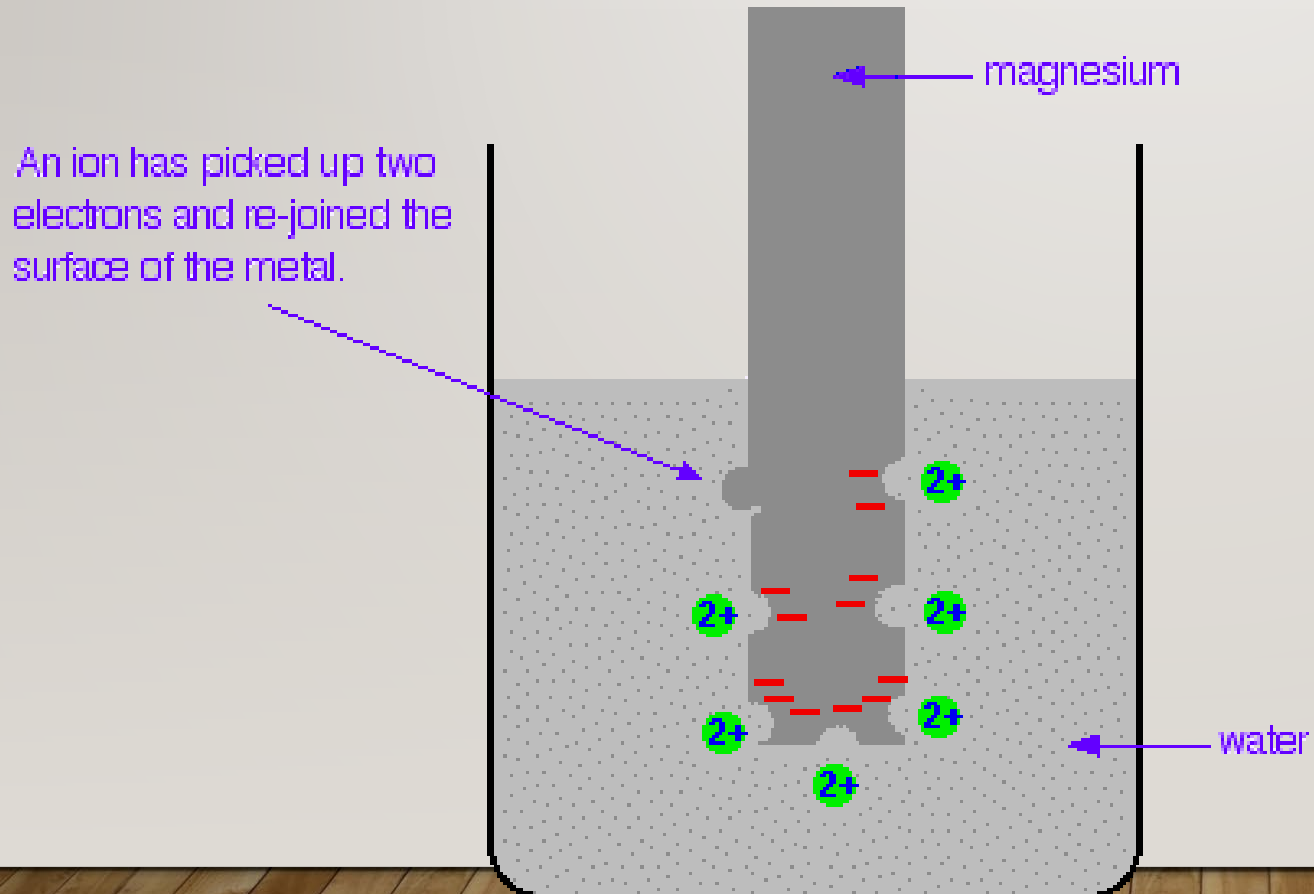


# General Principles of Metallurgy

1. Chief mode of occurrence of metals based on standard electrode potential.
2. Ellingham diagram for reduction of metal oxides using carbon and CO as reducing agent.
3. Electrolytic reduction
4. Hydrometallurgy with reference to cyanide process for silver and gold.
5. Methods of purification of metals.
6. Electolytic process, Van Arkel de Boer process and Mond process
7. Zone refining

# WHAT IS STANDARD ELECTRODE POTENTIAL?



When a metal is immersed in water or a solution of its own ions it tends to lose positive metal ions into the solution.



The cell potential results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is called the **standard hydrogen electrode (SHE)**. The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature.

Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is



$E^\circ$  is the standard reduction potential.

The superscript “°” on the  $E$  denotes standard conditions (1 bar or 1 atm for gases, 1  $M$  for solutes).

The voltage is defined as zero for all temperatures.

# How to calculate Electrode potential?

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$\begin{aligned} E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{H}^+/\text{H}_2} &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - 0 = E^\circ_{\text{Cu}^{2+}/\text{Cu}} \\ &= +0.34\text{V} \end{aligned}$$

# Electrochemical Series

The standard reduction potentials of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. The arrangement of elements in order of increasing reduction potential values is called **electrochemical series**. It is also called **activity series**, of some typical electrodes.

Table 1: Electrochemical Series		
	Equilibrium (Oxidants $\leftrightarrow$ Reductants)	E° (volts)
Metal Reducing Activity Increasing ↑	Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
	Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
	Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
	Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
	Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
	Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
	Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76
	Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44
	Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
	Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
	Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
	Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
	Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50
		Metal Oxidizing Activity Increasing ↓

# Reduction Potential & Extraction Methods

Table 1: Electrochemical Series

Equilibrium (Oxidants $\leftrightarrow$ Reductants)	$E^\circ$ (volts)
Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76
Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44
Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50

## Extraction Methods

Electrolysis of fused salts, usually chlorides

Electrolysis of  $\text{MgCl}_2$  High temp. reduction with Carbon

Electrolysis of  $\text{Al}_2\text{O}_3$  dissolved in  $\text{Na}_3[\text{AlF}_6]$

Chemical reduction of oxides with Carbon

Found as native metal or compounds easily decomposed by heat.

# Ellingham Diagram

Gibbs equation helps us to predict the spontaneity of a reaction on the basis of enthalpy and entropy values directly.

H.G.T Ellingham proposed the Ellingham diagram to predict the spontaneity of reduction of various metal oxides.

Ellingham diagram was basically a curve which related the Gibbs energy value with the temperature. Gibbs energy is given as:

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

Where  $\Delta H$  is the change in enthalpy and  $\Delta S$  is the change in entropy.

Thus, when the reaction is exothermic, enthalpy of the system is negative, thus making Gibbs free energy negative. Hence, we can say that the reaction will proceed in the forward direction due to a positive value of the equilibrium constant.

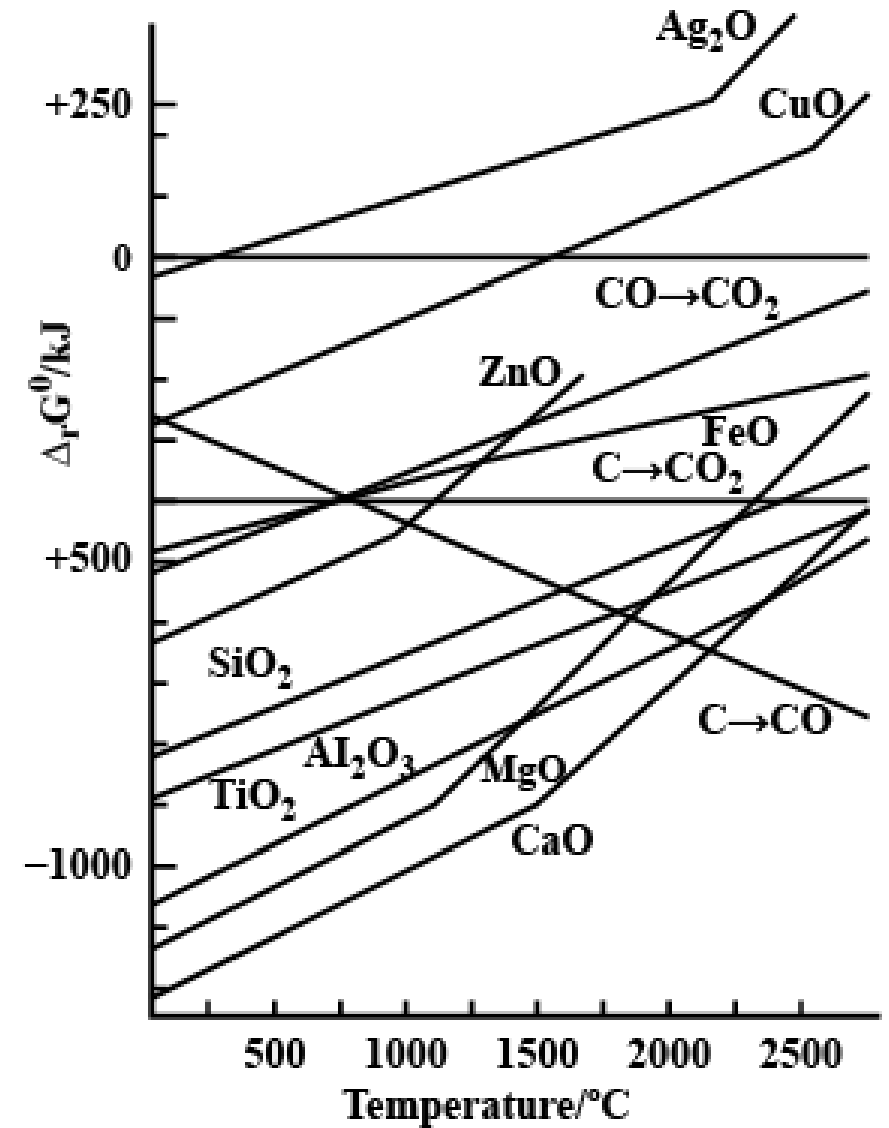
A general reaction expressing oxidation is given by:



