Decomposition of iodide	(s) Boron

2. Match the conversions in **Column I** with the type(s) of reaction(s) given in **Column II**. *(2008 - 6M)*

Column I	*Column II*
(A) $PbS \rightarrow PbO$	(p) roasting
(B) $CaCO_3 \rightarrow CaO$	(q) calcination
(C) $ZnS \rightarrow Zn$	(r) carbon reduction
(D) $Cu_2S \rightarrow Cu$	(s) self reduction

3. Match the anionic species given in Column-I that are present in the ore(s) given in Column-II. *(JEE Adv. 2015)*

Column-I	**Column-II**
(A) Carbonate	(p) Siderite
(B) Sulphide	(q) Malachite
(C) Hydroxide	(r) Bauxite
(D) Oxide	(s) Calamine
	(t) Argentite

Section-B JEE Main / AIEEE

1. Aluminium is extracted by the electrolysis of **[2002]**
   (a) bauxite
   (b) alumina
   (c) alumina mixed with molten cryolite
   (d) molten cryolite.

2. The metal extracted by leaching with a cyanide is **[2002]**
   (a) Mg
   (b) Ag
   (c) Cu
   (d) Na.

3. Which one of the following ores is best concentrated by froth-flotation method ? **[2004]**
   (a) Galena
   (b) Cassiterite
   (c) Magnetite
   (d) Malachite

4. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are **[2005]**
   (a) Fe and Ni
   (b) Ag and Au
   (c) Pb and Zn
   (d) Sn and Ag

5. Which of the following factors is of ***no significance*** for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly? **[2008]**
   (a) Metal sulphides are thermodynamically more stable than CS_2
   (b) CO_2 is thermodynamically more stable than CS_2
   (c) Metal sulphides are less stable than the corresponding oxides
   (d) CO_2 is more volatile than CS_2

6. 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is **[2010]**
   (a) 59.0
   (b) 47.4
   (c) 23.7
   (d) 29.5

7. Which method of purification is represented by the following equation ? **[2012]**

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

   (a) Zone refining
   (b) Cupellation
   (c) Polling
   (d) Van Arkel

8. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is: **[JEE M 2014]**

(a) Ag

(b) Ca

(c) Cu

(d) Cr

9. In the context of the Hall - Heroult process for the extraction of Al, which of the following statements is **false** ? **[JEE M 2015]**

(a) Al^{3+} is reduced at the cathode to form Al

(b) Na_3AlF_6 serves as the electrolyte

(c) CO and CO_2 are produced in this process

(d) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivit112y

10. Which one of the following ores is best concentrated by froth floatation method? **[JEE M 2016]**

(a) Galena (b) Malachite

(c) Magnetite (d) Siderite

15 General Principles and Processes of Isolation of Elements

Section-A : JEE Advanced/ IIT-JEE

A **1.** Tin **2.** Aluminium **3.** Magnesia and lime; Calcium silicate **4.** sintering, smelting

C **1.** (c) **2.** (c) **3.** (b) **4.** (a) **5.** (c) **6.** (b)
7. (d) **8.** (b) **9.** (a)

D **1.** (b, d) **2.** (a, c, d) **3.** (c, d) **4.** (b,c,d) **5.** (b,c,d) **6.** (a, b, c)

F **1.** (A)- p, r; (B) - p, r; (C) - q; (D) - s **2.** (A) - p; (B) - q; (C) - p, r; (D) - p, s
3. (A)- p,q,s, (B)- t, (C)- q, r, (D)- r

Section-B : JEE Main/ AIEEE

1. (c) **2.** (b) **3.** (c) **4.** (b) **5.** (c) **6.** (c) **7.** (d) **8.** (b)
9. (b) **10.** (a)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **Tin.** It is SnO_2. [The formula of Casseterite ore in SnO_2

2. **Aluminium**

$$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe + Heat$$

[Thermite reaction]

3. **Magnesia and lime; calcium silicate**

NOTE : The lining of converter is made of magnesia & lime. Slag formed consists of $CaSiO_3$.

4. **sintering, smelting.**

C. MCQs with One Correct Answer

1. **(c)** Malachite is $CuCO_3$. $Cu(OH)_2$ it is ore of copper.

2. **(c)** Al reduces Fe_2O_3 or Cr_2O_3 to respective metals and acts as a reducing agent.
$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2\,Fe$

3. **(b)** **NOTE :** During the extraction of copper, iron is present in the ore as impurity (FeS).
The ore together with a little coke and silica is smelted; FeS present as impurity in the ore is oxidized to iron oxide, which then reacts with silica to form fusible ferrous silicate which is removed as slag.

