HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

2. **(A)** Tin-cassiterite (SnO_2)
(B) Zinc - calamine ($ZnCO_3$)
(C) Iron - siderite ($FeCO_3$)
(D) Lead - Cerussite ($PbCO_3$)
Therefore, **(B)** option is correct.

3. Sulphide ore is roasted in presence of excess of air or O_2 below its melting point to convert into the oxide and to remove the impurities of S, P, Sb etc., as their volatile oxides. In some cases roasting of certain sulphide ores provide directly the metals.

5. **(A)** $AlO_x(OH)_{3-2x}$ [Where $0 < x < 1$] **(B)** Al_2O_3
(C) $K_2Mg_2(SO_4)_3$ (D) $[Al_2(OH)_4Si_2O_5]$
Therefore, **(C)** option is correct.

9. $ZnS + 4NaCN \rightarrow Na_2[Zn(CN)_4] + Na_2S$
$PbS + NaCN \rightarrow$ No such complex formation.

10. Sodium and Aluminium reacts with water so often extracted from their fuses salts.

12. **(A)** When the oxide undergoes a phase change, there will be an increase in the entropy of the oxide.
(B) It is true statements, $HgO \xrightarrow{\Delta} Hg + 1/2O_2$
(C) For a reduction process the change in the free energy, ΔG^0 must be negative and to make ΔG^0 negative temperature should be high enough so that $T\Delta S^0 > \Delta H^0$.

14. **(A)** $\frac{\Delta G}{T} = -\Delta S$, $\frac{\Delta G}{T}$ is slope in Ellingham diagram.
Which is same below the boiling point.
(B) Below the boiling point slope is same as factor $T\Delta S$ is same.
(C) Above $\Delta G = 0$ line free energy becomes positive so oxide decomposes.
(D) Random increases i.e. ΔS increases, so slope also increases.

16. As PbS on self reduction with PbO and $PbSO_4$ gives metallic lead.

17. Sulphide ore of Hg, Cu, Pb are heated in air, a part of these is changed in to oxides or sulphate that then react with the remaining part of the sulphide ore to give its metal and SO_2. This is called self reduction, auto reduction or air reduction method.

19. Matte is obtained in blast furnace and that contains mostly Cu_2S and FeS. It is transferred to bessemer converter where self reduction takes place according to the following reactions.
$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$;
$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$.

20. The solidified copper obtained after bessemerisation is impure and contains Fe, Ni, Zn, Ag, Au etc., as impurity. It has blistered like appearance due to the evolution of SO_2 and so it is called blister copper.

22. **(A)** true **(C)** small amount of Mn is added to molten steel to remove sulphur and oxygen.

23. $Na_3[AlF_6] \longrightarrow 3NaF + AlF_3$
NaF and AlF_3 both are ionic compounds and so ionise to give ions. This increases the electrical conductivity and lowers the melting point of Al_2O_3.
At cathode : $Al^{3+}(melt) + 3e^- \longrightarrow Al$.
At anode : $C(s) + O^{2-}(melt) \longrightarrow CO(g) + 2e^-$;
$C(s) + 2O^{2-}(melt) \longrightarrow CO_2(g) + 4e^-$.

25. Cyanide process used for Au and Ag complexes formed in this, are : $Na[Au(CN)_2]$, $Na[Ag(CN)_2]$, $Na_2[Zn(CN)_4]$.

26. It is obtained by electrolytic reduction of molten anhydrous $KCl.MgCl_2$ (other methods are not economical/ feasible for the extraction of Mg metal).

28. Aluminium is extracted by electrolytic reduction of mixture of molten $Al_2O_3 + Na_3AlF_6 + CaF_2$.
Due to very high energy of dissociation of Al_2O_3, the reduction at such high temperature will give carbide in place of metallic Al according to the following reaction.
$2Al_2O_3 + 6C \xrightarrow{\Delta} Al_4C_3 + 3CO_2$.

29. Anode mud obtained in electrolytic refining of lead contains, Sb, Cu, Ag and Au.
Therefore, **(C)** option is correct.

31. Molten silver preferentially dissolves in molten zinc forming silver-zinc alloy - Which is lighter and has higher melting point. Therefore, (D) option is correct.

33. The Hooper process is a process for the electrolytic refining of aluminium. Impure Al forms the anode and pure Al forms the cathode of the Hooper's cell which contains three liquid layers. The bottom layer is molten impure Al, the middle is a fused salt layer containing sodium fluoride, aluminum fluoride and barium fluoride, and the top layer is pure Al. At the anode (bottom layer), Al passes with solution as aluminium ion (Al^{3+}), and at the cathode (top layer), these ions are reduced to the pure metal. In operation, molten metal is added to the bottom of the cell and pure aluminium is drawn off the top.

At anode : $Al \longrightarrow Al^{3+} + 3e^-$

At cathode : $Al^{3+} + 3e^- \longrightarrow Al.$

36. It is not called van Arkel method. Van Arkel method is used for the purification of Zr and Ti. Reaction **(C)** is simple thermal decomposition of Ag_2CO_3.

37. Gold is not attacked by sulphuric acid, nitric acid and Cl_2 use to separate it from borax so, parting of gold can be done with these.

39. Al_2O_3 (bauxite) + 2NaOH (aq) + H_2O (l) $\xrightarrow{\text{leaching}}$ $2Na[Al(OH)_4]$ (aq).

41. In smelting the concentrated oxide ores like haematite, tin stone even after concentration, is heated with flux to remove the acidic or basic impurities forming the slag. All other processes are used for removing the earthy/silicious impurities.

42. Carnallite is the important ore of aluminium and it has chemical composition $KCl.MgCl_2.6H_2O$.

44. It is used to separate haematite ore as it is attracted by electromagnet.

46. Potassium or sodium ethyl xanthate get attached with the particle of the sulphide ore and thus make them water repellant i.e. hydrophobic.

47. Ore is heated below its melting point in a reverberatory furnace in the presence of air to convert it into its oxides. It removes easily oxidisable volatile impurities like arsenic as As_2O_3, antimony as Sb_2O_3 and sulphur as SO_2. Roasting is an exothermic process; once started it does not require additional heating.

49. A hydrometallurgical process for the extraction of metals from ores, concentrates, or secondary materials essentially contains three basic steps—dissolution of the valuable metal in the aqueous solution (leaching) purification of leach solution and subsequent recovery of metal from the purified solutions either by electrolysis or by adding some electropositive metal to it.

50. $CaO + SiO_2 \longrightarrow CaSiO_3$ (slag) (Haematite ore contains silica as impurities).

Slag being lighter and insoluble in molten metal floats over and thus forms upper layer.

52. The Gibb's free energy of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. Therefore, the $\Delta_f G^0$ of M_xS is not compensated. So reduction of M_xS is difficult. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

55. (X) Red bauxite contains the impurities of oxides of iron and silicates. In Bayer process, alumina is dissolved by reacting sodium hydroxide solution leaving behind the insoluble oxide of iron.

(Y) White bauxite contains the impurity of silica which is removed by Serpeck's method.

