6 General Principles and Processes of Isolation of Elements

LESSON AT A GLANCE

- **Minerals:** A naturally occurring substance that has a characteristic chemical composition, and in general, a crystalline structure. This term is also often applied generally to organic substances that are obtained by mining (*e.g.* petroleum and natural gas) but strictly speaking these are not minerals, being complex mixtures without definite chemical formulas.
- **Ores:** A naturally occurring mineral from which a metal can be extracted, usually on a commercial basis.
- **Concentration of ore:** Removal of unwanted impurities to a certain extent is called concentration of ore.
- Concentrated ore is then treated chemically to obtain metal founded in metal in the form of oxides or sulphides.
- Metal oxides react with a reducing agent. The oxide is reduced to metal and the reducing agent is oxidised. In the two reactions net Gibbs energy change is negative which becomes more negative on raising the temperature.
- The concept is graphically displayed by Ellingham diagram.
- The metals obtained by usual method still contain minor impurities.
- Pure metal obtained by refining. Refining process depends upon the differences in properties of metal and their impurities. Aluminium is extracted by bauxite ore.
- Metals are widely used and have significantly contributed in the development of varieties of industries.
- **Gangue:** The impurities associated with the minerals are known as gangue or matrix.
- **Metallurgy:** The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

- **Occurrence of metals:** Among metals, aluminium is the most abundant. It is the third most abundant element in earth's crust. (8.3% approxmately by weight). It is a major component of many igneous minerals including mica and clays.
- **Depressants:** It is used to separate two sulphide ores by adjusting proportion of oil and water. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.
- **Leaching:** It is a process in which ore is treated with suitable reagent which dissolves ore but not the impurities.
- **Pig iron:** The iron obtained from blast furnace is called pig iron. It is impure form of iron contains 4% carbon and small amount of S, P, Si and Mn. It can be cast into variety of shapes.
- **Cast iron:** It is made by melting pig iron with scrap iron and contains 3% of carbon content. It is hard and brittle.
- **Wrought iron:** A highly refined form of iron containing 1–3% of slag which is evenly distributed throughout the material in threads and fibres so that the product has a fibrous structure quite dissimilar to that of crystalline cast iron. It is the purest form of iron. It is also called malleable iron. It is prepared by oxidative refining of pig iron in reverberatory furnace used with haematite which oxidises carbon to carbon monoxide.
- **Distillation:** Method used for the metals having low boiling point. Like zinc and mercury. Impure metal is evaporated to obtain pure metal as distillate.
- **Liquation:** In this method low melting metal like tin can be made to flow on a sloping surface, On this way it is separated from higher melting impurities.
- **Electrolysis:** In this method, impure metal is taken as anode, pure metal is taken as cathode, soluble salt of metal is used as an electrolyse. When electric current is passed impure metal forms metal ions which are discharged at cathode forming pure metal.
- **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. A circular mobile heater is fixed at one end of a rod of the impure metal.

- **Vapour phase refining:** Nickel is purified by Mond's process. Nickel when heated in stream of carbon monoxide forms volatile $Ni(CO)_4$ which decomposes to pure nickel.

$$Ni + 4CO \xrightarrow{330-350K} Ni(CO)_4 \xrightarrow{450-470K} \underset{\text{Pure}}{Ni} + 4CO$$

- **Van Arkel-de Boer Method:** Zr and Ti are purified by this process. Zr or Ti are heated in iodine vapours at about 870 K to form volatile ZrI_4 or TiI_4 which are heated over tungsten filament at 2075 K to give pure Zr or Ti.

TEXTBOOK QUESTIONS SOLVED

6.1 *Copper can be extracted by hydrometallurgy but not zinc. Explain.*

Ans. Copper is less reactive than hydrogen, therefore, it can be extracted by hydro-metallargy, whereas Zn cannot be extracted by hydrometallurgy because zinc is more reactive than hydrogen.

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

Ans. It prevents certain sulphides like ZnS to enter the froth in presence of PbS therefore, helps in their separation. Sodium Cyanide is used as depressant in separation of ZnS from PbS.

