Chapter- General principles and process of isolation of elements

6.1. Which of the ores mentioned in Table 6.1 can be concentrated by magnetic separation method?

Ans. If the ore or gangue can be attracted by a magnetic field, then magnetic separation can be used to concentrate the ore. Magnetic separation can be used to separate iron ores such as haematite $\left(Fe_2O_3\right)$, magnetite $\left(Fe_3O_4\right)$, siderite $\left(FeCO_3\right)$,, and iron pyrites $\left(FeS_2\right)$.

6.2. What is the significance of leaching in the extraction of aluminium?

Ans. Leaching is important in the extraction of aluminium because it concentrates pure alumina $\left(Al_2O_3\right)$ from bauxite ore. Impurities in bauxite include silica, iron oxide, and titanium oxide. Alumina is concentrated in the leaching process by digesting powdered ore with a concentrated solution of $NaOH$ at 473-523 K and 35-36 bar. Alumina $\left(Al_2O_3\right)$ dissolves as sodium meta-aluminate and silica $\left(SiO_2\right)$ dissolves as sodium silicate under these circumstances, leaving the impurities behind.

$$\underset{\text{Alumina}}{Al_2O_{3(x)}}+2NaOH_{(aq)}+3H_2O \underset{35\text{-}36bar}{\overset{473\text{-}523K}{\rightarrow}} 2Na\left[Al(OH)_4\right]_{(aq)}$$

$$\underset{\text{Silica}}{SiO_{2(l)}}+2NaOH_{(aq)} \underset{35\text{-}36bar}{\overset{473\text{-}523K}{\rightarrow}} NaSiO_{3(aq)}+H_2O_{(l)}$$

After filtering out the contaminants, the solution is neutralised by passing CO_2 gas through it. Hydrated $\left(Al_2O_3\right)$ is precipitated in this procedure, leaving sodium silicate in the solution. Seeding the solution with freshly prepared samples of hydrated $\left(Al_2O_3\right)$ causes precipitation.

$$2Na\left[Al(OH)_4\right]_{(aq)}+CO_{2(g)} \rightarrow \underset{\text{Hydrated aluminia}}{Al_2O_3.xH_2O_{(x)}}+2NaHCO_{3(aq)}$$

The resulting hydrated alumina is filtered, dried, and heated to get pure alumina $\left(Al_2O_3\right)$.

$$Al_2O_3.xH_2O_{(x)} \xrightarrow{1470K} Al_2O_{3(s)}+xH_2O_{(g)}$$

6.3 The reaction,

$$Cr_2O_3+2Al \rightarrow Al_2O_3+2Cr \quad (\Delta G_0=-241kJ)$$

is thermodynamically feasible as is apparent from the Gibbs energy value. Why does it not take place at room temperature?

Ans. The equilibrium constant, K, is related to the change in Gibbs energy.

$\Delta G = - RT \ln K$

All the reactants and products of a particular reaction are solid at room temperature. As a result, there is no equilibrium between the reactants and products. As a result, the reaction does not occur at room temperature. At a greater temperature, however, chromium melts and the reaction occur. We also know that the equation says that

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

As the temperature rises, the value of the value of the value of the value of the value of the value of the value of the value of the value of the value of the value of the value When a result, as the temperature rises, the reaction becomes more viable.

6.4 Is it true that under certain conditions, Mg can reduce SiO and Si can reduce MgO? What are those conditions?

Ans.

$$Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)} \left[\Delta G_{(Mg.MgO)}\right]$$

$$Si_{(s)} + O_{2(g)} \rightarrow SiO_{2(s)} \left[\Delta G_{(Si.SiO_2)}\right]$$

Mg can convert SiO_2 to Si in the temperature range when $\left[\Delta G_{(Mg.MgO)}\right]$ is smaller than $\left[\Delta G_{(Si.SiO_2)}\right]$

Si, on the other hand, can convert MgO to Mg at temperatures where $\left[\Delta G_{(Si.SiO_2)}\right]$ is smaller than $\left[\Delta G_{(Mg.MgO)}\right]$.

$SiO_2 + 2Mg \rightarrow SiO_2 + 2Mg;\ \Delta G^{-} = \text{-ve}$

The temperature at which these two chemicals' $\Delta_f G$ curves cross is 1966 K. Mg can reduce SiO_2 at temperatures below 1966 K, while Si can reduce MgO at temperatures over 1966 K.

Example Exercises

Ex 6.1 Suggest a condition under which magnesium could reduce alumina.

Ans. The two equations are as follows:

(a) $\frac{4}{3}\ Al \rightarrow O_2\ \frac{2}{3}\ Al_2O_3$

(b) $2Mg + O_2 \rightarrow 2MgO$

The $\Delta_r G^{-}$ for the reaction becomes ZERO at the point of junction of the Al_2O_3 and MgO curves (marked "A" in illustration 6.4).

$$\frac{2}{3}\ Al_2O_3 + 2Mg \rightarrow 2MgO + \frac{4}{3}\ Al$$

Magnesium can decrease alumina below that point.