$Al_2O_3 + N_2 + 3C \xrightarrow{1800°C} 2AlN + 3CO$;

$SiO_2 + 2C \xrightarrow{1800°C} Si\uparrow + 2CO\uparrow$

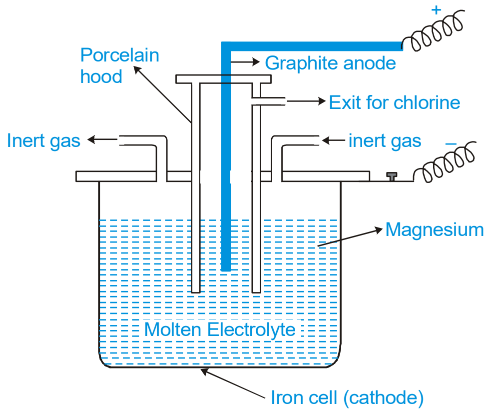
$AlN + 3H_2O \longrightarrow Al(OH)_3\downarrow + NH_3$;

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O.$

56. $MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$

At cathode : $Mg^{2+} + 2e^- \longrightarrow Mg$ (99% pure) ;

At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$



60. Na_3AlF_6 or $3NaF.AlF_3$

$NaF \underset{\text{compound}}{\overset{\text{Ionic}}{\rightleftharpoons}} Na^+ + F^-$; $AlF_3 \underset{\text{compound}}{\overset{\text{Ionic}}{\rightleftharpoons}} Al^{3+} + 3F^-$

62. **(A)** Cupellation is used when lead is present in traces.

(B) In argentiferous lead the silver is removed by Parkes process because silver has higher solubility in molten zinc than lead.

(C) Silver has higher solubility in molten zinc than lead and thus forms zinc-silver alloy from which zinc can be distilled off leaving behind the silver.

(D) Silver has higher solubility in molten zinc and thus forms zinc-silver alloy from which zinc can be distilled off leaving behind the silver.

63. Zr (impure) $+ 2I_2 \xrightarrow{<1800°C} ZrI_4$;

$ZrI_4 \xrightarrow{>1800\ K}$ Zr (pure) $+ 2I_2$ and hence over 1800ºC practically no reaction can take place between Zr and I_2. Therefore, (D) option is correct.

64. This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb); copper pyrites $CuFeS_2$ (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wet ability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.

65. An ore of tin containing $FeCr_2O_4$ is concentrated by magnetic separation as $FeCr_2O_4$ is ferromagnetic.

66. Roasting is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point. During roasting impurities of As, Sb, P and S escape as their volatile oxides.

$$S\,(s) + O_2\,(g) \longrightarrow SO_2\,(g)$$

67. The rocky and silicious impurities associated with an ore is called matrix or gangue.

68. Lighter gangue particles are washed in a current of water by a process called levigation. In levigation the powdered ore is agitated with water or washed with a upward stream of running water, the lighter particles of sand , clay etc. are washed away leaving behind heavier ore particles.

69. Hydraulic washing or Gravity separation or Levigation method is based on the difference in the densities of the gangue and ore particles.

70. Roasting removes easily oxidisable volatile impurities like arsenic (as As_2O_3) sulphur (as SO_2), phosphorus (as P_4O_{10}) and antimony (as Sb_2O_3).

$$4M\,(M = As, Sb) + 3O_2 \longrightarrow 2M_2O_3\uparrow$$

$$S + O_2 \longrightarrow SO_2\uparrow\ ;\ P_4 + 4O_2 \longrightarrow P_4O_{10}\uparrow$$

Organic matter, moisture if present in the ore, also get expelled and the ore becomes porous.

71. Generally the sulphides of Zn, Pb, Fe, Cu etc. are subjected to roasting to convert in to their oxides prior to reduction by carbon.

72. In many extraction processes, an oxide is added deliberately to combine with other impurities and form a stable molten phase immiscible with molten metal called a slag. The principle of slag formation is essentially the following.

Nonmetal oxide (acidic oxide) + Metal oxide (basic oxide) $\longrightarrow$ Fusible (easily melted) slag.

73. Electrolytic reduction method is used in the extraction of highly electropositive elements as they themselves are stronger reducing agents. They lie above hydrogen in electrochemical series. The heat of formation of Al_2O_3 is very high and therefore, at higher temperature there will be the possibility of formation of Al_4C_3 with carbon.

74. **(A)** $Cu_2O + C \xrightarrow{\Delta} 2Cu + CO$;

$SnO_2 + 2C$ (anthracite) $\xrightarrow{1800°C} Sn + 2CO$.

(B) $2Fe_2O_3 + 3C \longrightarrow 4Fe$ (spongy iron) $+ 3CO_2$;

$ZnO + C \xrightarrow{1200°C} Zn + CO$.

(C) Oxides of highly reactive metals (like K_2O) are not reduced by carbon. K lie above hydrogen in electrochemical series and so it acts as strong reducing agent. K is obtained by electrolytic reduction of their fused salts.

(D) $FeO + C \longrightarrow Fe + CO$; $PbO + C \longrightarrow Pb + CO$

75. A hydrometallurgical process for the extraction of metals from ores, concentrates, or secondary materials essentially contains three basic steps—dissolution of the valuable metal in the aqueous solution (leaching) purification of leach solution and subsequent recovery of metal from the purified solutions either by electrolysis or by adding some electropositive metal to it.

76. Acidic flux is used. It is an acidic oxide (oxide of a non-metal) like SiO_2, P_2O_5, B_2O_3 (from borax). It is used to remove the basic impurity like CaO, FeO, MgO etc. The acidic flux combines with the basic impurity and forms a slag.

77. **(A)** Calamine is $ZnCO_3$ and siderite is $FeCO_3$.

(B) Argentite is Ag_2S while cuprite is Cu_2O.

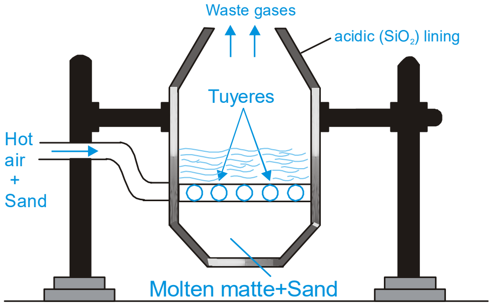
(C) Zinc blende is ZnS and iron pyrites is FeS_2.

(D) Malachite is $CuCO_3$ $Cu(OH)_2$ and azurite is $2CuCO_3$ $Cu(OH)_2$.

78. Electrolytic reduction method is used in the extraction of highly electropositive elements as they themselves are stronger reducing agents. They lie above hydrogen in electrochemical series.

79. Cryolite is Na_3AlF_6 and is used in the electrolysis of alumina. It reduces the melting point of alumina and increase the electrical conductivity of electrolyte.

80.



Bessemer convertor

Reactions involved :

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

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

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

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2 \text{ (self reduction)}$$

81. In actual process the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags off' as iron silicate and copper is produced in the form of copper matte which contains mostly Cu_2S and some FeS.

82. This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not, i.e., the impurities are infusible. This process is used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy, which is obtained at the end of Parkes process and contains Pb as impurity.

83. Conversion of a carbonate into oxide is an example of calcination

$$MgCO_3 \xrightarrow[\text{Absence of air}]{\Delta} MgO + CO_2 \uparrow .$$

84. (I) $$4Au/Ag(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \longrightarrow 4[Au/Ag(CN)_2]^-(aq) + 4OH^-(aq)$$

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

(II) This method is based on the fact that gangue and ore particles have different degree of wet ability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.

(III) Electrolytic reduction (Hall-Heroult process) :

The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar)) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed. The electrolytic reactions are:

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

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

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

(IV) This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.