6.3 *Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?*

Ans. Considering carbon as the reducing agent for copper pyrites (Cu_2S), the reduction reaction would be

$$2Cu_2S(s) + C(s) \longrightarrow 4Cu(s) + CS_2(g)$$

The condition for this reaction is

$$\Delta_f G^\ominus(CS_2) < \Delta_f G^\ominus (Cu_2S)$$

which is not the case. The line for CS_2 in Ellingham diagram lies much higher than that for Cu_2S. Hence, carbon cannot be used as a reducing agent. For similar reasons even hydrogen gas cannot be used as a reducing agent. For this,

$$\Delta_f G^\ominus(H_2S) > \Delta_f G^\ominus (Cu_2S)$$

That is why Cu_2S is first roasted to Cu_2O and then reduced with carbon.

$$Cu_2O(s) + C(s) \longrightarrow 2Cu(s) + CO(g)$$

and for this we have

$$\Delta_f G^\ominus(CO) < \Delta_f G^\ominus (Cu_2O)$$

6.4 *Explain: (i) Zone refining (ii) Column chromatography.*

Ans. (*i*) **Zone refining:** The method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal.

As the heater moves forward the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and heater is moved in the same direction. At one end impurities get concentrated. This end is cut off. This method is very useful for producing semiconductor and other metals of very high purity.

For example, germanium, silicon, boron gallium and indium.

(*ii*) **Column chromatography:** In column chromatography Al_2O_3 is taken as adsorbent which acts as stationary phase. The mixture of substances to be separated is dissolved in suitable solvent called eluent which acts as mobile phase. The components get separated due to differential adsorbing power. The component which has maximum adsorbing power moves slowest whereas substances which has least adsorbing power moves fastest and thus, they get separated.

6.5 *Out of C and CO, which is a better reducing agent at 673 K?*

Ans. CO (Carbon monoxide).

6.6 *Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present?*

Ans. The common elements present in the anode mud are antimony, selenium, tellurium, silver, gold and platinum. Since these elements are less reactive and not affected by Cu, Cu^{2+} ion and H_2SO_4 solution and hence settle down under anode as anode mud.

6.7 *Write down the reactions taking place in different zones in the blast furance during the extraction of iron.*

Ans. Zinc blende is ZnS. Following steps are involved in the extraction of zinc from it:

(*i*) Concentration by froth floatation method.

(*ii*) Roasting to the oxide form.

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

(*iii*) Reduction of ZnO to Zn by coke at about 1673 K.

$$ZnO(s) + C(s) \xrightarrow{1673K} Zn(g) + CO(g)$$

At this temperature zinc vapours are collected as zinc metal.

(*iv*) *Purification* of zinc is done by electrolytic refining using Al as cathode and Pb as anode. The electrolyte is $ZnSO_4$.

Reaction at cathode: $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$

Reaction at anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

$ZnSO_4$ electrolyte is added from time to time.

6.8 *Write down the reactions taking place in the extraction of zinc from zinc blende.*

Ans. At 500–800 K

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O4 + CO_2;$$
$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$
$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

At 900–1500 K

$$C + CO_2 \longrightarrow 2CO$$
$$FeO + CO \longrightarrow Fe + CO_2$$
$$C + O_2 \longrightarrow CO_2$$

At above 1570 K

$$FeO + C \longrightarrow Fe + CO$$
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (slag)}$$

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

Ans. During the metallurgy of copper from copper pyrites, $CuFeS_2$, its roasting gives FeO besides Cu_2O and SO_2, respectively.

$$4CuFeS_2(s) + 11O_2(g) \longrightarrow 4FeO(s) + 2Cu_2O(s) + 8SO_2(g)$$

(Copper pyrites)

To remove FeO, SiO_2 is added to form slag.

$$FeO(s) + SiO_2(s) \longrightarrow FeSiO_3(l)$$

(basic oxide) (acidic oxide) slag

6.10 *What is meant by the term "chromatography"?*

Ans. Chromatography is a technique for analysing or separating mixtures of gases, liquids or dissolved substance. The technique was discovered by a Russian botanist Mikhail

Tsvet. The term chromatography was derived from the Greek word *chroma* meaning colour and *graphy* for writing. It was used for the first time to separate the colour pigments of plants.

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

Ans. In chromatography the stationary phase is generally an adsorbent material such as silica gel or alumina. The adsorbent can be spread over a flat glass plate (Thin-layer chromatography) or taken in a glass tube (column chromatography). The criterion of selecting an adsorbent, *i.e.*, the stationary phase depends on the different adsorbing powers of the components of a mixture to be separated. The least absorbed component is eluted first followed by other components.

