General Principles and Processes of Isolation of Elements - Part 2

Objectives

After going through this lesson, the learners will be able to understand the following:

- Apply the concept of thermodynamics in metallurgical processes
- Appreciate coupling of reactions to make non-feasible reactions, as feasible
- Evaluate the use of CO or coke as a favourable reducing agent at given temperatures
- Explain why specific reducing agents are used for the reduction purposes
- Apply the knowledge of electrochemistry and redox reactions to extraction of elements

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Introduction

In the previous module of this chapter you studied about the first two steps in metallurgy of metal, *viz.*

- Concentration of ore
- Conversion of metal compound into metal oxide.

Now in this module you will learn how to reduce the metal oxide to metal. In class XI you learnt the concept of feasibility of a reaction on the basis of Free Energy. Recall that only the reactions having a negative value of Gibbs Free Energy are feasible. The basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations.

You must be able to recall that the change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

where, ΔH is the enthalpy change and ΔS is the entropy change for the process.

For any reaction, this change could also be explained through the equation:

$$\Delta G^0 \quad = \quad - RT lnK \qquad (2)$$

where, K is the equilibrium constant of the 'reactant – product' system at the temperature, T. A negative ΔG implies a +ve equilibrium constant K in equation (2). And this can happen only when reaction proceeds towards products.

From these facts we can make the following conclusions**:**

1. When the value of ΔG is negative in equation (1), only then the reaction will proceed. If ΔS is positive, on increasing the temperature (T), the value of $T\Delta S$ would increase ($\Delta H < T\Delta S$) and then ΔG will become –ve as $\Delta G \; = \; \Delta H - T\Delta S$

A very interesting concept is coupling of reactions. If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is –ve, the overall reaction will occur even if individually the reaction is not feasible. So the process of interpretation of free energy values involves coupling of the two reactions, getting the sum of their ΔG and looking for its magnitude and sign. Such coupling is easily understood through Gibbs energy (ΔG^0) *vs* T plots for formation of the oxides (Figure 1). These plots are called the Ellingham Diagram. These graphical representations of Gibbs energy were first used by H.J.T. Ellingham. (Read extra about Ellingham Diagram, in box below)

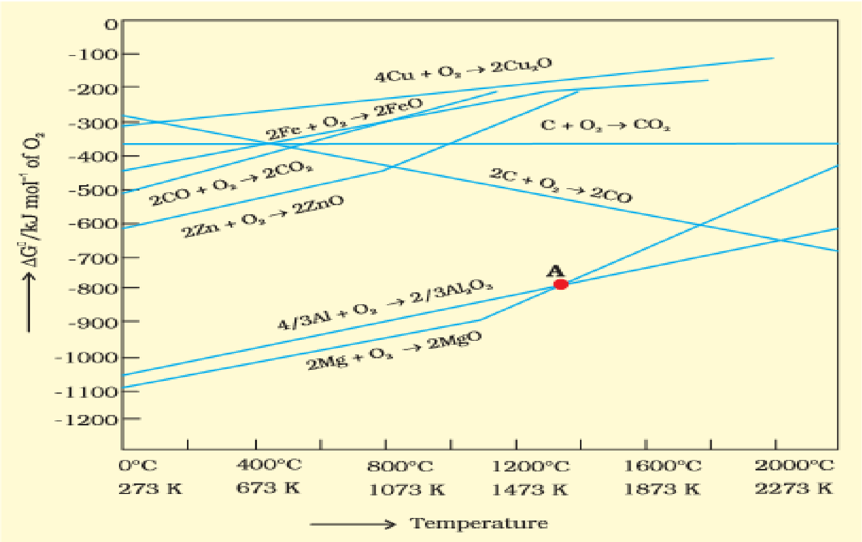

Figure 1: Gibbs energy (ΔG^0) *vs* T plots (schematic) for formation of some oxides: Ellingham Diagram.

