



THERMODYNAMICS OF METAL EXTRACTION

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INTRODUCTION

In general, a process or extraction of metals has two components:

1. Severance: produces, through chemical reaction, two or more new phases, one of which is much richer in the valuable content than others.
2. Separation : involves physical separation of one phase from the others

Three types of processes are used for accomplishing severance :

1. Pyrometallurgical: Chemical reactions take place at high temperatures.
2. Hydrometallurgical: Chemical reactions carried out in aqueous media.
3. Electrometallurgical: Involves electrochemical reactions.

Advantages of Pyrometallurgical processes

1. Option of using a cheap reducing agent, (such as C, CO). As a result, the unit cost is 5-10 times lower than that of the reductants used in electrolytic processes where electric power often is the reductant.
2. Enhanced reaction rates at high temperature .
3. Simplified separation of (molten) product phase at high temperature.
4. Simplified recovery of precious metals (Au,Ag,Cu) at high temperature.
5. Ability to shift reaction equilibria by changing temperatures.

THERMODYNAMICS

The Gibbs free energy(G) , of the system is the energy available in the system to do work . It is relevant to us here, because at constant temperature and pressure it considers only variables contained within the system .

$$G = H - TS$$

Here, T is the temperature of the system S is the entropy, or disorder, of the system. H is the enthalpy of the system, defined as:

$$H = U + PV$$

Where U is the intern energy , P is the pressure and V is the volume.

If the system is changed by a small amount , we can differentiate the above functions:

$$dG = dH - TdS - SdT$$

And

$$dH = dU - PdV + VdP$$

From the first law,

$$dU = dq - dw$$

And from second law,

$$dS = dq/T$$

We see that,

$$\begin{aligned}dG &= dq - dw + PdV + VdP - TdS - SdT \\dG &= -dw + PdV + VdP - SdT \quad (dw = PdV) \\dG &= VdP - SdT\end{aligned}$$

The above equations show that if the temperature and pressure are kept constant, the free energy does not change. This means that the gibbs free energy is unique at each temperature and pressure.

At a constant temperature $dT=0$ and so

$$dG = VdP$$

And we know that $V = RT/P$, putting that in equation and integrating ,we get

$$dG = RT\ln(P) + constant$$

Can be expressed as

$$G = G^0 + RT\ln(P/P^0)$$

G^0 and P^0 are standard free energy and standard pressure respectively

CHEMICAL REACTION

GIBBS FREE ENERGY

The energetic of process for system at constant temperature and pressure, the appropriate quantity is known as gibbs free energy.

$$\Delta G_{\text{reaction}} = \Delta G_{\text{product}} - \Delta G_{\text{reactant}}$$

- **FOR SPONTANEOUS REACTION**

It decreases for spontaneous reaction at constant temperature and constant pressure.

$$\Delta G < 0$$

- **FOR NON-SPONTANEOUS REACTION**

It increases for spontaneous reaction at constant temperature and constant pressure.

$$\Delta G > 0$$

While at equilibrium, $\Delta G = 0$.

Also we know that,

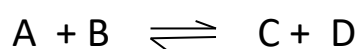
$$\Delta G = \Delta H - T\Delta S$$

ΔH	ΔS	ΔG	Types of process
-ve	+ve	-ve	Spontaneous at all temperature
+ve	-ve	+ve	Non-spontaneous at all temperature
+ve	+ve	-ve or +ve	Spontaneous if temperature is high enough
-ve	-ve	+ve or -ve	Spontaneous if temperature is low enough

- ΔG is independent of the path of the transformation and is unaffected by the mechanism of reaction.
- ΔG cannot tell us about the rate of reaction.

Gibbs free energy in equilibrium

Let's consider the following reversible reaction –



The following equation relates the standard state free energy of reaction with the free energy of reaction with the free energy at any point in a given reaction

(not necessarily at standard state conditions):-

$$\Delta G = \Delta G^0 + RT \ln Q, \quad \text{where}$$

ΔG = Free energy at any moment

R = Ideal gas constant = 8.3 J/K-mole

T = Absolute temperature

$\ln Q$ = Natural logarithm of reaction quotient.