In paper chromatography the stationary phase is water held in the pores of the paper. Here, the separation depends upon the different distribution of the components between water in stationary phase and the element.

6.12 *Describe a method for refining nickel.*

Ans. When impure nickel is heated in a current of CO at 330–350 K, it forms volatile nickel tetracarbonyl leaving behind the impurities. The nickel tetracarbonyl thus obtained is then heated to a higher temperature (450–470 K), when it undergoes thermal decomposition to give pure nickel.

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

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

This method is commonly called as Mond process for refining of nickel.

6.13 *How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.*

Ans. Alumina is contaminated with impurities like silica and iron (III) oxide. It is purified by the Bayer process by making use of the amphoteric nature of the oxides. Silica (SiO_2) is an acidic oxide, Al_2O_3 is amphoteric, while Fe_2O_3 is basic oxide. Alumina is treated with hot concentrated solution of caustic soda, NaOH when Al_2O_3 dissolves.

$$\underset{\text{Amphoteric}}{Al_2O_3}\,(s) + \underset{\text{Acidic}}{SiO_2}\,(s) + \underset{\text{Basic}}{Fe_2O_3}\,(s) + 4\,(30\%)\,NaOH\,(aq)$$

$$+ 5H_2O\,(aq) \xrightarrow{463K} 2Na\,[Al(OH)_4]\,(aq)$$

$$+ Na_2\,[Si(OH)_6]\,(aq) + Fe_2O_3\,(s)$$

The insoluble materials are removed by filteration and $Al_2O_3 \cdot xH_2O$ is precipitated by treating the solution with CO_2 gas.

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

Silicate compound remains in the solution.

The hydrated alumina is filtered and heated to get pure Al_2O_3:

$$Al_2O_3 \cdot xH_2O(s) \xrightarrow{1473K} Al_2O_3\,(s) + xH_2O(g)$$

6.14 *Giving examples differentiate between 'roasting' and 'calcination'.*

Ans. **Calcination:** It is a process in which ore is heated in absence of air so as to remove volatile impurities. It is used to convert carbonate ore into oxide. It is also used to remove moisture and water of crystallization in hydrated ores *e.g.*,

$$Fe_2O_3 \cdot xH_2O \xrightarrow{heat} Fe_2O_3 + xH_2O$$

$$\underset{\text{Calamine}}{ZnCO_3} \xrightarrow{heat} ZnO + CO_2$$

$$\underset{\text{Siderite}}{FeCO_3} \xrightarrow{heat} FeO + CO_2$$

$$\underset{\text{Malachite}}{CuCO_3 \cdot Cu(OH)_2} \xrightarrow{heat} 2CuO + H_2O + CO_2$$

$$\underset{\text{Dolomite}}{MgCO_3 \cdot CaCO_3} \xrightarrow{heat} MgO + CaO + 2CO_2$$

Roasting: It is a process in which sulphide ore is heated in presence of oxygen so as to convert into oxide.

Sulphur dioxide.

$$2ZnS\,(s) + 3O_2\,(g) \longrightarrow 2ZnO\,(s) + 2SO_2\,(g)$$

$$\underset{\text{Galena}}{2PbS\,(s)} + 3O_2\,(g) \longrightarrow 2PbO\,(s) + 2SO_2\,(g)$$

$$\underset{\text{Ironpyrite}}{4FeS_2\,(s)} + 11O_2\,(g) \longrightarrow 2Fe_2O_3\,(s) + 8SO_2\,(g)$$

$$\underset{\text{Copper glance}}{2Cu_2S\,(s)} + 3O_2\,(g) \longrightarrow 2Cu_2O\,(s) + 2SO_2\,(g)$$

6.15 *How is 'cast iron' different from 'pig iron"?*

Ans. Impure iron obtained from blast furnace is known as pig iron and cast into pigs (blocks). It contains 4-5 per cent of carbon along with some phosphorus, silicon, manganese and sulphur.

Cast iron contains a less percentage of carbon (1.8 to 3 per cent) made by melting pig iron with scrap iron and coke using hot air blast.

6.16 *Differentiate between minerals and ores.*

Ans. A mineral is the naturally occurring compound of a metal. An ore is a mineral used to extract metal economically. All ores are minerals whereas all minerals are not ores.