Source: NCERT, Chemistry, PartI, XII

The reducing agent gets oxidised to its oxide and in turn the metal oxide is reduced. The role of reducing agent is to provide ΔG^0negative and large enough to make the sum of ΔG^0 of the two reactions (oxidation of the reducing agent and reduction of the metal oxide) negative.

As we know, during reduction, the oxide of a metal decomposes:

$$M_xO(s) \rightarrow xM\ (solid\ or\ liq)\ +\ \tfrac{1}{2}O_2(g) \quad (3)$$

ΔG^0 for reaction (3) is positive as this is a highly endothermic process.The reducing agent takes away the oxygen. Equation (3) can be visualised as the reverse of the oxidation of the metal. And then, the $\Delta_f G^0$ value is written in the usual way:

$$xM(s\ or\ l)\ +\tfrac{1}{2}O_2(g) \rightarrow M_xO(s)\ [\Delta G^{\circ}\ (M, MxO)] \quad (4)$$

If reduction is being carried out through equation (3), the oxidation of the reducing agent (e.g., C or CO) will be there:

$$C(s)\ +\ \tfrac{1}{2}O_2(g) \rightarrow CO(g)\ [\Delta G\ (C,\ CO)] \quad (5)$$

$$CO(g)\ +\tfrac{1}{2}O_2(g) \rightarrow CO_2(g)\ [\Delta G\ (CO,\ CO_2)] \quad (6)$$

If carbon is taken, there may also be complete oxidation of the element to CO_2:

$$\tfrac{1}{2}C(s)\ +\ \tfrac{1}{2}O_2(g) \rightarrow \tfrac{1}{2}CO_2(g)\ [\tfrac{1}{2}\Delta G\ (C,\ CO_2)] \quad (7)$$

On subtracting equation 4 [it means adding its negative or the reverse form as in equation 3] from one of the three equations (5, 6 or 7), we get respectively following reactions (8, 9 or 10):

$$M_xO\ (s)\ +\ C\ (s) \rightarrow xM\ (s\ or\ l)\ +\ CO\ (g) \quad (8)$$

$$M_xO\ (s)\ +\ CO\ (g) \rightarrow xM\ (s\ or\ l)\ +\ CO_2(g) \quad (9)$$

$$M_xO\ (s)\ +\ \tfrac{1}{2}C\ (s) \rightarrow xM\ (s\ or\ l)\ +\ \tfrac{1}{2}CO_2(g) \quad (10)$$

These reactions describe the actual reduction of the metal oxide, M_xO, that we want to accomplish. The ΔG^0 values for these reactions in general, can be obtained by similar subtraction of the corresponding $\Delta_f G^0$values.

As we have seen, heating (i.e., increasing *T*) for a reaction with positive entropy change (+Δ*S*) favours a negative value of $\Delta_r G^0$. Therefore, the temperature is chosen such that the sum of $\Delta_r G^0$in the two combined redox processes is negative. In $\Delta_r G^0$*vs T* plots, this is indicated by the point of intersection of the two curves (curve for M_xO and that for the oxidation of the reducing substance). After that point, the $\Delta_r G^0$value becomes more negative for the combined process including the reduction of M_xO. The difference in the two $\Delta_r G^0$ values after that point determine whether reduction of the oxide of the upper line is feasible by the element represented by the lower line. If the difference is large, the reduction is easier.

Ellingham Diagram

The graphical………..(s→l) or vapourises (l→g) since molecular randomness increases on changing the phase from solid to liquid or from liquid to gas.

Ellingham Diagram

The graphical representation of Gibbs energy was first used by H.J.T. Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as the Ellingham Diagram. Such diagrams help us in predicting the feasibility of thermal reduction of an ore. The criterion of feasibility is that at a given temperature, Gibbs energy of the reaction must be negative.

a) Ellingham diagram normally consists of plots of $\Delta_f G^0$ *vs* T for formation of oxides of elements i.e., for the reaction,

$$2xM(s) \ + \ O_2(g) \rightarrow 2M_xO(s)$$

In this reaction, the gaseous amount (hence molecular randomness) is decreasing from left to right due to the consumption of gases leading to a –ve value of ΔS which changes the sign of the second term in equation (1). Subsequently ΔG shifts towards the higher side despite rising T.

