GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

ELLINGHAM DIAGRAM

❖ THERMODYNAMICS OF EXTRACTION:

ELLINGHAM DIAGRAM OF A METAL

Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations. Gibbs energy is the most significant term here. 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:

$$\Delta GV = -RTlnK \qquad ....(2)$$

where, K is the equilibrium constant of the 'reactant – product' system at the temperature T. A negative ΔG implies a +ve 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.
2. 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. So the process of interpretation 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^-) vs T plots for formation of the oxides

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 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 $\Delta_f G^-$ vs T for formation of oxides of elements i.e., for the reaction,

$$2xM(s) + O_2(g) \rightarrow 2M_x O(s)$$

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

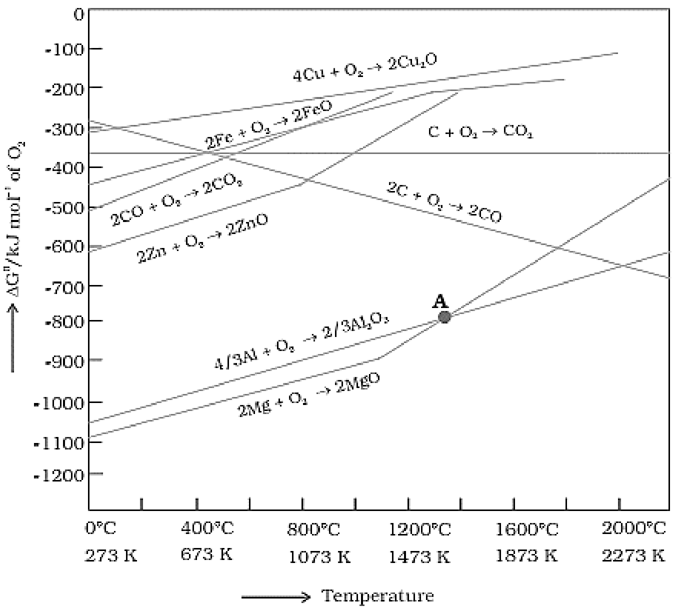
(1) Subsequently ΔG shifts towards higher side despite rising T (normally, ΔG decreases i.e., goes to lower side with increasing temperature). The result is +ve slope in the curve for most of the reactions shown above for formation of Mx O(s).

(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 Mx O is stable). Above this point, Mx O will decompose on its own.

(d) In an Ellingham diagram, the plots of ΔG^- for oxidation (and therefore reduction of the corresponding species) of common metals and some reducing agents are given. The values of $\Delta_f G^-$, 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 Mx S is difficult. There, the $\Delta_f GV$ of M_x S 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 the 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^{-} is based on K ($\Delta GV = -RT \ln K$). Thus, it is presumed that the reactants and products are in equilibrium:

$$M_xO + A_{red} \leftrightarrow xM + AO_{ox}$$

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 on varying temperature. So the only dominant variable in equation (1) becomes T. However, ΔS 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 melt (s → l) or vaporizes (l → g) since molecular randomness increases on changing the phase from solid to liquid or from liquid to gas].

The reducing agent forms its oxide when the metal oxide is reduced. The role of reducing agent is to provide ΔG^{-} negative and large enough to make the sum of ΔG^{-} 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:

$$M_xO(s) \rightarrow xM\ (\text{solid or liq}) + \frac{1}{2}\ O_2\ \ (g) \qquad \text{............}(3)$$

The reducing agent takes away the oxygen. Equation (3) can be visualized as reverse of the oxidation of the metal. And then, the $\Delta_f G^{-}$ value is written in the usual way:

$$xM(\text{s or l}) + \frac{1}{2} O_2(g) \rightarrow M_xO(s)\ [\Delta G^{-}\ \ (M, M_xO)] \qquad \text{............}(4\ )$$

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

$$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g) \qquad [\Delta G_{(C.CO)}]$$

$$CO(g) +\ \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad [\Delta G_{(CO.CO2)}]$$

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

$$\frac{1}{2}C(s) + \frac{1}{2} O_2(s) \rightarrow\ \frac{1}{2}CO_2(g) \qquad [\frac{1}{2}\Delta G_{(C.CO2)}]$$

On subtracting equation (4) [it means adding its negative or the reverse form as in equation (3) from one of the three equations, we get:

$$M_xO(s) + C(s) \rightarrow xM(\text{s or 1}) + CO(g)$$

$$M_xO(s) + CO(g) \rightarrow xM(\text{s or 1}) + CO_2(g)$$

$$M_xO(s) +\ \frac{1}{2}C(s) \rightarrow xM(\text{s or 1}) + \frac{1}{2}CO_2(g)$$

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

As we have seen, heating (i.e., increasing T) favours a negative value of $\Delta_r G^{-}$. Therefore, the temperature is chosen such that the sum of $\Delta_r G^{-}$ in the two combined redox process is negative. In $\Delta_r G^{-}$ 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 Δ_rG^- value becomes more negative for the combined process including the reduction of M_XO. The difference in the two Δ_rG^- values after that point determines whether reductions 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.