85. $$Ti\text{ (impure)} + 2I_2(g) \xrightarrow{50\text{-}250°C} TiI_4(g) \xrightarrow[\text{Tungsten filament}]{1400°C} Ti\text{ (pure)} + 2I_2(g)$$

86. This process is used for the purification of copper and tin to remove the impurities of their oxides.

Green wood $\rightarrow$ Hydrocarbons $\rightarrow CH_4$;

$4CuO + CH_4 \rightarrow 4Cu\text{ (pure metal)} + CO_2 + 2H_2O$

Green wood $\rightarrow$ Hydrocarbon $\rightarrow CH_4$;

$2SnO_2 + CH_4 \rightarrow 2Sn + CO_2 + 2H_2O$

87. This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.

88. **(a)** Limonite is $Fe_2O_3.3H_2O$.

(b) Argentite is Ag_2S.

(c) Carnallite is $KCl.MgCl_2.6H_2O$.

(d) Calamine is $ZnCO_3$.

89. **(a)** Bauxite is leached with NaOH (concentrated) to form soluble $Na[Al(OH)_4]$ complex and insoluble impurities are filtered off.

(b) Carbonate and hydroxide ores are heated in absence of air below their melting point to convert in to their oxides in reverberatory furnace. This is called calcination. So siderite, $FeCO_3$ is subjected to calcination.

(c) This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb) ; copper pyrites $CuFeS_2$ (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wet ability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.

(d) Chromite ore $(FeO.Cr_2O_3)$ having magnetic properties is separated from non–magnetic silicious impurities by magnetic separator.

90. **(a)** **Self-reduction method**

This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb etc. are heated in air, a part of these is changed into oxide or sulphate that then reacts with the remaining part of the sulphide ore to give its metal and SO_2.

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

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

(b) **Reduction with carbon / carbon monoxide**

$$2Fe_2O_3 + 3C \longrightarrow 4Fe\ (\text{spongy iron}) + 3CO_2$$

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

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + CO_2$$

(c) **Electrolytic reduction (Hall-Heroult process)**

The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar)) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed.

The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2.

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

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

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

(d) **Complex formation and displacement by metal**

Extraction of Ag and Au. Metals like Au and Ag can be precipitated for their salt solution by electropositive metals for example, Zn.

Metallic Ag is dissolved from its ore in dilute NaCN solution, and the solute so obtained is treated with scrap Zn when Ag is precipitated. Air is blown into the solution oxidize Na_2S. Leaching the metals like silver, gold with CN^- is an oxidation reaction ($Ag \rightarrow Ag^+$ or $Au \rightarrow Au^+$)

$$Ag_2S\,(s) + 4CN^-\,(aq) \longrightarrow 2\,[Ag(CN)_2]^-\,(aq) + S^{2-}\,(aq)$$

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

Here Zn acts as reducing agent.

91. **(i)** $\overset{+3}{Cr_2}O_3 + 2\overset{0}{Al} \xrightarrow{\Delta} \overset{+3}{Al_2}O_3 + 2\overset{0}{Cr}$

(ii) Mg is extracted by electrolytic reduction of fused $MgCl_2$. As Mg lies above hydrogen in electrochemical series.

(iii) $PbO + C \xrightarrow{\Delta} Pb + CO\,;\ CaO + SiO_2 \xrightarrow{\Delta} CaSiO_3$

(iv) Red bauxite (contains impurity of iron oxide) is purified by Bayer's / Hall's process.

92. $Ag_2S\ (\text{conc. ore}) + 2NaCN \overset{\text{Air}}{\rightleftharpoons} 2AgCN + Na_2S.$

Ag_2S and AgCN are in equilibrium so Na_2S is oxidised by air in to Na_2SO_4. Hence equilibrium shifts towards right side.

$$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

$$AgCN + NaCN \longrightarrow Na[Ag(CN)_2]\ (\text{soluble complex})$$

$$2Na[Ag(CN)_2] + Zn\,(\text{dust}) \longrightarrow 2Ag\downarrow + Na_2[Zn(CN)_4].$$

93. **(i)** Extraction of tin (carbon reduction) :

$SnO_2 + C \rightarrow SnO + CO\uparrow$

(ii) Extraction of zinc (carbon reduction) :

$ZnO + C \xrightarrow{\text{coke, 673}} Zn + CO$

(iii) Extraction of lead (self reduction) :

$PbS + 2O_2 \longrightarrow PbSO_4\,;$

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

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

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

(iv) Extraction of copper (self reduction) :

$2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$

$Cu_2S + FeO + SiO_2 \longrightarrow FeSiO_3\ (\text{fusible slag}) + Cu_2S\ (\text{matte})$

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

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

(v) Extraction of aluminium (electrolytic reduction, Hall-Heroult process) :

The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed.

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

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

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

(vi) Extraction of gold/silver (leaching and displacement method) :

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

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

94. Molten iron from blast furnace is taken in to sand pigs for solidification. Therefore iron obtained from blast furnace is called pig iron.

95. $2\,ZnS + 3O_2 \xrightarrow{\text{roasting}} 2ZnO + 2SO_2$

$ZnO + C \xrightarrow{1100°C} Zn + CO.$

Therefore, **(B)** option is correct.

96. In Ellingham diagram, the $\Delta_fG°$ of Al_2O_3 lies below that of CO_2. If reduction is carried out at very high temperature, the Al produced will react with carbon forming Al_4C_3.

97 (I) Ti (s) (impure) $+\ 2I_2(g) \xrightarrow{150\text{ -}250°C}$

TiI_4 (volatile) $\xrightarrow[\text{Tungsten filament}]{1400°C}$ Ti (s) (pure) $+ 2I_2(g)$

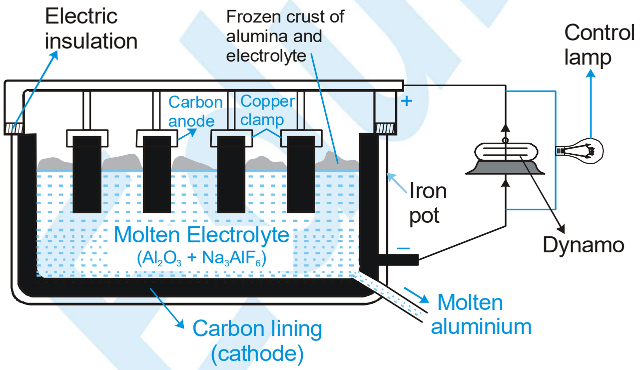
(II) $2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$

$PbS + 2PbO \xrightarrow[\text{temp.}]{\text{high}} 3Pb + SO_2$

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

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

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



98. S_1 : At 500 – 800 K (lower temperature range in the blast furnace)

$$3\,Fe_2O_3 + CO \longrightarrow 2\,Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \longrightarrow 3Fe + 4\,CO_2$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

At 900 – 1500 K (higher temperature range in the blast furnace) : $FeO + CO \longrightarrow Fe + CO_2$

S_2 : calamine is $ZnCO_3$

S_3 : It contains Fe_2O_3, SiO_2 and TiO_2 as impurities

S_4 : The surface of solidified copper has blistered like appearances due to the evolution of SO_2 and so it is called blister copper.

99. **S_1 :** The mud obtained below the anode contains unreactive Sb, Se, Te, Ag, Au and Pt.

S_2 : $SiO_2 + 2C \xrightarrow[N_2(g)]{1800°C} Si\uparrow + 2CO\uparrow$ (Serpeck's method)

At this temperature silicon is volatile.

S_3: Chalco pyrite is $CuFeS_2$ and azurite is $2CuCO_3.Cu(OH)_2$

S_4 : Purified cassiterite ore containing 60-70% SnO_2 is called black tin.

SnO_2 (black tin) $+ 2C \longrightarrow Sn + 2CO$ (carbon reduction).