Ex. 6.2 Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium. Why?

Ans. Magnesium can reduce alumina at temperatures below the point of junction of the Al_2O_3 and MgO curves. However, the procedure will be costly.

Ex. 6.3 Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

Ans. When a metal is in a liquid condition, its entropy is higher than when it is in a solid state. When the metal created is liquid and the metal oxide being reduced is solid, the entropy change (S) of the reduction process is more on the positive side. As a result, the value of $\Delta_r G^{-}$ shifts to the negative side, making reduction easier.

Ex. 6.4 At a site, low grade copper ores are available, and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?

Ans. Zinc is more reactive than iron in the electrochemical series, the reduction will be faster if zinc scraps are employed. However, because zinc is a more expensive metal than iron, it will be more cost effective to use iron waste.

Exercises

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

Ans. Zinc and iron can be employed in hydrometallurgy to remove copper from a solution. More reactive metals, i.e., metals with lower reduction potentials than zinc, such as Mg, Ca, K, and others, are needed to supplant zinc. As a result, hydrometallurgy may extract copper but not zinc.

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

Ans. Certain sorts of particles are prevented from frothing with bubbles by depressants. We can now distinguish two sulphide ores because of this. For an ore containing ZnS and PbS sodium cyanide, for example, is a depressant. $NaCN$ prevents the formation of a froth on the surface of ZnS by producing a layer of the complex $Na_2[Zn(CN)_4]$. As a result, it has a depressive effect. $NaCN$, on the other hand, does not prevent PbS from generating froth and permits it to do so.

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

Ans. Copper-copper oxide line is almost at the top of the Ellingham diagram (graph of $\Delta_r G^o$ vs T) for oxide production. As a result, burning copper oxide ores with coke can quickly convert them to copper. At high temperatures, the ΔG^o vs T lines for CO have a negative slope. As a result, copper oxide can be easily reduced to copper. Sulphide ores, on the other hand, have a greater ΔG^o than CS_2 ores (which is an endothermic compound). As a result, copper extraction from pyrite ore is challenging.

6.4 Explain:

(i) Zone refining

(ii) Column chromatography.

Ans. (i) Zone refining

It's utilised to refine Si, B, Ga and ln, among other things. In the molten form of metal, impurities are more soluble than in the solid state. At one end of an impure metal rod is a circular mobile heater. The molten zone and the heater migrate from one end to the other. Impurities pass into the adjacent molten zone as pure metal crystallises out of the melt. This method is repeated numerous times to separate contaminants at one end of a rod. The impurity-filled end can then be removed.

(ii) Column chromatography

It's used to separate and purify things. It is based on the difference in a metal's and its impurities' adsorption tendencies on a suitable adsorbent. Different components of a mixture are adsorbed on an adsorbent in different ways.

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

Ans. The ΔG^o vs T line for CO, CO_2 is lower than the C, CO line at 673 K. As a result, at 673 K, CO is a superior reducing agent than C.

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

Ans. Antimony, selenium, tellurium, silver gold, and platinum are all found in the anode mud used in the electrolytic purification of copper. Blister copper contains contaminants. They are less reactive and unaffected by $CuSO_4$-H_2SO_4 solution, thus they settle as anode mud beneath the anode.

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

Ans. Iron oxides are reduced at various temperatures in a blast furnace. The temperature in the lowest half of the blast furnace can reach 2200 K. It's known as the combustion zone. The temperature reaches as low as 500800 K at the summit. It's known as a reduction zone. Carbon is the reducing agent at lower temperatures, while CO is the reducing agent at higher temperatures. The following reactions take place in the reduction zone (500–800 K).

$$3Fe_2O_3+CO \rightarrow 2Fe_3O_4+CO_2$$
$$Fe_3O_4+4CO \rightarrow 3Fe+4CO_2$$
$$Fe_2O_3+CO \rightarrow 2FeO+CO_2$$

The following reactions take place in the temperature range of 900-1500 K.

$$C+CO_2 \rightarrow 2CO$$
$$FeO+CO \rightarrow Fe+CO_2$$

Decomposition of limestone produces lime (CaO) and CO_2 at 1270 K (middle section). Lime is a flux that reacts with silicate impurities to generate calcium silicate slag.

$$CaCO_3 \rightarrow CaO+CO_2$$
$$CaO+SiO_2 \rightarrow CaSIO_3$$

6.8 Write chemical reactions taking place in the extraction of zinc from zinc blende

Ans. The reactions that occur during the extraction of Zn from zinc blende (ZnS) are as follows:

(i) ZnS is roasted at 1200 K in excess air to produce ZnO.

