LAW OF MASS ACTION :- The law of mass action states the rate of a chemical reaction is directly proportional to the product of reactant concentration values.

For the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

The law gives a formula for the equilibrium constant

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

FUGACITY: It is a thermodynamic property of a real gas which if substituted for the pressure of partial pressure in the equations for an ideal gas gives equation applicable to the real gas.

We know that -

$$dG = VdP - SdT$$

So if T is constant then $dT = 0$

$\therefore$ ~~PV~~ $dG = VdP$

$\because PV = RT$

$\therefore dG = \frac{RT}{P} dP$

$\boxed{dG = RT \ln P}$ This equation for ideal gas

$\boxed{dG = -RT \ln f}$ This equation for non ideal gas where f is the fugacity.

ACTIVITY: Activity of a substance is the ratio of fugacity of the substance to the fugacity of a substance in the standard state.

$$a = \frac{f}{f^\circ} \quad \frac{\text{Fugacity in any state}}{\text{fugacity in standard state}}$$

EQUILIBRIUM CONSTANT: The ratio of the product of active masses of the products to the product of active masses of reactants is known as equilibrium constant ("K_c").

$$K_c = \frac{[\text{Product}]}{[\text{Reactants}]}$$

Exa. $aA + bB \rightleftharpoons cC + dD$
Reactant — Product

$$\because K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where- K_c - equilibrium constant
[ ] - concentration at equilibrium
A, B - Reactants in (gram)
C, D - Products in (gram)
a, b, c, d are the coefficient in the balanced chemical reaction.

Relation Between Free energy and Equilibrium constant:-

$$\Delta G^\circ = -RT \ln K$$

Where- ΔG - Free energy
R - Gass constant $8.314\ J\,mol^{-1}K^{-1}$
$0.08314\ L\,mol^{-1}K^{-1}$
T - Temperatur
K - equilibrium constant

Ellingham Diagram :-

It is a diagram between the free energy of formation of compounds ~~vs~~ such as oxides and the temp. For oxide Ellingham diagram, the free energy change ΔG°, when one mole of gaseous oxygen at 1 atm combine with a pure element to form an oxide, is plotted against temp for various elements.

Construction of Ellingham diagram :-

Free energy equation, $\Delta G^\circ = \Delta H - T\Delta S$

It is a equation of straight line $Y = mX + C$ where m = slope and c = intercept. Comparing the free energy equation with the eq^n of straight line,

m = slope = ΔS (entropy)

c = intercept = ΔH (enthalpy)

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Important features of Ellingham Diagram for oxide:-