100. **S_1** :$2ZnS$ (sphalerite) $+ 3O_2 \xrightarrow{\text{roasting}} 2ZnO + 2SO_2$;

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

S_2 : $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$

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

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

$FeO + SiO_2 \longrightarrow FeSiO_3$;

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

S_3 : $PbSiO_3 + CaO \longrightarrow CaSiO_3 + PbO$

S_4 : $2Cu_2O + 4H_2SO_4 + O_2 \longrightarrow 4CuSO_4 + 4H_2O$

$Cu_2S + 4H_2SO_4 + 4O_2 \longrightarrow 4CuSO_4 + 4H_2O + 2SO_2\uparrow$

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

101. **S1 :** It is used for copper and tin which contain the impurities of their own oxides.

S2 : It remove the impurities of N_2 and O_2 dissolved in molten steel.

S3 : Matte contains mostly Cu_2S and some FeS.

S4 : Cryolite undergoes dissociation :

$Na_3AlF_6 \rightarrow 3NaF + AlF_3 : AlF_3 \rightarrow Al^{3+} + 3F^-$; $NaF \longrightarrow Na^+ + F^-$

EXERCISE - 2

Part # I : Multiple Choice

2. All processes are correct.

(A) $Fe_2O_3 + 4CO \xrightarrow{\Delta} 3Fe + 4CO_2$

(B) $ZnO + C \xrightarrow{\Delta} Zn + CO$

(C) $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$

(D) $PbO + C \xrightarrow{\Delta} Pb + CO$

4. **(A)** Sulphides ores are generally concentrated by froth floatation.

(B) $2CuFeS_2 + 4O_2 \xrightarrow{\text{roasting}} Cu_2S + 2FeO + 3SO_2$

$Cu_2S + FeO + SiO_2 \longrightarrow FeSiO_3$ (fusible slag) $+ Cu_2S$ (matte)

(C) Bessemerisation

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

$FeO + SiO_2 \longrightarrow FeSiO_3$

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

$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ (self reduction).

6. **(A)** White bauxite contains the impurity of silica which is removed by heating with coke in a stream of N_2

$SiO_2 + 2C \xrightarrow{1800°C} Si\uparrow + 2CO$;

$Al_2O_3 + 3C + N_2 \xrightarrow{1800°C} 2AlN + 3CO$

(B) $2PbS + 3O_2 \xrightarrow[\text{air}]{\text{low temperature}} 2PbO + SO_2$;

$2PbO + PbS \xrightarrow{\text{high temperature}} 3Pb + SO_2$

(C) SnO_2 (black tin contains 60–70% SnO_2) $+ 2C \xrightarrow{\Delta} Sn + 2CO$.

7. **(A) Roasting.** It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point.

Roasting at high temperature. The sulphide ores of some of the metals like Cu, Pb, Hg, Sb etc., when heated strongly in the free supply of air or O_2 are reduced directly to the metal rather than to the metallic oxides.

(C) Calcination. It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air.

8. **(A)** $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$;

$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$;

$FeO + CO \longrightarrow Fe + CO_2$

(B) The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar)) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed.

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

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

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

Electrons act as reducing agent in electrolytic reduction.

(C) The molten mixture containing $MgCl_2$, NaCl and $CaCl_2$ is electrolysed.

$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$

At cathode : $Mg^{2+} + 2e^- \longrightarrow Mg$(99% pure) ;
At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Electrons act as reducing agent in electrolytic reduction.

(D) $2ZnS + 3O_2 \xrightarrow{\text{roasting}} 2ZnO + 2SO_2$
$ZnO + C \xrightarrow{\text{Carbon reduction}} Zn + CO$

9. $C + O_2 \longrightarrow CO_2$ (combustion zone)
$C + CO_2 \longrightarrow 2CO$ (fusion zone) ;
$FeO + C \longrightarrow Fe + CO$ (fusion zone)
$CaO + SiO_2 \longrightarrow CaSiO_3$ (slag formation zone) ;
$FeO + CO \longrightarrow Fe + CO_2$ (slag formation zone)
$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$ (reduction zone) ;
$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$ (reduction zone)

10. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb etc. are heated in air, a part of these is changed into oxide or sulphate that then reacts with the remaining part of the sulphide ore to give its metal and SO_2.

$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$;
$2HgO + HgS \longrightarrow 2Hg + SO_2$
$Cu_2S + 3O_2 \longrightarrow 3Cu_2O + 2SO_2$;
$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$
$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$;
$2PbO + PbS \longrightarrow 3Pb + SO_2$

11. **(A)** Dolomite is $CaCO_3.MgCO_3$

(B) $2PbS + 3O_2 \xrightarrow{\text{roasting}} 2PbO + 2SO_2$;

$PbS + 2PbO \xrightarrow{\text{self reduction}} 3Pb + SO_2$

(C) $2ZnS + 3O_2 \xrightarrow{\text{roasting}} 2ZnO + 2SO_2$;

$ZnO + C \xrightarrow{\text{Carbon reduction}} Zn + CO$

(D) In extraction of iron the slag obtained is $CaSiO_3$ where as in copper it is $FeSiO_3$.

12. **(A)** Cassiterite ore (SnO_2) is separated from magnetic Wolframite ($FeWO_4$ + $MnWO_4$) by magnetic separator.

(B) The purified cassiterite ore containing 60-70% SnO_2 is called black tin.

(C) $SnO_2 + C \rightarrow SnO + CO\uparrow$

(D) Anglesite is $PbSO_4$.

13. **(A)** $B_2O_3 + 2Al \xrightarrow{\Delta} 2B + Al_2O_3$

(aluminothermic process-extraction of boron)

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

(extraction of chromium)

(C) $TiCl_4 + 2Mg \xrightarrow{\Delta} Ti + 2MgCl_2$

(Kroll process-extraction of titanium)

(D) $PbS + 2PbO \xrightarrow{\Delta} 3Pb + SO_2$ (extraction of lead)

14. CaO converts the $PbSiO_3$ to PbO, and also prevents the formation of $PbSO_4$.

$CaO + SiO_2 \longrightarrow CaSiO_3$ (slag) ;

$PbO + SiO_2 \longrightarrow PbSiO_3$;

$PbSiO_3 + CaO \longrightarrow PbO + CaSiO_3$

15. **(A)** In extraction of copper from chalcopyrite, self reduction takes place in Bessemer converter.

(B) In extraction of iron from haematite, carbon / carbonmonoxide reduction takes place in Blast furnace.

(C) The extraction of chromium from Cr_2O_3 by reduction with aluminium is called aluminothermic process.

(D) Tin is obtained by carbon reduction of SnO_2 (cassiterite ore).

16. $C + O_2 \longrightarrow CO_2$ (combustion zone)

$C + CO_2 \longrightarrow 2CO$ (fusion zone) ;

$FeO + C \longrightarrow Fe + CO$ (fusion zone)

$CaO + SiO_2 \longrightarrow CaSiO_3$ (slag formation zone) ;

$FeO + CO \longrightarrow Fe + CO_2$ (slag formation zone)

$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$ (reduction zone) ;

$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$ (reduction zone)

17. This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb); copper pyrites $CuFeS_2$ (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wet ability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.

18. **(A)** Bauxite is Al_2O_3 and limonite is $Fe_2O_3.3H_2O$.

(B) Haematite is Fe_2O_3 and siderite is $FeCO_3$.

(C) Cinnabar is HgS and cassiterite is SnO_2.