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

$$FeO + SiO_2 \longrightarrow \underset{(Slag)}{FeSiO_3}$$

4. **(a)** $\underset{(fused\ anhydrous)}{MgCl_2} \rightarrow Mg^{+2} + 2Cl^-$

At cathode : $Mg^{+2} + 2e^- \rightarrow Mg;$

At anode : $2Cl^- - 2e^- \rightarrow Cl_2\uparrow$

5. **(c)** Cuprite : Cu_2O; Chalcocite : Cu_2S; Chalcopyrite : $CuFeS_2$; Malachite: $Cu(OH)_2.CuCO_3$. We see that $CuFeS_2$ contais both Cu and Fe.

6. **(b)** **NOTE :** Extraction of Zn from ZnS (Zinc blende) is achieved by roasting followed by reduction with carbon.
$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
$ZnO + C \longrightarrow Zn + CO$

7. **(d)** (i) Haematite is Fe_2O_3 in which Fe is present in III oxidation state.
(ii) Magnetite (Fe_4O_3) is an equimolar mixture of FeO and Fe_2O_3.
Oxidation state of Fe in FeO is II.
Oxidation state of Fe in Fe_2O_3 is III.

8. **(b)** The reactions involved in cyanide extraction process are :

$$\underset{(argentite)}{Ag_2S} + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$$

$$4Na_2S + \underset{Oxiding\ agent}{5O_2} + 2H_2O \rightarrow 2Na_2SO_4 + 4NaOH + 2S$$

$$2Na[Ag(CN)_2] + \underset{(reducing\ agent)}{Zn} \rightarrow Na_2[Zn(CN)_4] + 2\,Ag\downarrow$$

9. **(a)** Silver, copper and lead are commonly found in earth's crust as Ag_2S (silver glance), $CuFeS_2$ (copper pyrites) and PbS (galena)

D. MCQs with One or More Than One Correct

1. **(b, d)** Both Mg and Al have their reduction potentials less than that of water [$E^\circ = -0.83$ V]. Hence, their ions in the aqueous solution can not be reduced. Instead water will be reduced : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

2. **(a, c, d)**

3. **(c, d)** Al from Al_2O_3 and Mg from $MgCO_3.CaCO_3$ are separately extracted by electrolytic reduction.

4. **(b, c, d)** $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

$Cu_2S + 2CuO \rightarrow 4Cu + SO_2$

$Cu_2S + CuSO_4 \rightarrow 3Cu + 2SO_2$

5. **(b, c, d)** In electrolytic refining of blister Cu, acidified $CuSO_4$ is used as electrolyte, pure Cu deposits at cathode and impurities settle as anode mud.

6. **(a, b, c)**

Copper pyrite [$CuFeS_2$]

↓ Crushing into fine powder

Concentrated by froth floatation process

↓

Roasting take place in reverberatory furnace

$$\begin{cases} 2CuFeS_2 + O_2 \xrightarrow[\text{(air)}]{\Delta} Cu_2S + 2FeS + SO_2 \\ FeS + O_2 \xrightarrow{\Delta} FeO + SO_2 \end{cases}$$

↓ Smelting [Iron is removed as slag of $FeSiO_3$; $FeO + SiO_2$ (flux) $\xrightarrow{\Delta} FeSiO_3(\ell)$(slag)]

Copper matte ($Cu_2S + FeS$)

↓ Self reduction [Self reduction occurs in Bessemer converter; $2Cu_2S + 3O_2 \longrightarrow 2Cu_2S + 2SO_2(\uparrow)$; $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2(\uparrow)$]

(Blister copper)

↓

Refining of blister copper is done by poling followed by electrorefining but not by carbon reduction method.

E. Subjective Problems

1. **(a)** Galena is roasted in excess of air in a reverberatory furnace

$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$ (air)

$PbS + 2O_2 \longrightarrow PbSO_4$

It is followed by self reduction

$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$

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

(b) (i) Silver ⟶ (D) Amalgamation

(ii) Calcium ⟶ (A) Fused salt electrolysis

(iii) Zinc ⟶ (B) Carbon reduction

(iv) Iron ⟶ (C) Carbon monoxide reduction

(v) Copper ⟶ (E) Self reduction

2. Bleaching agent ⟶ Chlorine

Smelling salt ⟶ Ammonium carbonate

Cryolite ⟶ Aluminium

Bell metal ⟶ Tin

Fluorspar ⟶ Calcium

Fertilizer ⟶ Ammonium phosphate

Anthracite ⟶ Carbon

3. (*i*) because they occur as oxides, carbonates, sulphides which have to be calcined or roasted.

(*ii*) **NOTE :** *Zone refining* is based on the difference in solubility of impurities in molten and solid state of the metal. This method is used for obtaining metals of very high purity.

