Fugacity:

a)It is a measure of escaping tendency of a substance. It was introduced by G.N.Lewis to permit the free energy calculations of real gas.

b)Fugacity is a term which substitutes pressure in ideal gas free energy calculation. It has same unit as pressure.

c)The relation of free energy with fugacity is given by

$$\mathbf{G = RT\ln f + C} \qquad \text{------------I}$$

where , f – fugacity of the substance

C – constant whose value depends upon temperature and nature of the substance.

To evaluate the constant C, standard states are taken into consideration.

Equation – I in standard state can be written as

$$G^0 = RT\ln f^0 + C \qquad \text{------------II}$$

Subtracting II from I, we get , $G - G^0 = RT\ln f - RT\ln f^0$

$$G - G^0 = RT\ln\frac{f}{f_0}$$

$$G = G^0 + RT\ln\frac{f}{f_0}$$

$$G = G^0 + RT\ln \mathbf{a}$$

where $\mathbf{a} = \frac{f}{f_0}$ = activity of the substance

Activity :

Activity can be defined as the ratio of fugacity of the substance in the given state to the fugacity of the same substance in standard state.

In standard state, **a = 1** . Therefore $G = G^0$

The concept of activity introduced to gas as well as for solution, it accounts for the following parameters:

i) Attractive forces existing between the gas molecules.

ii) Nature of solid substance whether ionic or covalent

iii) Ionizing nature of the solute.

The above three factors are responsible for the breaking of ideal system behavior than the real system. This can be accounted by the expression for free energy change.

For ideal system , $\Delta\mathbf{G = 2.303nRT\ log\frac{P_2}{P_1}}$ ------------(1)

For real system , $\Delta\mathbf{G = 2.303nRT\ log\frac{a_2}{a_1}}$ ------------(2)

Equation 2 gives exact value of ΔG when applied to real system.

Activity Coefficient:

a) It is represented by the symbol **γ**

b) For a gaseous system, it is a measure of extent of deviation of real behaviour of gas from ideal behaviour, which is expressed as a ratio of fugacity to pressure of the gas.

ie. $\boldsymbol{\gamma = \frac{f}{P}}$, where , $\boldsymbol{f}$ - is fugacity of gas and **P** – pressure of the gas

for ideal gas , **γ = 1,** therefore, fugacity = pressure. Thus a real gas approaches to ideal behavior at very low pressure and high temperature.

The activity coefficient of the solutions is defined as $\boldsymbol{\gamma = \frac{a}{m}}$ where a - activity of the electron , m – molality of the solution.

For an ideal solution , concentration = active mass

But for a real solution, some of the portion of the solute in solution may get partially solvated or may remain non-solvated. If the later part reacts, then this portion only account for the active mass. Hence, activity coefficient may be regarded as a measure of extent to which an ion or molecule departs from ideal behavior.

Law of mass action.

a) It gives the relation between rate of a chemical reaction with the active masses of the reactant.

b) It was put forward by Guldberg and Peter Waage in 1864.

c) The law of mass action states that **the ratio at which a substance reacts is proportional to its active mass and the rate of a chemical reaction**

is proportional to the product of the active masses of the reactants, with each active mass term raised to a power equal to its stoichiometric coefficient in the balanced chemical equation.

Eg. consider the following reaction

aA + bB + cC → products

if [A], [B] and [C] represent molar concentrations (active masses) of A, B nad C respectively, then by law of mass action,

Rate of reaction $\propto [A]^a[B]^b[C]^c$

Rate of reaction = $k[A]^a[B]^b[C]^c$

Where, k is rate constant of the reaction.

Equilibrium constant and its characteristics.

Equilibrium constant : It is defined as the ratio of the products of the equilibrium concentration (mol/dm^3) of products to the product of the equilibrium concentration of the reactants with the concentration of each substance raised to the power equal to its stoichiometric coefficient in the balanced chemical equation.

Explanation : Consider the following reversible reaction at equilibrium:

$$aA + bB \rightleftarrows cC + dD$$

By the law of mass action,

Rate of forward reaction $\propto [A]^a[B]^b$

ie. Rate of forward reaction(R_f) = $k_f [A]^a[B]^b$

Where, k_f is rate constant of the forward reaction.

