Chemical Equilibrium

In any chemical process there are two important things are to be known (1) how fast the reaction proceeds to form the products (2) how far the reaction will proceed in a given direction. Chemical kinetics gives the first answer & second question answer is provided by chemical equilibria.

For a reaction to proceed spontaneously it is possible only free energy of reactant is greater than free energy of products. In a spontaneous process the free energy decreases & attains a minimum value at equilibrium.

To study chemical equilibria there are two ways
(1) Based on Gibbs & Van't Hoff Treatment
(2) de Donder who introduced the concept of degree of advancement ξ in study of chemical equilibria

Formulation of Equilibrium Law

(1) Let us consider a general reaction represented by chemical equation $aA + bB \rightarrow mM + nN$ —(1)
where a, b, m, n are stoichiometric coefficients of the balanced equation or moles of respective species

If the system is closed one means no new material is added to the system, the stoichiometry of the reaction requires that any change in the no. of moles of reactants or products be accompanied by an equivalent change in all other reactant & product

When all the reactants as expressed in balanced chemical equation have combined to form products then progress of reaction is 100% but when all the reactants are not consumed, progress of reaction is less than 100%.

∴ A new variable "ξ" is representing progress or advancement of the chemical reaction. It is also called extent of reaction

Let chemical reaction represented by eq (1) advance by small amount $d\xi$ so that amount of reactants A & B and products M & N are changed by dn_A, dn_B, dn_M & dn_N respectively.

change in amount of A = $dn_A = -a\,d\xi$

" " " B = $dn_B = -b\,d\xi$

" " " M = $dn_M = m\,d\xi$

" " " N = $dn_N = n\,d\xi$

-ve sign means A & B are consumed in the reaction

$$d\xi = -\frac{dn_A}{a} = -\frac{dn_B}{b} = \frac{dn_M}{m} = \frac{dn_N}{n}$$ for small change,

$$\Delta\xi = -\frac{\Delta n_A}{a} = -\frac{\Delta n_B}{b} = \frac{\Delta n_M}{m} = \frac{\Delta n_N}{N}$$ for finite change

$d\xi$ or $\Delta\xi$ is equal to the change of the amount of the substance divided by its stoichiometric coefficient of the balanced chemical equation.

$$G = f(T, P, n_i)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial n_i}\right)_{T,P} dn_i \quad \text{— (2)}$$

$$= -S\,dT + V\,dP + \Sigma \mu_i\,dn_i$$

Since most of reactions at const T & P

$$(dG)_{T,P} = \Sigma \mu_i\,dn_i \quad \text{— (3)}$$

(3)

$$(dG)_{T,P} = \mu_A dn_A + \mu_B dn_B + \mu_M dn_M + \mu_N dn_N \quad (4)$$

Sub. eq (4) in eq the values of dn in eq (4)

$$(dG)_{T,P} = -a\,d\xi\,\mu_A - b\,d\xi\,\mu_B + m\,\mu_M\,d\xi + n\,\mu_N\,d\xi$$

$$(dG)_{T,P} = [m\mu_M + n\mu_N - a\mu_A - b\mu_B]\,d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = m\mu_M + n\mu_N - a\mu_A - b\mu_B \quad (5)$$

∴ Difference of (Products − Reactants) = ΔG.

$$m\mu_M + n\mu_N - a\mu_A - b\mu_B = \Delta G.$$

eq. (5) becomes

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G \quad (6)$$

↓ is rate of change of free energy of the system with extent of reaction & this is equal rate of change of total free energy per unit of reaction at const T & P

Sign of ΔG & $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ is a measure of the nature of chemical reaction. The decrease in free energy of reaction is defined as chemical affinity (A_f)

$$A_f = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G \quad (7)$$

A_f is regarded as the urge behind the reaction
A_f & ΔG are numerically exact but opposite in sign & represent different ways of viewing at the same situation.

When ΔG is used, the system is thought of large enough to allow 'a' moles A & 'b' moles of B to react.
While A_f is used means only $a d\xi$ moles of A & $b d\xi$ moles of B react. They help in predicting the feasibility of the chemical reaction

(1) When $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ is $-ve$, A_f is $+ve$, the free energy of the system decreases as the reaction proceeds in the forward reaction, $d\xi$ is $+ve$, dG is $-ve$.
Reaction is spontaneous when $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} < 0$

(2) when $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ $+ve$, A_f chemical Affinity is $-ve$, reaction is spontaneous in the reverse direction

(3) when $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$, $A_f = 0$, free energy has minimum value & reaction is at equilibrium

Condition of equilibrium of a chemical reaction is ΔG must be min. & $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = (n\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0 \quad \text{(1)}$$