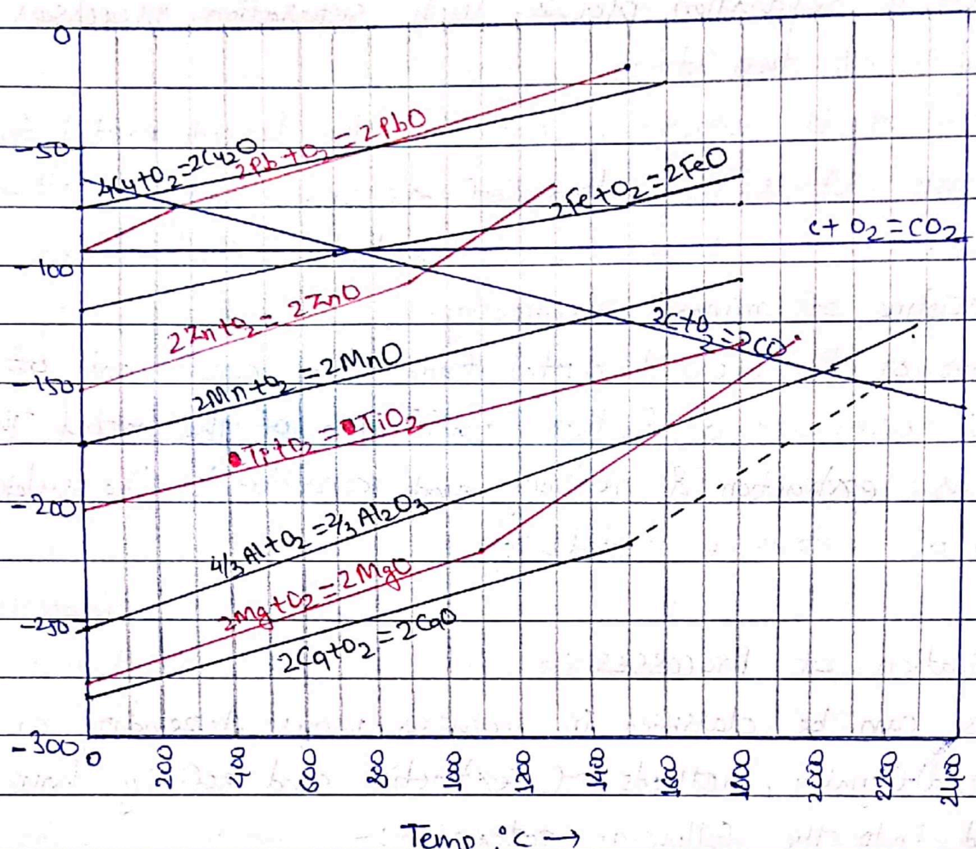


Fig:- Ellingham diagram for oxides:-

(1) As per standard relation for free energy change of a reaction $\Delta G^\circ = \Delta H - T\Delta S$, thus ΔH = std enthalpy or std heat of formation can be obtained by intercept of the line on the ΔG° axis and ΔS_f is the std entropy of formation of oxide, can be obtained from the slope of the line.

2(a). In all cases of $2M(s) + O_2(g) = 2MO(s)$

Gas vol. in mole → 0 + 1 → 0

Since gas phase has much higher entropy than solid phase i.e. entropy is decreased and hence entropy change, ΔS° = -ve. When ΔS° = -ve then ΔG will be +ve and slope line will be upward direction.

(b) In case of $2C(s) + O_2(g) = 2CO(g)$

Gas vol. in mole → 0 + 1 → 2

Entropy increases and hence entropy changes ΔS = +ve. When ΔS = +ve, then ΔG will be -ve and slope of the line will be -ve i.e. slope will be in downward direction.

(c) In case of $C(s) + O_2(g) = CO_2(g)$

Gas vol. in mole → 0 + 1 → 1

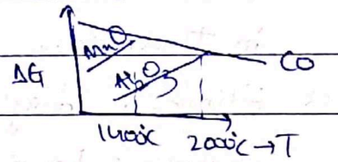
Entropy does not change and hence entropy change $\Delta S = 0$.
when $\Delta S = 0$, then $\Delta G = \Delta H$ i.e. ΔG does not vary with T and slope of the line is zero. Thus line is horizontal with T-axis.

Application or Importance of Ellingham Diagram:-

(1) Carbothermic Reduction:- The temp at which a line of any metal oxide (M–MO) intersects with carbon monoxide (C–CO) line, indicate the equilibrium temp of reduction of MO by C at 1 atm.
e.g:- the temp of reduction by C for various oxides are:-

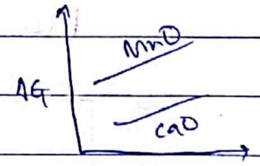
$MnO + C = Mn + CO$, $T = 1400°C$

$Al_2O_3 + 3C = 2Al + 3CO$, $T = 2000°C$



(2) Metallothermic Reduction:- In metallothermic reduction, metal is used as a reducing agent for MO. Highly stable oxides are found at the bottom & less stable oxides occupy higher position. So an element occupying a lower position in diagram can always reduce the oxide of another metal lying above it.
e.g:- MnO can be reduced by Ca.

$MnO + Ca \rightarrow CaO + Mn$

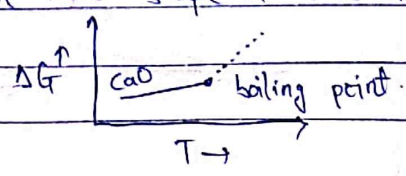


because CaO is more stable than MnO but reverse is not true.

(3) Ellingham diagram gives information about the stability of MO as explained in point (2).

(4) In Ellingham diagram, the lines are straight line with kinks (slope change). The kinks correspond to phase changes in either metal or its oxide due to melting, & boiling, sublimation or transition point. If phase is change, then ΔS will also change & thus slope of the line changes.

- inc in slope – reactant undergoes phase change
  decrease —— product —— " ——



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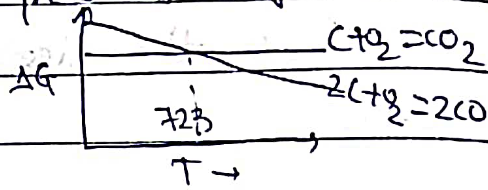
(5) The line for C–CO_2 & C–CO cross each other at 723°C. Thus below 723°C, $CO_2(g)$ is more stable & above 723°C CO(g) is more stable. Hence reduction of metal oxide (MO) by C below 723°C produces CO_2 and above 723°C produces CO(g).

$2MnO + C = 2Mn + CO_2$ (<723°C)

$MnO + C = Mn + CO$ (>723°C)



Limitations of Free Energy Diagram :-

(1) It gives ~~it~~ information only for pure substance, but only in rare cases the reactant present is in pure state.

(2) If the reactant and products are in solution then the thermodynamic data like ΔG is changed. Thus Ellingham diagram is not useful in this case.

(3) Ellingham diagram does not give the ~~ifo~~ information about intermediate product. For example reduction of hematite (Fe_2O_3) occurs in three steps: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$.

(4) Ellingham diagram gives no information about reaction rate, which is important for industry or process.