At equilibrium $\Delta G = 0$ and $Q = k$. Thus the equation can be can be arranged into-

$$\Delta G = \Delta G^0 + RT \ln([C][D] / [A][B])$$

$$\Delta G = \Delta G^0 + RT \ln([P_c][P_D] / [P_A][P_B])$$

At equilibrium $\Delta G = 0$ then,

$$\Delta G^0 = -RT \ln([C][D] / [A][B]) = -RT \ln([P_c][P_D] / [P_A][P_B])$$

The equilibrium constant is defined as –

$$K_{eq} = ([C][D] / [A][B]) = ([P_c][P_D] / [P_A][P_B])$$

Thus ,

$$\Delta G^0 = -RT \ln K_{eq}, \text{ or}$$

$$\Delta G^0 = -2.303 RT \log K_{eq}$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

1. It is reaction specific and at a constant temperature, it is fixed.
2. A catalyst changes the rate of forward and backward reaction equally not to affect the value of the equilibrium constant.

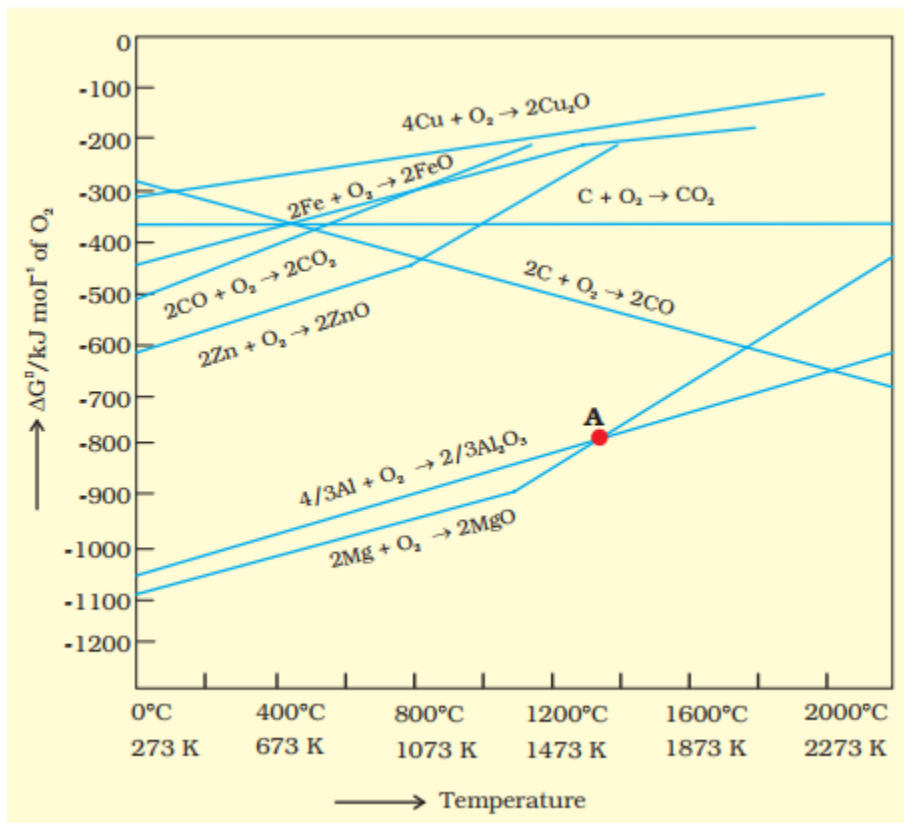
3. Changes in concentration, pressure, temperature and inert gases may affect the equilibrium, favoring either backward or forward reaction but not the equilibrium constant.
4. Is related to standard free energy as $\Delta G^0 = -RT \ln K_{eq}$.
5. For the same equilibrium reaction k_{eq} has different values at different temperatures.

ELLINGHAM DIAGRAM

Ellingham was the name of a scientist, his full name was Harold Johann Thomas Ellingham.