It is applicable for all types of reactions

Equilibrium Law for Ideal Gases

Consider a general chemical reaction

$aA + bB \rightarrow mM + nN$ All species are ideal gases

The chemical potential of each species $\mu_i = \mu_i^\circ(T) + RT \ln P_i$

The eqⁿ condition $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0$

$$(m\mu_M^\circ + mRT \ln \frac{P_M}{P^\circ} + m\mu_N^\circ + nRT \ln \frac{P_N}{P^\circ}) - (a\mu_A^\circ + aRT \ln \frac{P_A}{P^\circ} + bRT \ln \frac{P_B}{P^\circ} + b\mu_B^\circ) = 0 \quad -(8)$$

$$RT\left(\ln \frac{\left[\frac{P_M}{P^\circ}\right]^m \left(\frac{P_N}{P^\circ}\right)^n}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b}\right) + (m\mu_M^\circ + n\mu_N^\circ) - (a\mu_A^\circ + b\mu_B^\circ)$$

$$RT \ln \frac{\left(\frac{P_M}{P^\circ}\right)^m \left(\frac{P_N}{P^\circ}\right)^n}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b} + \Delta G^\circ \quad (\text{from eq. 6})$$

$$RT \ln \frac{\left(\frac{P_M^\circ}{P^\circ}\right)^m \left(\frac{P_N}{P^\circ}\right)^n}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b} = -\Delta G^\circ \quad -(9)$$

where ΔG° is standard free energy of reaction at temp T & standard Pressure P°. (1 atm or $101325\ Nm^{-2}$)

$$\ln \frac{\left(\frac{P_M}{P^\circ}\right)^m \left(\frac{P_N}{P^\circ}\right)^n}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b} = -\frac{\Delta G^\circ}{RT} \quad -(10)$$

$\left(\frac{P_M}{P^\circ}\right)^M \left(\frac{P_N}{P^\circ}\right)^n$

$$\frac{\left(\frac{P_M}{P^\circ}\right)^m \left(\frac{P_N}{P^\circ}\right)^n}{\left(\frac{P_A^\circ}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \quad \text{(11)} \qquad (6)$$

Since R.H.S. $\frac{\Delta G^\circ}{RT}$ is const at a particular temp. therefore at fixed T, L.H.S is also const & is given a symbol K_p

$$\frac{\left(\frac{P_M}{P^\circ}\right)^m \left(\frac{P_N}{P^\circ}\right)^n}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b} = K_p \text{ (equilibrium const)}$$

It is function of temp only it contains

(1) Partial P of products in the numerator & Partial P of reactants in the denominator

(2) It is dimensionless quantity because std P (abs) is ratio of two Pressures is zero

Interpretation of $\Delta G^\circ = -RT \ln K_p$

ΔG° = std. free energy of reaction at temp T

$$\Delta G^\circ = (m\mu_M^\circ + n\mu_N^\circ) - (a\mu_A^\circ + b\mu_B^\circ)$$

μ° = std. chemical pot. or partial ~~pressure~~ molar free energy or std. free energies of Products & Reactants

$$\Delta G^\circ = \sum G^\circ(P) - \sum G^\circ(R) = -RT \ln K_p \quad \text{(11)}$$

eq (11) provides some information

(1) If ΔG° is having a -ve value then $K_p > 1$ and the reactants in their standard state spontaneously react to give products in their standard state

(2) If ΔG° has a +ve value then $K_p < 1$ it indicates that std. states of reactants are not converted completely into products. It means ΔG° is not the only criterion for a reaction to be spontaneous. $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ should be -ve & A_f chemical affinity should be positive for a reaction to be spontaneous.

(3) $\Delta G^\circ = 0$ If then $K_p = 1$, reactants in their standard states are in equilibrium with products in their standard states.

Free Energy change ΔG in a chemical Reaction

For the given process, free energy change will be

$$aA + bB \rightleftharpoons mM + nN$$

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_M dn_M + \mu_N dn_N$$

At const T & P, $dT = dP = 0$

$$(dG)_{T,P} = \mu_A dn_A + \mu_B dn_B + \mu_M dn_M + \mu_N dn_N$$

If ξ is the degree of advancement of the reaction

$$d\xi = \frac{-dn_A}{a} = \frac{-dn_B}{b} = \frac{dn_M}{m} = \frac{dn_N}{n}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B)$$

$$\mu_i = \mu_i^\circ + RT \ln \frac{P_i}{P}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G^\circ + RT \ln Q_p$$

where $\Delta G^\circ = (m\mu_M^\circ + n\mu_N^\circ) - (a\mu_A^\circ + b\mu_B^\circ)$ (8)

$$Q_p = \frac{(P_M/P^\circ)^m (P_N/P^\circ)^n}{(P_A/P^\circ)^a (P_B/P^\circ)^b}$$

$\therefore \Delta G^\circ = -RT \ln K_p$ where K_p is eqⁿ const at which partial P of Products & reactants are at eqⁿ.

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -RT \ln K_p + RT \ln Q_p$$

ΔG = Free energy per stochiometric unit of reaction at const T & P for the reactants & Products at specified partial pressures

ΔG° = Std. Free energy of reaction with all reactants & Products at 1 atm P & specified temp

Relative values of ΔG° & $\ln Q_p$ determine thermodynamic prop

(1) when there is all Reactants & no Products of reaction $\ln Q_p$ is $-\infty$, then ΔG will be $-\infty$ & infinitely large no matter what is value of ΔG° & reaction will go spontaneously to the right

(2) when there is only Products & no reactants $\ln Q_p > 0$ the opposite situation will exists, there is formation of at least some of reactants

(3) At some intermediate amts of R & P, the ΔG° & $RT \ln Q_p$ balance each other & $\Delta G = 0$ reaction will be at equilibrium