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

As is evident from the reaction, the gaseous amount of reactant is decreasing from left to right as the product formed is solid metal oxide on the right side. Hence, we can say that molecular randomness is also decreasing. Thus,  $\Delta S$  is negative and  $\Delta G$  shifts towards higher side despite rising  $T$ . Hence, for most of the reactions shown above for the formation of  $\text{M}_x\text{O}$  (s), the curve is positive.

The metal oxide ( $\text{M}_x\text{O}$ ) is stable at the point in a curve below which  $\Delta G$  is negative. Above this point, the metal oxide is unstable and decomposes on its own.



Ellingham diagram for Reduction of Oxides:



# Oxidation of Carbon: An Exception

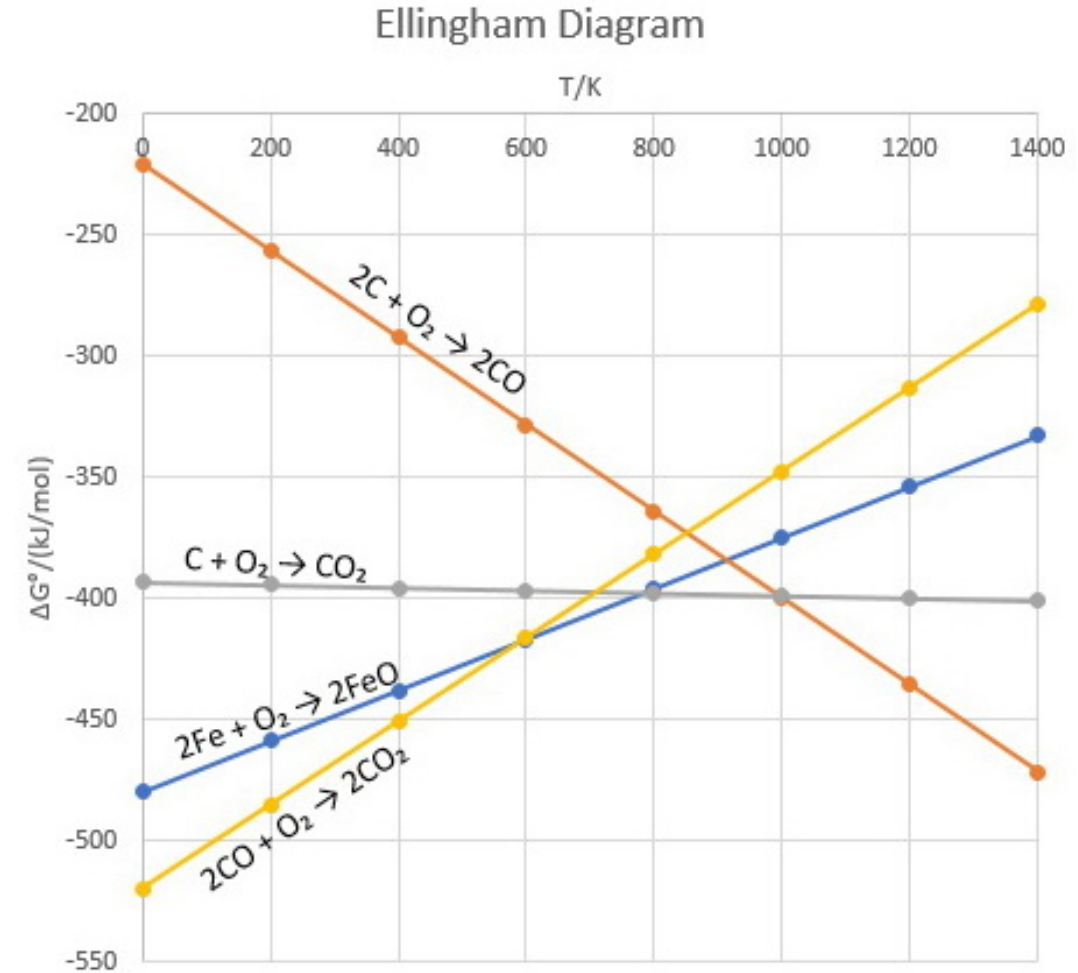
The majority of the lines slope upwards, because both the metal and the oxide are present as condensed phases (solid or liquid). The reactions are therefore reacting a gas with a condensed phase to make another condensed phase, which reduces the entropy. A notable exception to this is the oxidation of solid carbon.