The result is +ve slope in the curve for most of the reactions shown above for formation of M_xO (s).

b) Each plot is a straight line except when some change in phase (s→liq or liq→g) takes place. The temperature at which such change occurs, is indicated by an increase in the slope on +ve side (e.g., in the Zn, ZnO plot, the melting is indicated by an abrupt change in the curve).

c) There is a point in a curve below which ΔG is negative (So M_xO is stable). Above this point, M_xO will decompose on its own.

d) In an Ellingham diagram, the plots of $\Delta G^0$for oxidation (and therefore reduction of the corresponding species) of common metals and some reducing agents are given. The values of $\Delta_f G^0$, etc.(for formation of oxides) at different temperatures are depicted which make the interpretation easy.

e) Similar diagrams are also constructed for sulfides and halides and it becomes clear why reductions of M_xS is difficult. There, the $\Delta_r G^0$ of M_xS is not compensated.

Limitations of Ellingham Diagram

1. The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on thermodynamic concepts. It does not say about the kinetics of the reduction process (Cannot answer questions like how fast it could be ?).
2. The interpretation of ΔG^0 is based on K

$$(\Delta G^0 \; = \; - RT\; lnK)$$

Thus it is presumed that the reactants and products are in equilibrium:

$$M_xO \; + \; A_{red} \; \rightarrow \; xM \; + \; AO$$

This is not always true because the reactant/product may be solid. [However it explains how the reactions are sluggish when every species is in solid state and smooth when the ore melts down.

It is interesting to note here that ΔH (enthalpy change) and the ΔS (entropy change) values for any chemical reaction remain nearly constant even at varying temperatures.

So the only dominant variable in equation (1) becomes T.

However, ΔS, i.e. the change in entropy, depends much on the physical state of the compound. Since entropy depends on disorder or randomness in the system, it will increase if a compound melts (s→l) or vapourises (l→g) since molecular randomness increases on changing the phase from solid to liquid or from liquid to gas.

a. Extraction of Iron from its Oxides

Oxide ores of iron, after concentration through calcination/roasting (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with limestone and coke and fed into a Blast furnace from its top.

Here, the oxide is reduced to the metal.

Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is:

$$FeO\,(s) \; + \; C\,(s) \rightarrow Fe\,(s/l) \; + \; CO\,(g) \qquad (11)$$

It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO

$$FeO(s) \rightarrow Fe(s) \; + \; 1/2O_2(g)\; [\Delta G\ (\mathrm{FeO,Fe})] \qquad (12)$$

$$C(s) \; + \; 1/2O_2\,(g) \rightarrow CO\,(g)[\Delta G(\mathrm{C,CO})] \qquad (13)$$

When both the reactions take place to yield the equation (10), the net Gibbs energy change becomes:

$$\Delta G\,(C, CO) \;+\; \Delta G\,(FeO,\, Fe) \;=\; \Delta_r G \qquad (14)$$

Naturally, the resultant reaction will take place when the right hand side in equation (14) is negative. In ΔG^0 vs T plot representing reaction (12), the plot goes upward and that representing the change C→CO (C,CO) goes downward. At temperatures above 1073K (approx.), the C,CO line comes below the Fe,FeO line [ΔG (C,CO) < ΔG(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 Figure 1.

