

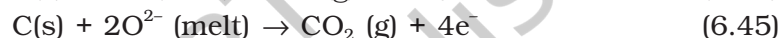
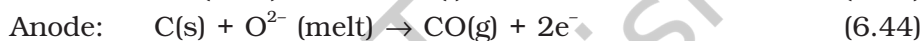
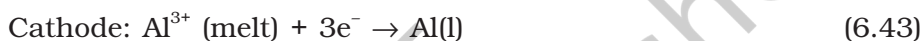
Aluminium

In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel vessel with lining of carbon acts as cathode and graphite anode is used. The overall reaction may be written as:



This process of electrolysis is widely known as **Hall-Heroult process**.

Thus 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 . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are:



Copper from Low Grade Ores and Scraps

Copper is extracted by *hydrometallurgy* from low grade ores. It is leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2 (equations 6.40; 6.46).



Example 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?

Solution

Zinc being above iron in the electrochemical series (more reactive metal is zinc), the reduction will be faster in case zinc scraps are used. But zinc is costlier metal than iron so using iron scraps will be advisable and advantageous.

6.6 Oxidation Reduction

Besides reductions, some extractions are based on oxidation particularly for non-metals. A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is abundant in sea water as common salt) .



The ΔG^\ominus for this reaction is + 422 kJ. When it is converted to E^\ominus (using $\Delta G^\ominus = -nE^\ominus F$), we get $E^\ominus = -2.2$ V. Naturally, it will require an external emf that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions (Unit-3, Section 3.5.1). Thus, Cl_2 is obtained by electrolysis giving out H_2 and aqueous NaOH as by-products. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.

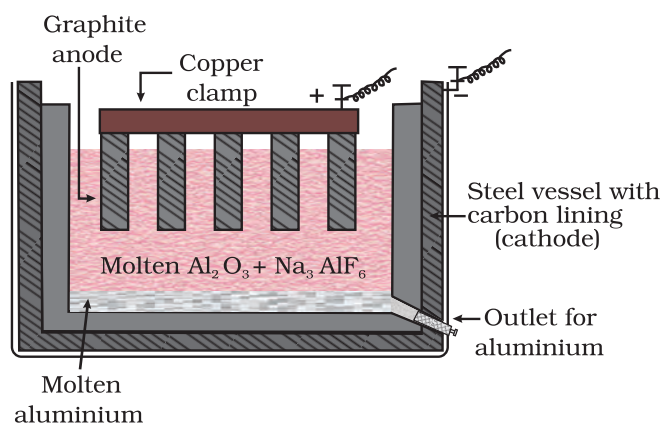
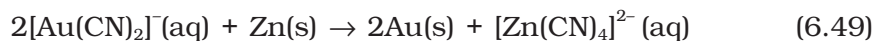
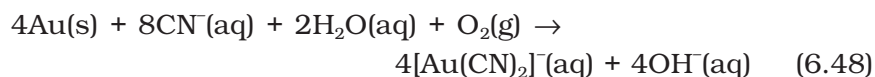


Fig. 6.7: Electrolytic cell for the extraction of aluminium

As studied earlier, extraction of gold and silver involves leaching the metal with CN^- . This is also an oxidation reaction ($\text{Ag} \rightarrow \text{Ag}^+$ or $\text{Au} \rightarrow \text{Au}^+$). The metal is later recovered by displacement method.



In this reaction zinc acts as a reducing agent.

6.7 Refining

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

- | | |
|---------------------------|-----------------------------|
| (a) Distillation | (b) Liquation |
| (c) Electrolysis | (d) Zone refining |
| (e) Vapour phase refining | (f) Chromatographic methods |

These are described in detail here.