The line for the reaction  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

is a solid reacting with a mole of gas to produce a mole of gas, and so there is little change in entropy and the line is nearly horizontal.

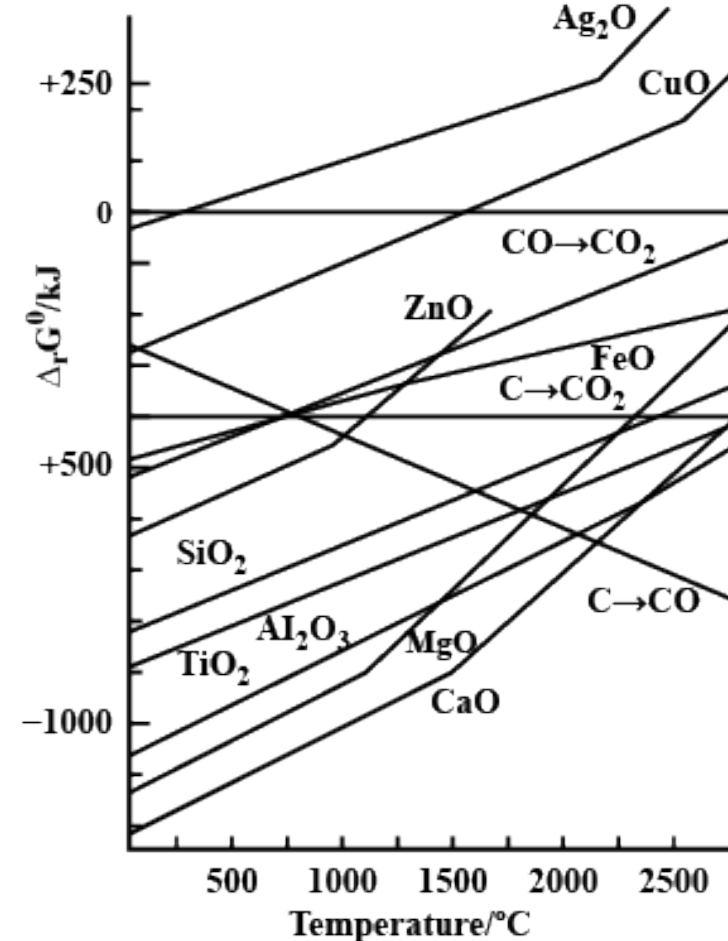
For the reaction  $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$

we have a solid reacting with a gas to produce two moles of gas, and so there is a substantial increase in entropy and the line slopes rather sharply downward.

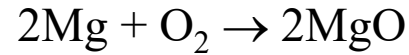


# Ease of Reduction

□ The position of the line for a given reaction on the Ellingham diagram shows the stability of the oxide as a function of temperature. Reactions closer to the top of the diagram are the most “noble” metals (for example, silver), and their oxides are unstable and easily reduced. As we move down toward the bottom of the diagram, the metals become progressively more reactive and their oxides become harder to reduce.



- ❑ A given metal can reduce the oxides of all other metals whose lines lie above theirs on the diagram. For example, the



line lies below the  $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$  line,

and so magnesium can reduce titanium oxide to metallic titanium.