In the Blast furnace, reduction of iron oxides takes place in different temperature ranges. Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself. The burning of coke therefore supplies most of the heat required in the process. The CO and heat move to the upper part of the furnace. In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO. Thus, the reduction reactions taking place in the lower temperature range and in the higher temperature range, depend on the points of corresponding intersections in the $\Delta_f G^0$ *vs T* plots. These reactions can be summarised as follows:

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

$$3Fe_2O_3 \;+\; CO \rightarrow 2Fe_3O_4 \;+\; CO_2 \qquad (15)$$

$$Fe_3O_4 \;+\; 4CO \rightarrow 3Fe \;+\; 4\,CO_2 \qquad (16)$$

$$Fe_2O_3 \;+\; CO \rightarrow 2FeO \;+\; CO_2 \qquad (17)$$

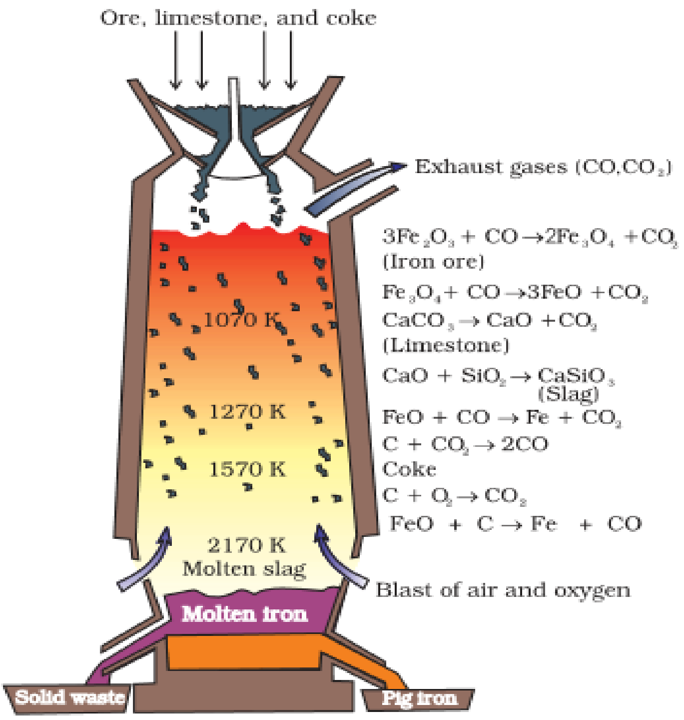

Figure 2: Blast furnace

Source: NCERT, Chemistry, Part I, XII

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

$$C + CO_2 \rightarrow 2\,CO \qquad (18)$$

$$FeO + CO \rightarrow Fe + CO_2 \qquad (19)$$

Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

The iron obtained from the Blast furnace contains about 4% carbon and many impurities in smaller amounts (e.g., S, P, Si, Mn). This is known as pig iron and cast into a variety of shapes.

Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast.

It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Further Reductions Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \qquad (20)$$

Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

b. Extraction of Copper from Cuprous Oxide [Copper(I) Oxide]

In the graph of $\Delta_r G^0$ *vs* T for formation of oxides (Figure 1), the Cu_2O line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO_2 are at much lower positions in the graph particularly after 500 – 600K). However most of the ores are sulphide and some may also contain iron. The sulphide ores are roasted/smelted to give oxides:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \qquad (21)$$

The oxide can then be easily reduced to metallic copper using coke:

$$Cu_2O + C \rightarrow 2\,Cu + CO \qquad (22)$$

In the 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. This contains Cu_2S and FeS.

$$FeO + SiO_2 \rightarrow FeSiO_3 \qquad (23)$$

(Slag)

Copper matte is then charged into a silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining FeS_2, FeO and Cu_2S/Cu2O to the metallic copper. Following reactions take place:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 \qquad (24)$$

$$FeO + SiO_2 \rightarrow FeSiO_2 \qquad (25)$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \qquad (26)$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2 \qquad (27)$$

The solidified copper obtained has a blistered appearance due to the evolution of SO_2 and so it is called blister copper.

c. Extraction of zinc from zinc oxide

The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in the case of copper. For the purpose of heating, the oxide is made into briquettes with coke and clay.

$$ZnO + C(coke) \xrightarrow{673K} Zn + CO$$

The metal is distilled off and collected by rapid chilling.