(D) Galena is PbS and cerussite is $PbCO_3$

19. **(A)** $2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$ (molten) ;

$\Delta H = -3230$ kJ (The reaction is used for thermite welding)

(B) Aluminothermic process :

$Cr_2O_3 + Al \rightarrow 2Cr$ (molten) $+ Al_2O_3$

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

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

(D) Self-reduction method : $Cu_2S + 3O_2 \longrightarrow 3Cu_2O +$

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

20. **(A)** $Ag + 2CN^- + O_2 + 2H_2O \longrightarrow [Ag(CN)_2]^- + 4OH^-$

$[Ag^I(CN)_2]^- + Zn^0 \longrightarrow Ag^0 + [Zn^{II}(CN)_4]^{2-}$

(B) $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$

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

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

(C) Magnesite, $MgCO_3$ is the ore of magnesium.

(D) Tin is extracted by carbon reduction.

$SnO_2 + 2C \longrightarrow Sn + 2CO$

Lead is extracted by carbon and self reduction.

21. **(A)** Calamine, $ZnCO_3$ is the ore of zinc.

(B) Proustite, Ag_3AsS_3 is the ore of silver.

(C) Cassiterite, SnO_2 is the ore of tin.

(D) Diaspore, $Al_2O_3.H_2O$ is the ore of aluminium.

22. Leaching is done with suitable chemical reagents to dissolve the ores of Al, Ag and Au.

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

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

23. **(A)**, **(C)** Heating of carbonates and hydroxide ores in absence of air to convert into their corresponding oxides is called calcination.

(B) Heating of sulphide in presence of air or O_2 to convert in to oxides is called roasting.

(D) This reaction represents the self reduction.

Part # II : Assertion & Reason

2. **Statement-1** Sphalerite is ZnS ;

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

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

Statement-2 Zinc is highly reactive metal, it cannot be displace from a solution of $ZnSO_4$ so easily. Thus reason is incorrect.

3. **S-1 :** $FeO + SiO_2 \longrightarrow FeSiO_3$.

S-2: Reason is incorrect as SiO_2 is a covalent compound and thus does not ionise to give ions responsible for conducting the electric current.

5. **Statement-1 :** The statement is incorrect because being strong reducing agents, they are extracted by electrolytic reduction of their fused salts.

Statement-2 : The statement is correct as they themselves are strong reducing agents and lie above hydrogen in electrochemical series. So they are extracted by the electrolytic reduction of their fused salts.

6. **Statement-1 :** True but its reason is that aluminium cannot be extracted (i) from Al_2O_3 by its reduction with carbon at high temperatures (there is possibility of formation of Al_4O_3) (ii) by electrolysis of their salts solution as aluminium liberated at cathode will immediately react with H_2O forming $Al(OH)_3$.

Statement-2 : The statement is correct as cryolite or fluorspar lowers the melting point of alumina as impurity. Both being ionic compounds ionize to give ions and thus increase the electric conductivity.

9. **Statement-1 :** The Gibb's energies of formation of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. There, the $\Delta_f G^\ominus$ of M_xS is not compensated. So reduction of M_xS is difficult. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

Statement-2 : $ZnO + C \xrightarrow{\Delta} Zn + CO$;

$PbO + C \xrightarrow{\Delta} Pb + CO$ (carbon reduction)

EXERCISE - 3

Part # I : Matrix Match Type

4. **(A)** Haematite is Fe_2O_3. To remove the impurity of $FeCO_3$, the ore is heated in absence of air (calcination).

At 500 – 800 K (lower temperature range in the blast furnace)

$$3\,Fe_2O_3 + CO \longrightarrow 2\,Fe_3O_4 + CO_2 ;$$

$$Fe_3O_4 + CO \longrightarrow 3Fe + 4\,CO_2 ;$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

At 900 – 1500 K (higher temperature range in the blast furnace):

$$C + CO_2 \longrightarrow 2\,CO ;$$

$$FeO + CO \longrightarrow Fe + CO_2$$

(B) Copper pyrites is $CuFeS_2$. During smelting /roasting (now a day) and bessemerisation the impurity of iron sulphide is removed as fusible slag, $FeSiO_3$.

$$2CuFeS_2 + 4O_2 \xrightarrow{\text{roasting}} Cu_2S + 2FeO + SO_2$$

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

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

(C) Carnallite $(KCl.MgCl_2.MgCl_2.6H_2O) \xrightarrow[\text{dry HCl(g)}]{\Delta\text{(calcination)}} MgCl_2 + 6H_2O$

Mg extraction is done by electrolytic reduction of molten mixture of anhydrous $MgCl_2 + NaCl + CaCl_2$.

(D) Bauxite is Al_2O_3 ;

$$2Al(OH)_3 \xrightarrow[\text{calcination}]{1275\text{ K}} Al_2O_3 + 3H_2O;$$

Extraction of Al from purified Al_2O_3 is done by electrolytic reduction of molten alumina dissolved in cryolite or fluorspar.

6. **(A)** Hall- Heroult process is the electrolytic reduction of molten Al_2O_3 dissolved in cryolite or fluorspar.

(B) Dow's sea water process involves the isolation of Mg from sea water as $MgCl_2$ and then electrolytic reduction of molten $MgCl_2$ dissolved in $CaCl_2$ and NaCl.

(C) Hoop's process is the electrolytic purification of impure aluminium. The cell has three liquid layers upper most layer contains impure Al, middle one contains fluorides of Na^+, Ba^{2+} and Al^{3+}, lower most layer has pure Al (obtained by cathodic oxidation).

(D) Mac-Arthur forest cyanide process is the process used for the extraction of gold and silver.

Extraction of gold and silver involves leaching the metal with CN^-. The metal is later recovered by displacement method.

8. **(A)** $FeO + SiO_2 \longrightarrow FeSiO_3$ (slag) ; this reaction occurs in extraction of copper from copper pyrites in smelting as well as in bessemerisation processes.

(B) Reduction of oxides of Mn, Cr with electropositive metal aluminium is called thermite process.

(C) Self reduction generally occurs in bessemer converter in extraction of copper from copper pyrites.

(D) Conversion of $Al(OH)_3$ into Al_2O_3 by heating in absence of air represents the calcination.

(E) Displacement of silver from its salt solution by more electropositive zinc.

Part # II : Comprehension

Comprehension # 1 :

1. $[X] = CuCO_3.Cu(OH)_2$ or $2CuCO_3.Cu(OH)_2$;
$[Y] = Cu_2S$ or $CuFeS_2$

$CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} CuO\,(S) + CO_2 + H_2O$;
$[Y] = Cu_2S$ or $CuFeS_2$

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

$Cu_2S + 2Cu_2O \longrightarrow 6Cu\,(M) + SO_2(g)$

$5SO_2 + 2IO_3^- + 4H_2O \longrightarrow I_2 + SO_4^{2-} + 8H^+$

I_2 + starch $\longrightarrow$ blue colour

2. It is sulphide ore (Cu_2S or $CuFeS_2$) & is called as copper glance or copper pyrite ; S^{2-} gives yellow ppt. of CdS with $CdCO_3$ suspension.

5. $CuCO_3.Cu(OH_2) \xrightarrow{\Delta} CuO\downarrow$ (black) $+ CO_2 + H_2O$

$CuCO_3 . Cu(OH)_2 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$;

$2CuCl_2 + 4KI \longrightarrow Cu_2I_2\downarrow$ (white) $+ I_2 + 4KCl$

Comprehension # 2 :

1. Dissolution of gold in NaCN forming soluble complex is reversible, so it is carried out in presence of air bubbling. Oxygen contained in air oxidises Au to Au^+ which then complexes with CN^- to form soluble complex.