- ❑ Since the  $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$  line is downward-sloping, it cuts across the lines for many of the other metals. This makes carbon unusually useful as a reducing agent, because as soon as the carbon oxidation line goes below a metal oxidation line, the carbon can then reduce the metal oxide to metal. So, for example, solid carbon can reduce chromium oxide once the temperature exceeds approximately  $1225^\circ\text{C}$ , and can even reduce highly-stable compounds like silicon dioxide and titanium dioxide at temperatures above about  $1620^\circ\text{C}$  and  $1650^\circ\text{C}$ , respectively.

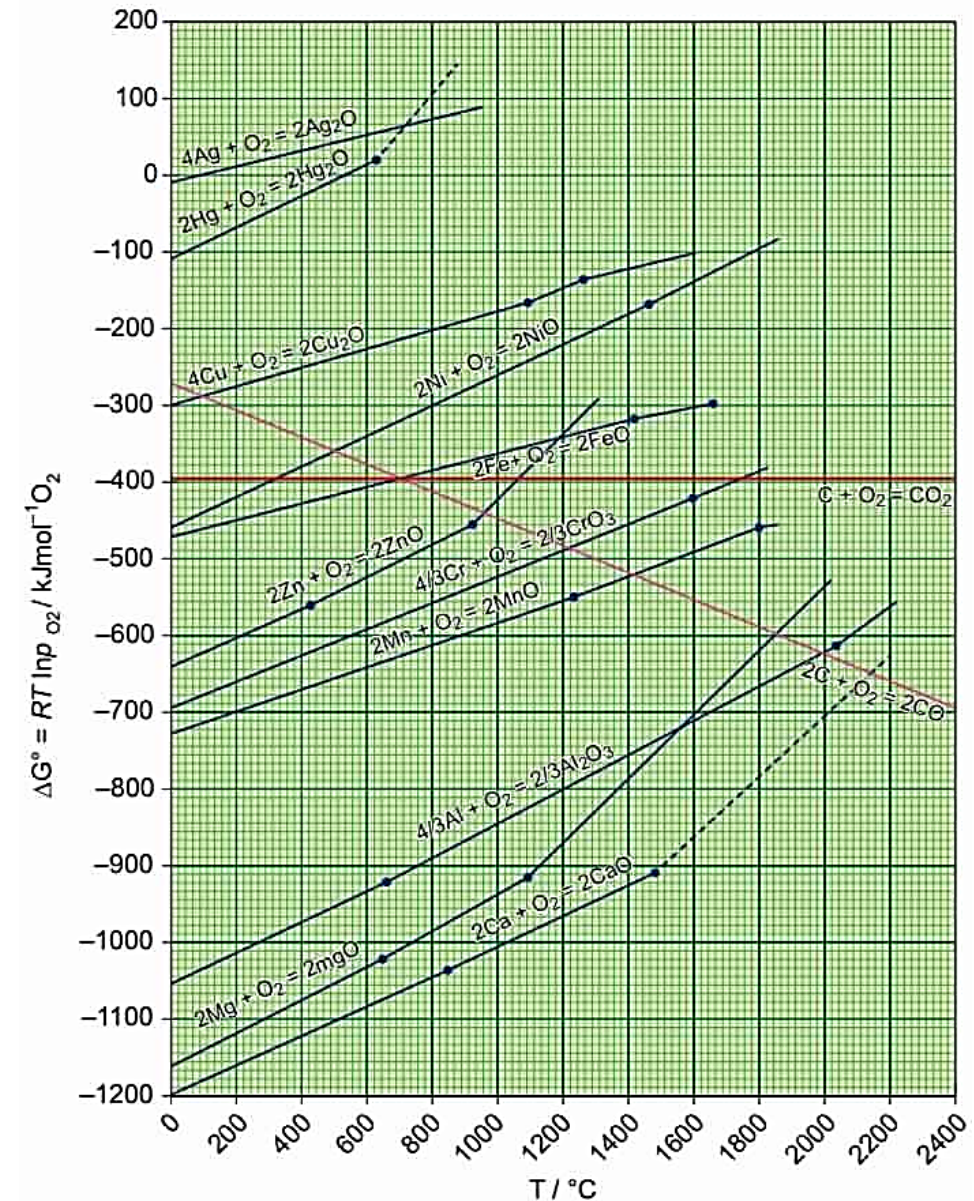


Figure 1.4 Ellingham diagram

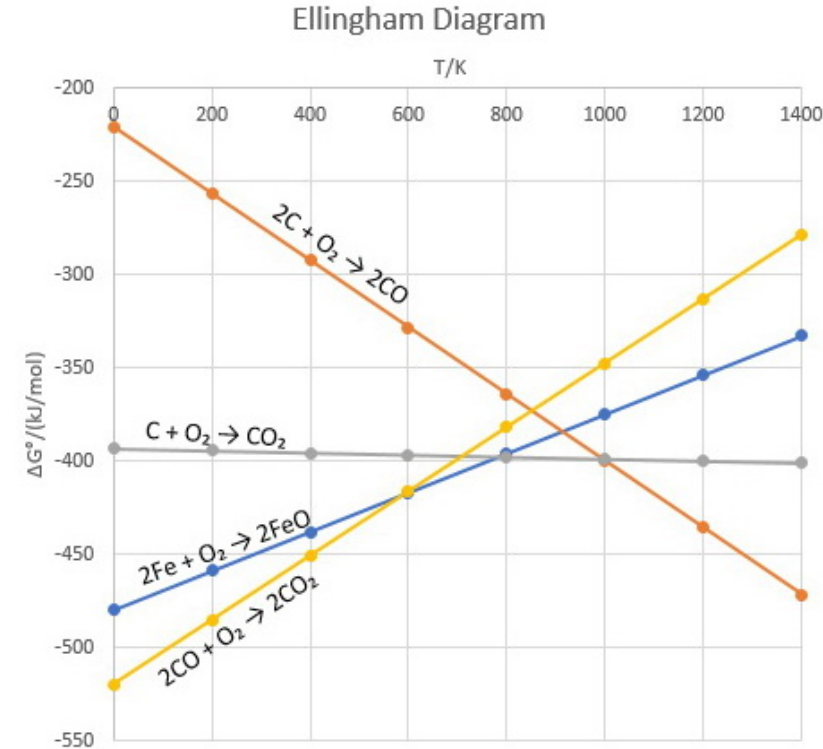
# Applications of the Ellingham diagram:

Ellingham diagram helps us to select a suitable reducing agent and appropriate temperature range for reduction. The reduction of a metal oxide to its metal can be considered as a competition between the element used for reduction and the metal to combine with oxygen. If the metal oxide is more stable, then oxygen remains with the metal and if the oxide of element used for reduction is more stable, then the oxygen from the metal oxide combines with elements used for the reduction. From the Ellingham diagram, we can infer the relative stability of different metal oxides at a given temperature.

1. Ellingham diagram for the formation of  $\text{Ag}_2\text{O}$  and  $\text{HgO}$  is at upper part of the diagram and their decomposition temperatures are 600 and 700 K respectively. It indicates that these oxides are unstable at moderate temperatures and will decompose on heating even in the absence of a reducing agent.