Electrochemical Principles of Metallurgy

We have seen how principles of thermodynamics are applied to pyrometallurgy.

Similar principles are effective in the reductions of metal ions in solution or molten state. Here they are reduced by electrolysis or by adding some reducing element. In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^0 = -nE^0F \quad (29)$$

here n is the number of electrons and E^0 is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E^0 values corresponds to a positive E^0 and consequently negative ΔG^0in equation (29), then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,

$$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq) \quad (30)$$

In simple electrolysis, the Mn^+ ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added to make the molten mass more conducting.

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 mix and brings conductivity.

The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \quad (31)$$

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

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

Cathode: $Al^{3+}(melt) + 3e^{-} \rightarrow Al(l)$ (32)

Anode: $C(s) + O^{2-}(melt) \rightarrow CO(g) + 2$ (33)

$C(s) + 2O^{2-}(melt) \rightarrow CO_2(g) + 4e^{-}$ (34)

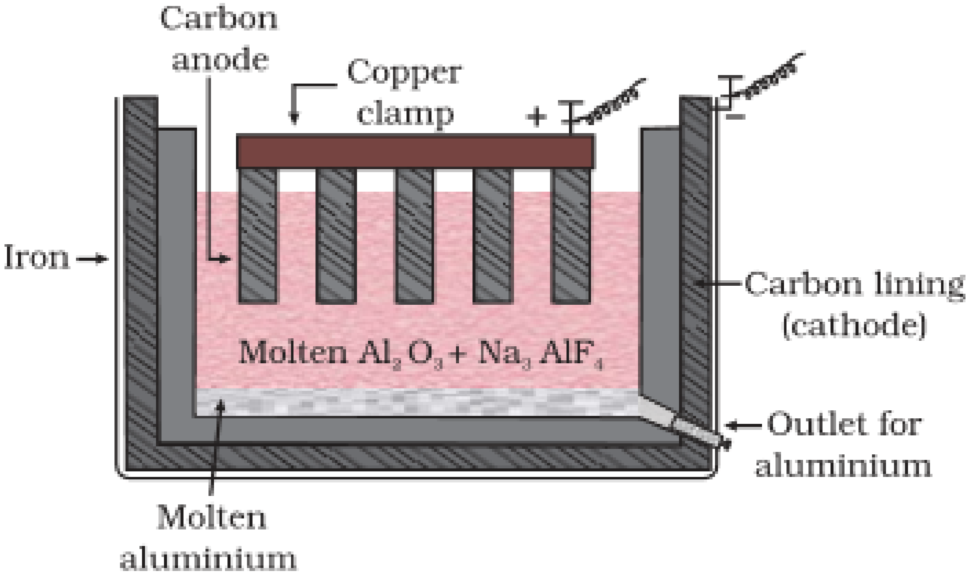

Figure 3: Electrolytic Cell for Extraction of Aluminium

Source: NCERT, Chemistry, PartI, XII

Hydrometallurgy

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 29; 35).

$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^{+}(aq)$ (35)

Oxidation and Reduction to get Elements

Extraction of Chlorine

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, NaCl (aq) from sea water which is an abundant source of sodium and chlorine in the form of common salt.

$$2Cl^{-}\,(aq) \;+\; 2H_2O\,(l) \rightarrow 2OH^{-}\,(aq) \;+ H_2\,(g) \;+ Cl_2\,(g) \qquad (36)$$

The ΔG^0 for this reaction is + 422 kJ, using $\Delta G^0 \;=- \;nFE^{\circ}$, we get E° = – 2.2 V. Naturally, it will require an external e.m.f. that is greater than 2.2 V during electrolysis. Thus, Cl_2 is obtained at the anode as Cl^- is oxidized and by-products of this electrolysis process are H_2 at the cathode and aqueous NaOH.