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

(ii) ZnO is converted to Zn by heating it with crushed coke at 1673 K.

$$ZnO+C \xrightarrow{1676K} Zn+CO$$

(iii) In order to refine impure zinc, electrorefining is used. The anode is made of impure zinc, while the cathode is made of pure zinc. Zinc sulphate and dilute sulphuric acid make up the electrolyte (small amount). Zinc is deposited on the cathode and collected when current is passed.

$$\text{At anode : } Zn \rightarrow Zn^{2+}+2e^-$$
$$\text{At cathode: } Zn^{2+} \rightarrow +2e^- \rightarrow Zn$$

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

Ans. A combination of FeO and Cu_2O is formed during the roasting of pyrite ore. The function of silica in copper metallurgy is to remove iron oxide formed during the extraction of pure copper from copper pyrite. SiO functions as an acidic flux that reacts with iron oxide (FeO) to generate iron silicate ($FeSiO$).

6.10 Which method of refining may be more suitable if element is obtained in minute quantity?

Ans. If an element is obtained in small quantities, column chromatography is the refining technique to use.

6.11 Which method of refining will you suggest for an element in which impurities present have chemical properties close to the properties of that elements?

Ans. If an element is obtained in small quantities, column chromatography is the refining technique to use.

6.12 Describe a method for refining nickel.

Ans. Mond's technique is used to refine nickel. Nickel is heated in the presence of carbon monoxide in this process, resulting in nickel tetracarbonyl, a volatile complex. The nickel tetracarbonyl produced is then decomposed at a higher temperature (450 - 470 K) to get pure nickel metal.

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

Ans. The powdered ore is first digested with a concentrated $NaOH$ solution at 473 - 523 K and 35 - 36 bar pressure to separate alumina from silica in bauxite ore coupled with silica. This causes alumina (Al_2O_3) and silica (SiO_2)to leach out as sodium aluminate and sodium silicate, respectively, leaving the impurities behind.

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

Ans. Roasting is the conversion of sulphide ore to oxide. The ore is heated in the furnace with a constant supply of air, below its melting temperature: for example, zinc, lead, and copper sulphide ore.

$$2ZnS+3O_2 \rightarrow 2ZnO+2SO_2$$
$$2PbS+3O_2 \rightarrow 2PbO+2SO_2$$
$$2Cu_2S+3O_2 \rightarrow 2Cu_2O+2SO_2$$

Calcination is a process that converts hydroxide and carbonate ore to oxide in the presence of a restricted amount of oxygen. In this procedure, the temperature should be below the melting point of the metal because volatile stuff escapes, leaving behind the metal oxide.

$$Fe_2O_3.xH_2O \xrightarrow{\Delta} Fe_2O_3(s)+xH_2O(g)$$
$$ZnCO_3 \xrightarrow{\Delta} ZnO(s)+CO_2(g)$$
$$CaCO_3.MgCO_3 \xrightarrow{\Delta} CaO(s)+MgO(s)+2CO_2(g)$$

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

Ans. Although both pig iron and cast iron contain main elements of iron, their preparation, characteristics, and applications are distinct. For various uses, iron is employed in a variety of businesses and factories. As a result, we must separate iron from its ore.

In a blast furnace, iron is recovered from its oxide ore through reduction. Different reducing chemicals reduce iron at different stages in the furnace. Finally, molten iron is obtained from the blast furnace. To make pig iron, the molten iron can solidify. Carbon and other impurities such as Si, P, S, and Mn make up around 4% of pig iron.

Cast iron has a carbon content of roughly 3%, which is slightly lower than pig iron. Cast iron is made by remelting pig iron and casting it into metal pieces. In comparison to pig iron, cast iron is extremely hard and brittle.

6.16 Differentiate between "minerals" and "ores"

Ans. Minerals are naturally occurring substances that contain metals in some form. They are obtained via mining and are present in the earth's crust.

Metals may be cheaply recovered from ore, which are unique minerals. It has a distinct make-up. Every ore is a mineral, but not all minerals are ore.

6.17 Why copper matte is put in silica lined converter?

Ans. Cu_2S and FeS are found in copper matte. The remaining FeO and FeS contained in the copper matte are removed as slag in a silica-lined converter $(FeSiO_3)$. In addition, a small amount of silica is added to the silica-lined converter. Then a burst of hot air is blown. As a result, the remaining FeS and FeO are transformed to iron silicate $(FeSiO_3)$., while Cu_2S becomes metallic copper.

6.18 What is the role of cryolite in the metallurgy of aluminium?

Ans. Cryolite is added to bauxite ore before electrolysis for the following reasons.

(1) It could serve as a solvent.

(2) It lowers the alumina melting temperature to 1173 K.

(3) It improves the electrical conductivity of the material.