Comprehension # 3 :

3. $FeO(s) + C(s) \longrightarrow Fe(s/l) + CO\,(g)$ ..... (1)

$FeO(s) \longrightarrow Fe(s) + \frac{1}{2}O_2(g)\,[\,\Delta G_{(FeO,\,Fe)}]$ ..... (2)

$C(s) + \frac{1}{2}O_2\,(g) \longrightarrow CO\,(g)\ \ [\,\Delta G_{(C,\,CO)}]$ ..... (3)

$\Delta G_{(C,CO)} + \Delta G_{(FeO,\,Fe)} = \Delta_r G$ ..... (4)

In ΔG^0 vs T plot representing reaction (2), the plot goes upward and that representing the change C $\rightarrow$ CO (C,CO) goes downward. At temperatures above 1073K (approx.), the C,CO line comes below the Fe,FeO line $[\Delta G_{(C,\,CO)} < \Delta G_{(Fe,\,FeO)}]$. So in this range, coke will be reducing the FeO and will itself be oxidised to CO. In a similar way the reduction of Fe_3O_4 and Fe_2O_3 at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO_2 curve in the given figure.

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

$ZnS + 2O_2 \longrightarrow ZnSO_4$;

$ZnSO_4 \xrightarrow{1200\text{ K}} 2ZnO + 2SO_2 + O_2$

The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper because ZnO line crosses C $\rightarrow$ CO line at higher temperature than that of CuO.

$ZnO + C \xrightarrow{\text{coke, 673}} Zn + CO$

EXERCISE - 4

Subjective Type

1. $C + O_2 \longrightarrow CO_2$; $C + CO_2 \longrightarrow 2CO$

$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$;

$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$;

$FeO + CO \longrightarrow Fe + CO_2$ $CaO + SiO_2$ (flux) $\longrightarrow$ $CaSiO_3$(slag)

So coke & lime stone are added during smelting in extraction of iron.

2. Zinc is highly reactive metal. It may not be possible to replace it from a solution of $ZnSO_4$ easily.

3. $2Al + \frac{3}{2} O_2 \longrightarrow Al_2O_3$;

$\Delta_f G^o = -827$ kJ/mol ; $2Cr + \frac{3}{2} O_2 \longrightarrow Cr_2O_3$;

$\Delta_f G^o = -540$ kJ/mol

So, $\Delta G_{overall} = -827 - (-540) = -287$ kJ/mol

Hence $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$.

4. Sulphide ores being lighter are easily wetted by oil to come on the surface of solution with froths during froth floatation process, leaving behind heavier gangue wetted by water.

5. The Gibbs energies of formation of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

6. $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$;

$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu\downarrow$

7. For reaction at 1000ºC $\Delta G_{overall} = \Delta G(C) - \Delta G_{(M)}$

$= -439 - (-941)$

$= +502$ kJ/mol

For reaction at 2000ºC $\Delta G = \Delta G(C) - \Delta G_{(M)}$

$= -628 - (-314)$

$= -314$ kJ/mol

Reduction of MgO with C can occur at 2000ºC and not at 1000ºC.

8. $Al_2O_3 + N_2 + 3C \xrightarrow{1800°C} 2AlN + 3CO$;

$SiO_2 + 2C \xrightarrow{1800°C} Si\uparrow + 2CO\uparrow$

$AlN + 3H_2O \longrightarrow Al(OH)_3\downarrow + NH_3$;

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

9. $2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$;

$PbO + C \xrightarrow{\Delta} Pb + CO$

10. Hence, the change in oxidation number of aluminium is 3 per mole. Since 4/3 moles of Al are produced n = 3 × 4/3 = 4

$$E_{ext} = \frac{960000}{4 \times 96490} = 2.5 \text{ V}$$

A potential difference of at least 2.5 V must be applied to the oxide to bring about reduction.

11. Parting process

$Cu + 2H_2SO_4$ (or conc. HNO_3) $\xrightarrow{Boil} CuSO_4 + SO_2 + 2H_2O$

$2Ag + 2H_2SO_4$ (or conc. HNO_3) $\xrightarrow{Boil} Ag_2SO_4 + SO_2 + 2H_2O$

% of Au in impure sample should not be more than 25%

12. $Ni(s) + 4CO(g) \xrightarrow{50°C} Ni(CO)_4(g) \xrightarrow{200°C} Ni(s) + 4CO(g)$

13. Graphite rods act as anode and get burnt away as CO and CO_2 during the process of electrolysis.

14. The metallurgical procedure based on the roasting of an ore, followed by its reduction (usually with carbon), is known as **pyro-metallurgy**. A key consideration in pyro-metallurgy is the temperature at which reaction becomes spontaneous. A key term **"pyro"** suggests, often this temperature is quite high:

Hydrometallurgy involves the leaching of ores with suitable chemical reagents like acid base, water etc. The metal is then extracted from salt solution either by electrolysis or precipitation with more electropositive elements like, Fe,Cu etc.

15. In the cyanide process, crushed rock containing traces of gold is treated with 0.1 — 0.2% solution of NaCN and aerated. O_2 (air) oxidises free metal to Au^+ which complexes with CN^-

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

The pure metal is displaced from solution by an active metal.

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

16. Silver coin $(Cu + Ag) \xrightarrow{conc.\ HNO_3} (Cu^{2+} + Ag^+)\,NO_3^-$

$\downarrow NaCl$

$AgCl\downarrow$ (white ppt)

$2AgCl + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2NaCl$

$Ag_2CO_3 \xrightarrow{\Delta} 2Ag\downarrow + CO_2\uparrow + \frac{1}{2} O_2\uparrow$

Or use cyanide process with **AgCl.**

17. Aqueous solution of CO_2 is acidic. Hence $CO_2(g)$ when passed into $[Al(OH)_4]^-$ solution makes it acidic and $Al(OH)_3$ get precipitated.

$$CO_2 + 2H_2O \longrightarrow H_3O^+ + HCO_3^-$$

$$[Al(OH)_4]^- + H_3O^+ \longrightarrow Al(OH)_3\downarrow + 2H_2O$$

18. $Al_2O_3 + 3C \longrightarrow 2Al + 3CO;$

$\Delta G^o = 3(-137.2) - (-1582) = 1170.4\ kJ.$

As value of ΔG^o is +ve so Al_2O_3 can not be reduced by carbon.

19. **For reaction (A)** $\Delta G^o = 2\Delta G^o_f(ZnO) + 2\Delta G^o_f(SO_2) - 2\Delta G^o_f(ZnS)$

$= 2[-318.2 - 300.4 + 205.4] = -826.4\ kJ$

For reaction (B) $\Delta G^o = \Delta G^o_f(CO) - \Delta G^o_f(ZnO)$

$= -137.3 + 205.4 = +68.1$

For reaction **(A)**, ΔG^o is negative hence reaction is spontaneous; reaction **(B)** is non-spontaneous ΔG^o being positive for it.

20. **(i)** Carbon reduction of SnO_2

$SnO_2 + 2C \rightarrow Sn + 2CO\uparrow;\ SnO_2 + C \rightarrow SnO + CO\uparrow$

$SnO + SiO_2 \rightarrow SnSiO_3;\ CaO + SiO_2 \rightarrow CaSiO_3$

$SnSiO_3 + CaO + C \rightarrow Sn + CaSiO_3 + CO\uparrow$

or use scrap iron

$SnSiO_3 + Fe \rightarrow Sn + FeSiO_3$

(ii) Self-reduction (i.e. air reduction) of PbS

$PbS + 2O_2 \longrightarrow PbSO_4$;

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

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

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

$SiO_2 + CaO\ (flux) \longrightarrow CaSiO_3$ (slag) ;

$PbSiO_3 + CaO \longrightarrow PbO + CaSiO_3$ (slag)

CaO, prevents the formation of $PbSiO_3$.