6.17 *Why copper matte is put in slica lined converter?*

Ans. Main components of copper matte are Cu_2S and FeS (obtained from copper pyrites). When a blast of hot air is passed both are converted into their respective oxides. Since the convertes is lined with silica, SiO_2, which combines with FeO to form slag thus purifying Cu_2O.

$$2Cu_2S(s) + 3O_2(g) \longrightarrow 2Cu_2O(s) + 2SO_2(g)$$

$$2FeS(s) + 3O_2(g) \longrightarrow 2FeO(s) + 2SO_2(g)$$

$$FeO(s) + SiO_2\,(s) \longrightarrow FeSiO_3(s)$$

(Basic) (Acidic) Slag

6.18 *What is the role of cryolite in the metallurgy of aluminum?*

Ans. Cryolite, Na_3AlF_6, dissolves alumina, Al_2O_3, and lowers the molten temperature of electrolyte.

6.19 *How is leaching carried out in case of low grade copper ores?*

Ans. Leaching of low grade copper ores is done by spraying dil. H_2SO_4 on the heap of ore in the presence of air when copper goes into solution as Cu^{2+} ions.

$$CuCO_3(s) + H_2SO_4(aq) \longrightarrow CuSO_4\,(aq) + CO_2(g) + H_2O(l)$$

$$CuO(s)\ H_2SO_4\,(aq) \longrightarrow CuSO_4\,(aq) + H_2O(l)$$

6.20 *Why is zinc not extracted from zinc oxide through reduction using CO?*

Ans. Following redox reaction will occur when ZnO is reduced with CO gas:

$$ZnO(s) + CO(g) \longrightarrow Zn(s) + CO_2(g)$$

For this reaction to occur Gibbs energy of formation for CO_2, $\Delta_f G^\ominus(CO_2)$ should be less than that of ZnO, *i.e.* $\Delta_f G^\ominus$ (ZnO).

From Ellingham diagrams it becomes evident that

$$\Delta_f G^\ominus(CO_2) > \Delta_f G^\ominus (ZnO)$$

Hence CO cannot be used as a reducing agent for ZnO.

6.21 *The value of $\Delta_f G^\ominus$ for formation of Cr_2O_3 is –540 kJmol^{-1} and that of Al_2O_3 is –827 kJmol^{-1}. Is the reduction of Cr_2O_3 possible with Al?*

Ans. Reduction of Cr_2O_3 by Al (Thermit process) is

$$Cr_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Cr(s \text{ or } l)$$

$\Delta_f G^\ominus$/kJ mol^{-1}	–540	0	–827	0

Gibbs energy change for the reduction reaction would be

$$\Delta_r G^\ominus = -827 - (-540)$$
$$= -287 \text{ kJ mol}^{-1}$$

Negative value of $\Delta_r G^\ominus$ suggests that the reaction is spontaneous and will occur. (The reaction represents **alumina thermit process**. It is highly exhothermic. However, to initiate the reaction high temperature is required. Once the reaction starts it goes to completion.)

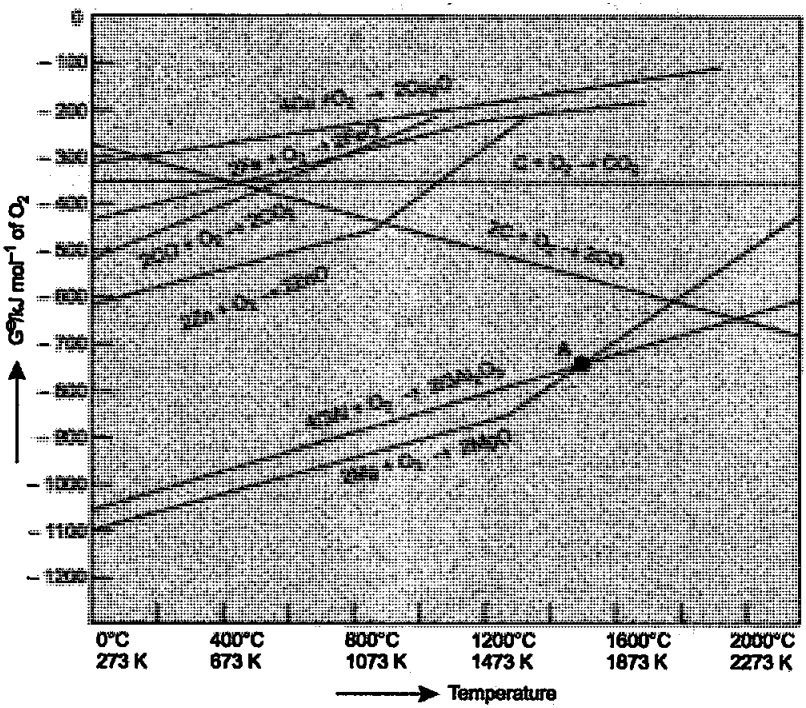
6.22 *Out of C and CO, which is a better reducing agent for ZnO?*

Ans. Carbon is a better reducing agent than CO for ZnO.