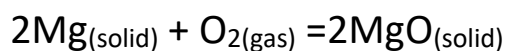
He gave the graph between $\Delta_f G^0$ (gibbs free energy) and T (temperature) in order to find the best reducing agent.

This diagram uses $\Delta G = \Delta H - T\Delta S$ equation.



The plot is straight line with slope as $-\Delta S$ and intercept as ΔH .

The sudden change in the slope is due to change in the state of the metal and the temperature at this point denotes the melting point, here the metal is converted from solid state to liquid state and hence the change in entropy becomes more negative due to this the slope is increased example,



If this equation has change in entropy as ΔS_1

Now when the metal meets melting point

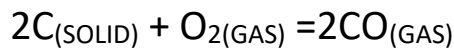


If This equation has change in entropy as ΔS_2 then,

ΔS_2 will be more negative than ΔS_1 Hence the slope is high after melting point.

→(1) The important point regarding Ellingham diagram is that since the entropy change ΔS for formation of a metal oxide is negative the

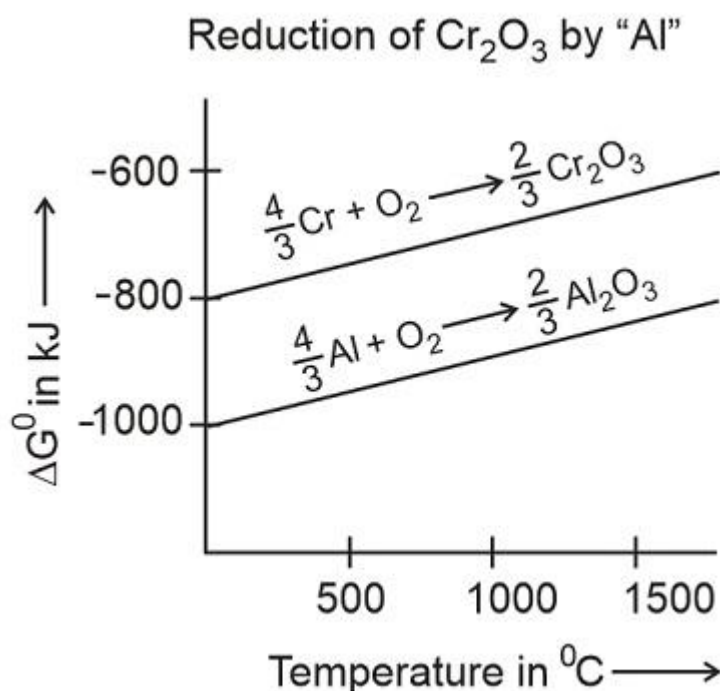
slope of the graph is positive and the value of ΔG becomes more and more positive as the temperature increases , i.e the formation of oxide becomes less feasible or in other words the stability of oxide decreases. But for the formation of CO , $\Delta_f G^0$ becomes more and more negative indicating the higher favourability of the reaction.



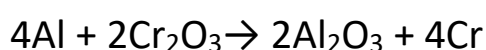
(2) Second important point is about the abrupt change in slope of the line shows the phase transition(melting of metal).

Q)How to read the Ellingham diagram?

→lets take an example to understand this,



Here $\Delta_f G^0$ for $\frac{2}{3}Al_2O_3$ is more negative than $\frac{2}{3}Cr_2O_3$ hence Al can easily reduce Cr_2O_3 to Al_2O_3 . i.e



This implies the graph which is up ,there oxide can be reduced by the metal , whose graph is down .

And the gap between two graph represents the tendency of reduction of metal oxide by the metal , more the gap, more is the tendency of reduction.

Limitations of Ellingham diagram

- No information about the kinetics of the reaction.
- The presumption that reactant-product are in equilibrium , which is not always true.
- It cannot provide the full information if more than one oxides are possible for that reaction.

Sources : embibe.com(image) , chemistry.stackexchange.com(image) , [youtube](https://www.youtube.com)(lecture), [wikipedia](https://www.wikipedia.com) .