(a) Distillation

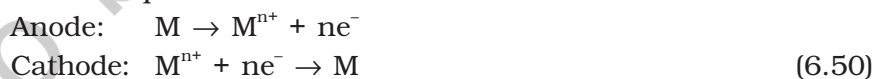
This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

(b) Liquation

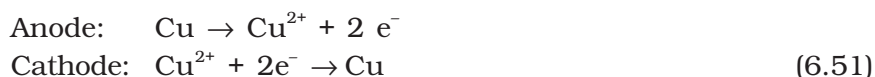
In this method a low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

(c) Electrolytic refining

In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud. This process is also explained using the concept of electrode potential, over potential, and Gibbs energy which you have seen in previous sections. The reactions are:



Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:



Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining. Zinc may also be refined this way.

(d) 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 mobile heater surrounding the rod of impure metal is fixed at its one end (Fig. 6.8). The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises

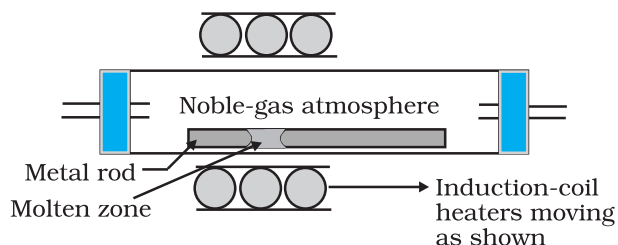


Fig. 6.8: Zone refining process

out of the melt left behind and the impurities pass on into the adjacent new molten zone created by movement of heaters. The process is repeated several times and the heater is moved in the same direction again and again. Impurities get concentrated at one end. This end is cut off. This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

(e) Vapour phase refining

In this method, the metal is converted into its volatile compound which is collected and decomposed to give pure metal. So, the two requirements are:

- the metal should form a volatile compound with an available reagent,
- the volatile compound should be easily decomposable, so that the recovery is easy.

Following examples will illustrate this technique.

Mond Process for Refining Nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex named as nickel tetracarbonyl. This complex is decomposed at higher temperature to obtain pure metal.



van Arkel Method for Refining Zirconium or Titanium: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:



The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal deposits on the filament.



(f) Chromatographic methods

You have learnt about chromatographic technique of purification of substances in Class XI (Unit-12).

6.8 Uses of Aluminium, Copper, Zinc and Iron

Column chromatography is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

Aluminium foils are used as wrappers for food materials. The fine dust of the metal is used in paints and lacquers. Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides. Wires of aluminium are used as electricity conductors. Alloys containing aluminium, being light, are very useful.

Copper is used for making wires used in electrical industry and for water and steam pipes. It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin) and coinage alloy (with nickel).

Zinc is used for galvanising iron. It is also used in large quantities in batteries. It is constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40-50%). Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc. It is used in the manufacture of wrought iron and steel. **Wrought iron** is used in making anchors, wires, bolts, chains and agricultural implements. Steel finds a number of uses. Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes. Chrome steel is used for cutting tools and crushing machines, and stainless steel is used for cycles, automobiles, utensils, pens, etc.

Summary

Although modern metallurgy had exponential growth after Industrial Revolution, many modern concepts in metallurgy have their roots in ancient practices that predated the Industrial Revolution. For over 7000 years, India has had high tradition of metallurgical skills. Ancient Indian metallurgists have made major contributions which deserve their place in metallurgical history of the world. In the case of zinc and high-carbon steel, ancient India contributed significantly for the development of base for the modern metallurgical advancements which induced metallurgical study leading to Industrial Revolution.

Metals are required for a variety of purposes. For this, we need their extraction from the minerals in which they are present and from which their extraction is commercially feasible. These minerals are known as **ores**. Ores of the metal are associated with many impurities. Removal of these impurities to certain extent is achieved in **concentration** steps. The concentrated ore is then treated chemically for obtaining the metal. Usually the metal compounds (e.g., oxides, sulphides) are reduced to the metal. The reducing agents used are carbon, CO or even some metals.