Ge, Si and Ga used as semi-conductors are refined in this manner. These metals can be easily melted and can easily crystallise out from the melt form.

(*iii*) Excess of Air (used during roasting) is necessary for converting chalcocite (a sulphide ore) to oxide. Calcination does not convert it to oxide.

4. **Recovery of Pb from galena :**

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

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

F. Match the Following

1. **(A)- p, r; (B) - p, r; (C) - q; (D) - s**

NOTE : The oxides and sulphides of less active metals like Hg, Cu & Pb are unstable to heat and hence no reducing agent is required. They undergo self reduction.

(A) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$;

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

(B) $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$;

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

Hence (A) → (p), (r)

NOTE : The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu, etc. are reduced by strongly heating them with coke or coal.

$PbO + C \longrightarrow Pb + CO_2$;

$2Cu_2O + C \longrightarrow 4Cu + CO_2$

Hence (B) → (p), (r)

Extraction from argentite (Ag_2S)

$Ag_2S + 2NaCN \rightleftharpoons Na_2S + 2AgCN;$

$AgCN + NaCN \longrightarrow \underset{\text{Sod. argentocyanide soluble}}{Na[Ag(CN)_2]}$

Zn, being more electropositive than Ag, displaces Ag from the complex.

$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$

Hence (C) → (q)

Among the halides of boron, BI_3 is unstable because of the large size of Iodine and small size of boron atom. Hence it decomposes to give boron. Thus, (D) → (s).

2. **(A) - p; (B) - q; (C) - p, r; (D) - p, s**
3. **A-(p, q, s), B-(t), C-(q, r), D-(r)**

Siderite → $FeCO_3$
Malachite → $CuCO_3 \cdot Cu(OH)_2$
Bauxite → $Al_2O_3.xH_2O$ or $AlO_x(OH)_{3-2x}\ 0 < x < 1$
Calamine → $ZnCO_3$
Argentite → Ag_2S

Section-B JEE Main/ AIEEE

1. **(c)** Pure aluminium can be obtained by electrolysis of a mixture containing alumina, crayolite and fluorspar in the ratio 20 : 24 : 20. The fusion temperature of this mixture is 900°C and it is a good conductor of electricity.
2. **(b)** Silver ore forms a soluble complex with NaCN from which silver is precipitated using scrap zinc.

$$Ag_2S + 2NaCN \rightarrow Na[Ag(CN)_2] \xrightarrow{Zn} \underset{\substack{\text{sodargento-cynanide}\\(\text{soluble})}}{Na_2[Zn(CN)_4] + Ag \downarrow}$$

3. **(c)** **NOTE :** Galena is PbS and thus purified by froth floatation method.
Froath floatation method is used to concentrate sulphide ores. This method is based on the preferential wetting properties with the froathing agent and water.
4. **(b)** During the process of electrolytic refining Ag and Au are obtained as anode mud.
5. **(c)** **NOTE :** The reduction of metal sulphides by carbon reduction process is not spontaneous because ΔG for such a process is positive. The reduction of metal oxide by carbon reduction process is spontaneous as ΔG for such a process is negative.
From this we find that on thermodynamic considerations CO_2 is more stable than CS_2 and the metal sulphides are more stable than corresponding oxides.
In view of above the factor listed in choice (c) is incorrect and so is of no significance.
Hence the correct answer is (c)
6. **(c)** Moles of HCl taken = $20 \times 0.1 \times 10^{-3} = 2 \times 10^{-3}$
Moles of HCl neutralised by NaOH solution
$= 15 \times 0.1 \times 10^{-3} = 1.5 \times 10^{-3}$
Moles of HCl neutralised by ammonia
$= 2 \times 10^{-3} - 1.5 \times 10^{-3}$
$= 0.5 \times 10^{-3}$

$$\% \text{ of nitrogen} = \frac{1.4 \times N \times V}{\text{w.t. of Substance}} \times 100$$

$$= \frac{1.4 \times 0.5 \times 10^{-3}}{29.5 \times 10^{-3}} \times 100 = 23.7\%$$

7. **(d)** Van Arkel is a method in which heat treatment is used to purify metal in this process metals are converted into other metal compound for loosly coupled like as iodine to make metal iodide which are easily decomposed and give pure metal.
The process is known as Van Arkel method.
8. **(b)** On electrolysis of aqueous solution of *s*-block elements H_2 gas discharge at cathode.

$$\text{At cathode: } H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$$

9. **(b)** In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mix and brings conductivity.
10. **(a)** Froth floatation method is mainly applicable for sulphide ores.
(1) Malachite ore : $Cu(OH)_2 . CuCO_3$
(2) Magnetite ore : Fe_3O_4
(3) Siderite ore : $FeCO_3$
(4) Galena ore : PbS (Sulphide Ore)