2. Ellingham diagram is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal. Any metal can reduce the oxides of other metals that are located above it in the diagram. For example, in the Ellingham diagram, for the formation of chromium oxide lies above that of the aluminium, meaning that  $\text{Al}_2\text{O}_3$  is more stable than  $\text{Cr}_2\text{O}_3$ . Hence aluminium can be used as a reducing agent for the reduction of chromic oxide. However, it cannot be used to reduce the oxides of magnesium and calcium which occupy lower position than aluminium oxide.



3. The carbon line cuts across the lines of many metal oxides and hence it can reduce all those metal oxides at sufficiently high temperature. Let us analyse the thermodynamically favourable conditions for the reduction of iron oxide by carbon. Ellingham diagram for the formation of FeO and CO intersects around 1000 K. Below this temperature the carbon line lies above the iron line which indicates that FeO is more stable than CO and hence at this temperature range, the reduction is not thermodynamically feasible. However, above 1000 K carbon line lies below the iron line and hence, we can use coke as reducing agent above this temperature. The following free energy calculation also confirm that the reduction is thermodynamically favoured.



From the Ellingham Diagram at 1500 K,



Reverse the reaction (1)



Now couple the reactions (2) and (3)



The standard free energy change for the reduction of one mole of FeO is,  $\Delta G_3/2$   
 $= -65 \text{ kJ mol}^{-1}$

# Limitations of Ellingham diagram

1. Ellingham diagram is constructed based only on thermodynamic considerations. It gives information about the thermodynamic feasibility of a reaction. It does not tell anything about the rate of the reaction. More over, it does not give any idea about the possibility of other reactions that might be taking place.
2. The interpretation of  $\Delta G$  is based on the assumption that the reactants are in equilibrium with the products which is not always true.