(iii) Cyanide process.

$Ag_2S\ (concentrated\ ore) + 2NaCN \underset{}{\overset{Air}{\rightleftharpoons}} 2AgCN + Na_2S.$

$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$

Na_2S is converted in to Na_2SO_4. Hence equilibrium shifts towards right side.

$AgCN + NaCN \longrightarrow Na[Ag(CN)_2]$ (soluble complex)

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

21. 1.6 V in Hall-Heroult process.

22. The impure lead metal serves as the anode and pure lead serves as the cathode. Impurities either remain at the anode or go into solution.

Anode : $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

Cathode : $PbSiF_6(aq) + 2e^- \longrightarrow Pb(s) + SiF_6^{2-}(aq)$

23. **(A)** $Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$

(B) $Na[Al(OH)_4] + HCl \longrightarrow NaCl + Al(OH)_3 + H_2O$

but strong acid like HCl will further dissolve $Al(OH)_3$ which is amphoteric. Aqueous solution of NH_4Cl is slightly acidic and this acidic solution will cause precipitation of $Al(OH)_3$ from $Na[Al(OH)_4]$

$NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+$

$[Al(OH)_4]^- + H_3O^+ \rightleftharpoons Al(OH)_3\downarrow + 2H_2O$

(C) $AgCl + Na_2CO_3 \xrightarrow{\Delta} Ag_2CO_3 \xrightarrow{\Delta} Ag_2O + CO_2$

$Ag_2O \xrightarrow{\Delta} 2Ag + \frac{1}{2}O_2$

24. Since N_2 can also combine with Mg giving magnesium nitride, and inert atmosphere no longer remains. So helium is used in place of N_2.

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

1. Froth-floatation method is used for the concentration of sulphide ores. The method is based on the preferential wetting properties with the frothing agent and water. Here galena (PbS) is the only sulphide ore.

2. $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$. (self reduction)

3. Anode mud contains Ag, Pt, Sb, Se, Te and Au as impurities.

4. **(3)** It is true that this statement has no significance for roasting sulphide ores to the oxides.

The Gibb's energies of formation of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. There, the $\Delta_f G^\ominus$ of M_xS is not compensated. So reduction of M_xS is difficult. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

5. The process is known as Van Arkel method.

9. $Al + 3H_2O \xrightarrow{NaOH} \underset{(x)}{Al(OH)_3}\downarrow + 3/2H_{2(g)}$

white gelatinous ppt.

↓

soluble in excess of NaOH and

and form $Na[Al(OH)_4]$

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

used as

adsorbent in chromatography

So, metal is Al.

Part # II : IIT-JEE ADVANCED

1. $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$

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

$SnO + C \longrightarrow Sn + CO$

$SnO + CO \longrightarrow Sn + CO_2$

2. Formation of CO_2 and H_2O indicates that ore A1 is hydrated carbonate ore.

A1 when treated with HCl and then KI gives white precipitate and iodine gas indicates that it is the ore of copper.

(A1) $CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} CuO\downarrow$ (black) $+ CO_2 + H_2O$.

$CuCO_3.Cu(OH)_2 + HCl \rightarrow CuCl_2 + H_2O + CO_2$.

$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2\downarrow + I_2$.

The precipitation of metal (by self reduction) and evolution of a gas (on roasting) which turns acidified $Cr_2O_7^{2-}$ green indicates that A_2 is sulphide ore of copper.

(A2) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$;

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

$3SO_2 + Cr_2O_7^{2-} + 2H^+ \longrightarrow 2Cr^{3+}$ (green solution) $+ 3SO_2 + H_2O$.

So, $A1 = CuCO_3.Cu(OH)_2$ or $2CuCO_3.Cu(OH)_2$;

$A2 = Cu_2S$; $S = CuO$; $P = Cu_2I_2$; $G = SO_2$

3. Chalcopyrite is $CuFeS_2$ which contains both Fe and Cu.

4. **(A)** $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$.

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

$PbO + C \longrightarrow Pb + CO$.

(B) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$.

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

Self reduction.

(C) $Ag + 2CN^- \xrightarrow[H_2O]{O_2} [Ag(CN)_2]^-$.

$2[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag\downarrow$.

(D) $2BI_3 \xrightarrow{\Delta} 2B + 3I_2$.

5. Zinc blende is roasted in excess of air to convert it into oxide. The oxide formed is then heated in presence of coke to get metallic zinc (reduction).

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

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

6. Reaction is reversible so to get the maximum yield of the product, the reaction is carried out in presence of oxygen. Also oxygen oxidises silver to silver (I) ion which then produces soluble complex with CN^- ions.

$$2Ag + 4\,NaCN + \frac{1}{2}O_2 + H_2O \rightleftharpoons 2Na[Ag(CN)_2] + 2NaOH.$$

7. **(A)** $2PbS + 3O_2 \xrightarrow[\text{roasting}]{\Delta} 2PbO + 2SO_2$

Sulphides are generally roasted for self reduction or for converting into their oxides which are then reduced by carbon or carbon monoxide to get metal.

(B) $CaCO_3 \xrightarrow[\text{in absence of air}]{\Delta} CaO + CO_2$

Carbonates and hydrated ores are calcined to convert into their oxides.

(C) $2ZnS + 3O_2 \xrightarrow[\text{roasting}]{\Delta} 2ZnO + 2SO_2$

$ZnO + C \xrightarrow[\text{roasting}]{\Delta} Zn\ CO$

(D) From copper glance i.e. Cu_2S, the copper is extracted by first heating the ore in reverberatory furnace at moderate temperature i.e. roasted and then supply of air is cut off and then temperature is increased so that roasted mass melts. At this point self reduction takes place and blister copper is obtained.

$Cu_2S + 3O_2 \xrightarrow{\Delta} 6Cu + SO_2$;

$Cu_2S + 2Cu_2O \xrightarrow{\Delta} 6Cu + SO_2$

8. $2\,CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$

9. Iron is removed in the form of slag of $FeSiO_3$

$FeO + SiO_2 \longrightarrow FeSiO_3$

10. S^{2-} acts as reducing species in self reduction reaction

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

11. Important ore of tin is cassiterite (SnO_2). SnO_2 is reduced to metal using carbon at 1200 – 1300°C in an electric furnace. The product often contains traces of Fe, which is removed by blowing air through the molten mixture to oxidise FeO which then floats to the surface.

$SnO_2 + 2C \longrightarrow Sn + 2CO$

$Fe + O_2 \longrightarrow FeO$

12. In haematite(Fe_2O_3), Fe is present in (III) oxidation state and in magnetite (Fe_3O_4) which is a mixed oxide of FeO and Fe_2O_3, Fe is present in (II) and (III) oxidation state.

13. In extraction of silver, Ag_2S is leached with KCN in presence of air :

$Ag_2S + NaCN + O_2 \rightleftharpoons Na[Ag(CN)_2] + Na_2S_2O_3$

Thus, O_2 is oxidant.

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

14. Common ore of Ag – Ag_2S, Cu – $CuFeS_2$, Pb – PbS, Sn – SnO_2, Mg – KCl. $MgCl_2$. $6H_2O$, Al – $Al_2O_3 . xH_2O$

So answer is **(A)**

15. SnO_2 and Fe_2O_3 are reduced by C reduction method. Al_2O_3 and $MgCO_3$. $CaCO_3$ are reduced by electrolytic reduction.