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

Ans. Copper from low-grade copper is leached off with acid in the presence of oxygen.

$$Cu+2^{H+}+0.5O_2\rightarrow Cu^{2+}+2H_2O$$

After that, the solution is treated with scrap iron or hydrogen.

$$Cu^{2+}+H_2\rightarrow Cu+2H^{+}$$

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

Ans. Zinc is not recovered from zinc oxide by using CO to reduce it. The reducing agent should have a lower ΔG value. However, because Zn has a lower negative G value than CO in this circumstance, it cannot be reduced by CO.

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

Ans. The lower the ΔG value, the more stable the compound is. The negative value of $\Delta_f G^-$ of Al_2O_3 is greater than that of Cr_2O_3 in this case. As a result, Al_2O_3 has a higher stability than Cr_2O_3. As a result, it is feasible to create Al_2O_3 by reducing Cr_2O_3 with Al_2O_3. As a result, it is conceivable.

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

Ans. In comparison to CO, C is a better reducing agent for ZnO. Furthermore, the Gibbs free energy of CO_2 formation from CO is always greater than the Gibbs free energy of ZnO formation. As a result, CO can't be utilised to decrease ZnO. When compared to CO, C is a better reducing agent for reducing 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. The thermodynamic factor aids in the selection of an appropriate reducing agent for the reduction of a metal oxide to metal. The Ellingham diagram, which depicts $\Delta_f G^-$ versus T for the generation of oxides, can be used to estimate the feasibility of thermal reduction. It may be predicted from the diagram that metals with a higher standard free energy of formation of their oxides will reduce metal oxides with a lower standard free energy of formation. In other words, because the standard free energy change ($\Delta_r G^-$) of the combined redox reaction will be -ve by an amount equal to the difference in $\Delta_f G^-$ of two metal oxides, a metal will reduce the oxides of other metals that lie above it in Ellingham diagram. FeO can be reduced to Fe by both Al and Zn, however Fe cannot reduce Al_2O_3 to Al or ZnO to Zn. C can also decrease ZnO to Zn, but not CO. As a result, the choice of a reducing agent is influenced by a thermodynamic component.

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. The electrolysis of $NaCl$ produces chlorine as a byproduct in Down's sodium manufacturing process.

$$\mathrm{NaCl(l)} \xrightarrow{\text{Electrolysis}} \mathrm{Na^{+}(melt)+Cl^{-}(melt)}$$

$$\text{At anode : } \mathrm{Cl^{-}(melt) \rightarrow Cl(g)+e^{-}}$$

$$\mathrm{Cl(g)+Cl(g) \rightarrow Cl_2(g)}$$

$$\text{At cathode : } \mathrm{Na^{+}(melt)+e^{-} \rightarrow Na(s)}$$

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

Ans. During the electrolysis of alumina, graphite rod serves as an anode and graphite line iron serves as a cathode. Aluminium is liberated at the cathode and oxygen is liberated at the anode during electrolysis. This oxygen combines with the graphite anode to produce CO and $\mathrm{CO_2}$, which prevents the oxygen from oxidising the aluminium. As a result, graphite's job in aluminium electrometallurgy is to prevent oxygen from being liberated, preventing the aluminium from being oxidised by oxygen.

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) Refining zones

It's utilised to refine $\mathrm{Si, B, Ga}$ and ln, among other things. In the molten form of metal, impurities are more soluble than in the solid state. At one end of an impure metal rod is a circular mobile heater. The molten zone and the heater migrate from one end to the other. Impurities pass into the adjacent molten zone as pure metal crystallises out of the melt. This method is repeated numerous times to separate contaminants at one end of a rod. The impurity-filled end can then be removed.

(ii) Refining by electrolysis

It is carried out to refine impure zinc. The cathode is pure zinc, while the anode is impure zinc. Zinc sulphate and dilute sulphuric acid make up the electrolyte (small amount). Zinc is deposited on the cathode and collected when current is passed.

(iii) Refining in the vapour phase

Metal is transformed into a volatile molecule, which is then degraded to yield pure metal. $\mathrm{Ni, Zr}$ and Ti are refined using this process.

The volatile nickel tetracarbonyl is formed when Ni is heated with CO.

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

Ans. Mg can reduce $\mathrm{Al_2O_3}$ below $1350^{0}\mathrm{C}$, while Al can reduce MgO beyond $1350^{0}\mathrm{C}$, .

ΔG^{-} Vs T plots can be used to deduce this. MgO lies below the ΔG^{-} Vs T plot for Al in the

ΔG^{-} Vs T plot for Mg . G^{-} for combined reaction is zero at the point of intersection (equivalent to 1350^0C,). Mg , MgO curve is higher than Al_2O_3 curve after 1350^0C, . Higher temperatures are difficult to achieve in practise.