6.23 *The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples.*

Ans. Thermodynamic factor helps us in choosing a suitable reducing agent for the reduction of a particular metal oxide to the metallic state as discussed below:

From the Ellingham diagram it is clear that metals for which the standard free energy of formation (DfG$^\ominus$) of their oxides is more negative can reduce metal oxides for which the standard free energy of formation (DfG$^\ominus$) of their respective oxides is less negative.



6.24 *Name the processes from which chlorine is obtained as a by-product. What will happen if an aqueous solution of NaCl is subjected to electrolysis?*

Ans. (*i*) During the preparation of sodium metal by Down's process. Chlorine is obtained as a by-product. In this process molten NaCl containing $CaCl_2$ (as flux to lower the fusion temperature) is electrolysed when sodium is obtained at the cathode and chlorine at the anode:

$$NaCl\ (s) \xrightarrow{873K} Na^+\ (melt) + Cl^-\ (melt)$$

At cathode $Na^+\ (melt) + e^- \longrightarrow Na\ (l)$

At anode $2\ Cl^-\ (melt) \longrightarrow Cl_2\ (g) + 2e^-$

(*ii*) When an aqueous solution of NaCl is electrolysed, H_2 gas is evolved at the cathode while Cl_2 is evolved at the anode. Consider the half-reactions occurring at cathode:

$$Na^+\ (aq) + e^- \longrightarrow Na\ (s)\quad E^\ominus_{red} = -2.71\ V$$

$$2H_2O\ (l) + 2e^- \longrightarrow H_2\ (g) + 2OH^-\quad E^\ominus_{red} = -0.83\ V$$

On comparing $E^{\ominus}$ values of the two half-reactions, it becomes clear that H_2O will be reduced to H_2 (g), rather than Na^+ (aq) to Na (s). That is, the H_2O/H_2 half-reaction has a less negative reduction potential than the Na^+ (aq)/ Na (s) half-reaction.

Likewise, we can inspect the oxidation reactions occurring at anode as:

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-;\ E^{\ominus}_{ox} = -1.36\ V$$

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-;\ E^{\ominus}_{ox} = -1.23\ V$$

Here Cl^- ions get oxidised in preference to H_2O molecules since its $E^{\ominus}_{ox}$ is lower than that of H_2O molecules.

Hence, the overall reaction of the electrolysis of an aqueous solution of NaCl would be:

At cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

At anode: $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

6.25 *What is the role of graphite rod in the electrometallurgy of aluminium?*

Ans. Graphite anode is used in the electrometallurgy of aluminium from alumina, Al_2O_3, to prevent the liberation of O_2 gas at the anode which may react with Al metal to give Al_2O_3 again. Oxygen so liberated at high temperature reacts with graphite to form both CO_2 and CO gases:

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

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

6.26 *Outline the principles of refining of metals by the following methods:*

(i) Zone refining

(ii) Electrolytic refining

(iii) Vapour phase refining

Ans. (i) **Zone refining:** It is based on the principle that impurities are more soluble in melt than in solid state of the metal. The impure metal rod is heated with the help of circular heater from one end. The impurities move along with the heater and reach the other end which is discarded and pure metal is obtained.

(ii) **Electrolytic refining:** In this method, impure metal is taken as anode whereas pure metal is taken as cathode.

Soluble salt of metal is taken as electrolyte. Impure metal changes into ions and get attracted towards cathode to form pure metal.

(*iii*) **Vapour phase refining:** In this process impure metal is treated with suitable reagent to form volatile compound which gets decomposed at high temperature to get pure metal.

6.27 *Predict conditions under which Al might be expected to reduce MgO.*

Ans. Above 1623 K, Al can reduce MgO to Mg, so that DrG° becomes –ve and the process becomes thermodynamically feasible.

$$3MgO + 2Al \xrightarrow{\text{heat}} Al_2O_3 + 3Mg$$

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