16. **(A)** NH_4NO_3 (decompose below 300ºC to produce N_2O & H_2O, but to produce N_2, it should be heated above 300ºC

(B) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N2 + Cr_2O_3 + H_2O$

(C) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + N_2$

(D) Mg_3N_2 (an ionic compound; will not decompose below 300ºC)

MOCK TEST

1. (A)

Argentite → Ag_2S ; Cuprite → Cu_2O ; Siderite → $FeCO_3$
Carnallite → $KCl.MgCl_2.6H_2O$

2. (B)

$ZnS + 4NaCN \longrightarrow Na_2[Zn(CN)_4]$ (soluble complex) + Na_2S.

3. (B)

PbS reduces PbO to Pb and SO_2 is liberated. This a called as self-reduction.

4. (B)

Copper pyrites contain Fe and Cu. Iron oxide is removed as fusible stage, $FeSi_3$.
$FeO + SiO_2 \rightarrow FeSiO_3$

5. (B)

Most of impurityof iron sulphide is removed during smelting, $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$
$FeO + SiO_2 \rightarrow FeSiO_3$ (slag)

6. (D)

$2Ag + 4CN^- + H_2O + 1/2O_2 \rightarrow 2[Ag(CN)_2]^- + 2OH^-$
$2Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + Ag\downarrow$

7. (A)

Cyanide process → Ag, Self reduction → Cu,
Electrolytic reduction → Al, Carbon reduction → Sn.

8. (A)

Alkali and alkaline earth metals are generally obtained by electrolysis of fused salts but not by carbon reduction.

9. (C, D)

(C) It occurs in fusin zone at higher tempt. with Fe_2O_3 with escapes reduction zone.
(D) It occus in slag formation zone.

10. (A, B, C)

(A) To remove the tungstate of Fe and Mn i.e. Wol-framite which are magnetic in nature.
(B) To convert of copper & iron pyrites to $CuSO_4$ & $FeSO_4$
(C) To remove the $CuSO_4$ and SO_4 by leaching with water as both are water soluble.

11. (A, B, C)

(A) Ture statement
(B) $CaO + SiO_2 \longrightarrow CaSiO_3$ (slag) ;
(C) $PbO + SiO_2 \longrightarrow PbSiO_3$
CaO converts the $PbSiO_3$ to
$PbO, PbSiO_3 + CaO \longrightarrow PbO + CaSiO_3$

12. (B, C, D)

(A) $FeSiO_3$
(B) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
$CaO + SiO_2 \longrightarrow CaSiO_3$
These reactions take place in slag formation zone at temperature = 1275 K
(C) True statement
(D) Infusible matter + Flux = Fusible matter (slag)

13. (A)

S1 : Cu_2O, $Fe_2O_3 . 3H_2O$, ZnO
S2 : $MgCO_3$, KCl, $MgCl_2$, $6H_2O$
S3 : Cu_2S, $3CuCO_3 . Cu(OH)_2$
S4 : Both contain aluminium.

14. (B)

(A) $Cr_2O_3 + 2Al \longrightarrow \overset{+3}{Al_2O_3} + 2Cr.$
(B) Reduction potentials of both Mg and Al are less then that of water [E° = 0.083V]. Thus the ions of both Mg and Al in aqueous solution cannot be reduced and in sucha a case water will be reduced.
$2H_2O + 2e \longrightarrow H_2 + 2OH^-$.
(C) True statement
(D) $Ag_2S + 4NaCN \xrightarrow{O_2} 2Na[Ag(CN)_2] + Na_2S$
$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$

15. (C)

$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$;
$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$
$FeO + SiO_2 \longrightarrow FeSiO_3$, ; thus remove the impurity of iron oxide.

16. (A)

Cast iron contains 3% carbon.

17. (C)

S-1 : It lowres the fusion temperature of $MgCl_2$ and provide conductivity to the electrolyte.
S-2 : $MgCl_2.6H_2O$ is calcined in a stream of dry HCl gas to have anhydrous $MgCl_2$. In absence of dry HCl, it forms $MgOCl_2$ ($MgO.MgCl_2$) because of hydrolysis.

18. (A)

(A) Reaction occurs during roasting in reverberatory furnace at moderate temperature in presence of air.

19. (A)

O_2 oxidases silver to silver (I) ion which then produces soluble complex with CN^- ions.

$2Ag + 4NaCN + ½O_2 + H_2O$ ③ $2\,Na\,[Ag(CN)_2] +$ $2\,NaOH$

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

20. (A)

Red bauxite contains the impurities of iron oxides, titanium oxide and silica which are removed by Baeyer's andHall's processes. The Serpeck's methos is used when bauxite contains only the impurity of silica.

21. (A)

22. (D)

$Au \longrightarrow [Au^+]$ which then form complex with CN^-

$2[Au(CN)_2] + Zn \longrightarrow 2Au\downarrow + [Zn(CN)_4]^{2-}$. Zinc acts both as complexing and reducing reagent.

23. (C)

The process which involves the dissolution of ore into a suitable reagent and then extraction of metal from the solution by more electropositive element is known as hydrometallurgy.

24. (A)

$[X] = CuCO_3\,Cu(OH)_2$ or $2CuCO_3.\,Cu(OH)_2$; $[Y] = Cu_2S$ or $CuFeS_2$

25. (D)

It is sulphide ore (Cu_2S or $CuFeS_2$) & is called as chalcopyrites or chalcocites, S^{2-} gives yellow precipitate of CdS with $CdCO_3$

26. (C)

$G_1 = SO_2$; sulphur can increase & decrease its oxidation state.

27. (A)

$CuCO_3 + 2HCl \longrightarrow CuCl_2 + CO_2 + H_2O$;

$CuCl_2 + 2KI \longrightarrow CuI_2 + 2KCl$;

$2CuI_2 \longrightarrow Cu_2I_2\downarrow(P) + I_2$

28. (A → p, q) ; (B → p, q, r) ; (C → q, s) ; (D → r)

(A) $CuFeS_2$; $Cu_2S + 2\,Cu_2O \longrightarrow 6\,Cu + SO_2$

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

$PbO + C \longrightarrow Pb + CO$

(C) Ag_2S; Cyanide process, leaching with alkali metal cyanide followed by displacement with zinc dust.

$Ag_2S + 4\,NaCN \xrightarrow{O_2} 2Na[Ag(CN)_2] + Na_2S$

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

(D) $CuCO_3.\,Cu(OH)_2$;

Calcination $\longrightarrow CuO + C \longrightarrow Cu + CO$

29. (A → p) ; (B → p) ; (C → q) ; (D → s)

(A) Gold dissolves in NaCN solution forming a soluble complex leaving behind impurities is calledleaching process. Hence the extraction of gold is called hydrometallurgy.

(B) Insoluble copper pyrites dissolves in H_2SO_4 forming soluble $CuSO_4$ is called leaching. Henc the extraction of copper is called hydrometallurgy.

(C) Reduction of Fe_3O_4 by CO in blast furmace is smelting.

(D) Healting $MgCl_2.\,6H_2O$ in dry HCl gas to convert into anhydrous $MgCl_2$ is calcination.

30. (A → q) ; (B → s) ; (C → r) ; (D → p)

Silver ⟶ Involves formation of soluble compex with dilute NaCN solution in presence of air followed by precipitation with zinc.

Lead ⟶ Involves roasting (of PbS) followed self reduction.

Iron ⟶ Involves calcination (of Fe_2O_3) followed by reduction with carbon monoxide.

Magnesium ⟶ Involves calcination (of $MgCl_2.\,6H_2O$ in presence of dry HCl gas) followed by fused salt electrolysis.