Extraction of Sodium and Chlorine

In case electrolysis of molten NaCl is carried out, Na metal is produced at the cathode as reduction product of Na^+ and Cl_2 is obtained at the anode as oxidation product of Cl^- . NaOH and hydrogen is not produced in this case as expected. Following reactions take place in case of electrolysis of molten NaCl.

Cathode:$Na^{+}\,(melt) \;+\; e^{-} \rightarrow Na(l)$……Reduction (37)

Anode:$2Cl^{-}\,(melt) \;\rightarrow Cl_2(g) \;+\; 2e^{-}$ ……Oxidation (38)

Extraction of Gold and Silver

As studied earlier, extraction of gold and silver involves leaching the metal with CN^-. This is also an oxidation reaction (Ag → Ag^+ or Au → Au^+). The metal is later recovered by the displacement method, which reduction process. In this reaction zinc acts as a reducing agent.

$$4Au\,(s) \;+\; 8CN^{-}\,(aq) \;+\; 2H_2O\,(aq) \;+\; O_2\,(g) \rightarrow 4[Au(CN)_2]^{-}\,(aq) \;+\; 4OH^{-}\,(aq)$$

(39)

$$2[Au(CN)_2]^{-}(aq) \;+\; Zn\,(s) \rightarrow 2Au\,(s) \;+\; [Zn(CN)_4]^{2-}(aq) \qquad (40)$$

Summary

1. The metal compounds (e.g., oxides, sulphides) are reduced to the metal.
2. The reducing agents used are carbon, CO or even some metals. In these reduction processes, the **thermodynamic** and **electrochemical** concepts are given due consideration.

3. 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.
4. Conversion of the physical states from solid to liquid or to gas, and formation of gaseous states favors decrease in the Gibbs energy for the entire system. This concept is graphically displayed in plots of G^0 vs T (Ellingham diagram) for such oxidation/reduction reactions at different temperatures.
5. 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 +ve so that the Gibbs energy change is negative.
6. Extraction of iron is done by reduction of its oxide ore in a blast furnace.
7. Copper is extracted by smelting and heating in a reverberatory furnace.
8. Extraction of zinc from zinc oxides is done using coke.
9. Extraction of aluminium is usually carried out from its bauxite ore. The molten purified alumina is mixed with cryolite as a flux and then electrolysed to obtain pure aluminium at the cathode.
10. Extraction of sodium is carried out from molten NaCl. The molten NaCl is electrolysed to obtain pure sodium at the cathode and chlorine gas at anode.
11. Electrolysis of brine, NaCl (aq) produces Cl_2 at the anode and by-products H_2 at the cathode and aqueous NaOH in the cell.
12. Extraction of gold and silver involves leaching the metal with CN^- and then using zinc as a reducing agent to recover pure metals.
13. A summary of the occurrence and extraction of some Metals is presented in the following table:

METAL	COMMON ORES		COMMON EXTRACTION PROCESS	REMARKS
Aluminium	1.	Bauxite, $Al_2O_3 . x\ H_2O$	Electrolysis of	For the extraction, a
	2.	Cryolite, Na_3AlF_6	Al_2O_3 dissolved in	good source of

			molten Na_3AlF_6	electricity is required.
Iron	1.	Haematite, Fe_2O_3	Reduction of the	Temperature
	2.	Magnetite, Fe_3O_4	oxide with CO	approaching 2170 K
			and coke in Blast	is required.
			furnace	
Copper	1.	Copper pyrites, $CuFeS_2$	Roasting of	It is self reduction in a
	2.	Copper glance, Cu_2S	sulphide	specially designed converter.
	3.	Malachite,	partially and	The reduction takes place easily.
		$CuCO_3.Cu(OH)_2$	reduction	Sulphuric acid leaching is also
	4.	Cuprite, Cu_2O		used in hydrometallurgy from
				low grade ores.
Zinc	1.	Zinc blende or	Roasting followed	The metal may be
		Sphalerite, ZnS	by reduction with	purified by fractional
	2.	Calamine, $ZnCO_3$	coke	distillation.
	3.	Zincite, ZnO		