In these reduction processes, the **thermodynamic** and **electrochemical** concepts are given due consideration. The metal oxide reacts with a reducing agent; the oxide is reduced to the metal and the reducing agent is oxidised. In the two reactions, the net Gibbs energy change is negative, which becomes more negative on raising the temperature. Conversion of the physical states from solid to liquid or to gas, and formation of gaseous states favours decrease in the Gibbs energy for the entire system. This concept is graphically displayed in plots of ΔG^\ominus vs T (Ellingham diagram) for such oxidation/reduction reactions at different temperatures. The concept of electrode potential is useful in the isolation of metals (e.g., Al, Ag, Au) where the sum of the two redox couples is positive so that the Gibbs energy change is negative. The metals obtained by usual methods still contain minor impurities. Getting pure metals requires **refining**. Refining process depends upon the differences in properties of the metal and the impurities. Extraction of aluminium is usually carried out from its bauxite ore by leaching it with NaOH. Sodium aluminate, thus formed, is separated and then neutralised to give back the hydrated oxide, which is then electrolysed using cryolite as a flux. Extraction of iron is done by reduction of its oxide ore in blast furnace. Copper is extracted by smelting and heating in a reverberatory furnace. Extraction of zinc from zinc oxides is done using coke. Several methods are employed in refining the metal. Metals, in general, are very widely used and have contributed significantly in the development of a variety of industries.

A Summary of the Occurrence and Extraction of some Metals is Presented in the following Table

Metal	Occurrence	Common method of extraction	Remarks
Aluminium	1. Bauxite, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6	For the extraction, a good source of electricity is required.
Iron	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4	Reduction of the oxide with CO and coke in Blast furnace	Temperature approaching 2170 K is required.
Copper	1. Copper pyrites, CuFeS_2 2. Copper glance, Cu_2S 3. Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ 4. Cuprite, Cu_2O	Roasting of sulphide partially and reduction	It is self reduction in a specially designed converter. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy for low grade ores.
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, ZnCO_3 3. Zincite, ZnO	Roasting followed by reduction with coke	The metal may be purified by fractional distillation.

Exercises

- 6.1 Copper can be extracted by hydrometallurgy but not zinc. Explain.
- 6.2 What is the role of depressant in froth floatation process?
- 6.3 Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?
- 6.4 Explain: (i) Zone refining (ii) Column chromatography.
- 6.5 Out of C and CO, which is a better reducing agent at 673 K ?
- 6.6 Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present ?
- 6.7 Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.
- 6.8 Write chemical reactions taking place in the extraction of zinc from zinc blende.
- 6.9 State the role of silica in the metallurgy of copper.
- 6.10 Which method of refining may be more suitable if element is obtained in minute quantity?
- 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?
- 6.12 Describe a method for refining nickel.
- 6.13 How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.
- 6.14 Giving examples, differentiate between 'roasting' and 'calcination'.
- 6.15 How is 'cast iron' different from 'pig iron'?
- 6.16 Differentiate between "minerals" and "ores".
- 6.17 Why copper *matte* is put in silica lined converter?
- 6.18 What is the role of cryolite in the metallurgy of aluminium?
- 6.19 How is leaching carried out in case of low grade copper ores?
- 6.20 Why is zinc not extracted from zinc oxide through reduction using CO?
- 6.21 The value of ΔG^\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 ?
- 6.22 Out of C and CO, which is a better reducing agent 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.
- 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?
- 6.25 What is the role of graphite rod in the electrometallurgy of aluminium?
- 6.26 Outline the principles of refining of metals by the following methods:
 - (i) Zone refining
 - (ii) Electrolytic refining
 - (iii) Vapour phase refining
- 6.27 Predict conditions under which Al might be expected to reduce MgO. (Hint: See Intext question 6.4)

Answers to Some Intext Questions

- 6.1** Ores in which one of the components (either the impurity or the actual ore) is magnetic can be concentrated, e.g., ores containing iron (haematite, magnetite, siderite and iron pyrites).
- 6.2** Leaching is significant as it helps in removing the impurities like SiO_2 , Fe_2O_3 , etc. from the bauxite ore.
- 6.3** Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.
- 6.4** Yes, below 1350°C Mg can reduce Al_2O_3 and above 1350°C , Al can reduce MgO. This can be inferred from ΔG^\ominus Vs T plots (Fig. 6.4).

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