Similarly,

Rate of backward reaction $\propto [C]^c[D]^d$

ie. Rate of forward reaction(R_b) = $k_b[C]^c[D]^d$

Where, $\mathbf{k_b}$ is rate constant of the backward reaction.

At equilibrium, $R_f = R_b$

$k_f [A]^a[B]^b = k_b[C]^c[D]^d$

therefore, $\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ or

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

Where , k_c is equilibrium constant o reaction in moles dm^{-3}

For a reaction involving gaseous reactants and products at equilibrium, the equilibrium constant is expressed in terms of partial pressure as k_p and is given by the expression,

$$K_p = \frac{{P_C}^c {P_D}^d}{{P_A}^a {P_B}^b}$$

Characteristics of equilibrium constant are as follows:

1) The magnitude of equilibrium constant is unaffected by changes in concentration of reactants or products, pressure and catalyst involved in reaction.

2)The equilibrium constant value changes with change in temperature. For exothermic reaction, the equilibrium constant decreases with rise in temperature.

3)The expression for equilibrium constant of a reaction is devoid of concentration of pure solids or pure liquid.

4) The value of equilibrium constant is dimensionless.

5) The form of equilibrium constant expression and the numerical value of equilibrium constant depend on the form of balanced chemical equation.

For eg. $2NO + O_2 \rightleftarrows 2NO_2$

$$k_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

If the reaction is written in reverse manner

$2NO_2 \rightleftarrows 2NO + O_2$, then

$$k'_c = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

$\therefore$ it follows that $k_c = \frac{1}{k'_c}$

Relation between k_p and k_c.

Consider the following reversible reaction at equilibrium,

aA + bB ⇄ cC + dD

the equilibrium constant in terms of partial pressure is given by ,

$$K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} \text{-------------------(1)}$$

The equilibrium constant k_c in terms of moles dm^{-3} is given by,

$$k_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{-------------------(2)}$$

From the ideal gas equation PV = nRT

$$\mathbf{P = \frac{nRT}{V} = cRT} \text{ ----------------(3)}$$

Therefore, $P_C{}^c = C_C{}^c(RT)^c$, $P_D{}^d = C_D{}^d(RT)^d$, $P_A{}^a = C_A{}^a(RT)^a$, $P_B{}^b = C_B{}^b(RT)^b$--(4)

Substituting (4) in equation (1), we get,

$$K_p = \frac{C_C{}^c(RT)^c . C_D{}^d(RT)^d}{C_A{}^a(RT)^a . C_B{}^b(RT)^b}$$

$$= \frac{C_C{}^c C_D{}^d}{C_A{}^a . C_B{}^b} . \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$K_p = Kc\ RT^{(c+d)-(a+b)}$ from equation (2)

$\therefore K_p = K_c . RT^{\Delta n}$, where $\Delta n = (c+d) - (a+ b)$

Variation of the equilibrium constant with pressure (*derivation of Vant Hoff reaction isotherm equation)*

The equilibrium constant, to a certain extent is found to change with change in pressure at constant temperature. The vant Hoff reaction isotherm gives a relationship between standard free energy change and equilibrium constant of the reaction. The relation is obtained as follows:

Consider the following reversible reaction at equilibrium

aA + bB ⇄ cC + dD

The equilibrium constant k_p for the change reaction is given by

$$K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} \text{-------------------(1)}$$

The Gibb's free energy for a system is defined as,

$G = H - TS$ where, H is enthalpy of the system ,
T – temperature ,
S – entropy of the system

But $H = U + PV$

Therefore, $G = U + PV - TS$ ------------------------------------(2)

On differentiation of equation (2) we get,

$$dG = dU + PdV + VdP - TdS - SdT$$

From 1st law $dU = dq - PdV$ ------------------------------------(3)

and $dq = T.dS$ --(4)

Substituting (3) and (4) in equation (2) we get,

$$dG = dq - PdV + PdV + VdP - dq - SdT$$

Therefore , $dG = VdP - SdT$ --------------------------------------(5)

At constant temperature dT= P, therefore $dG = VdP$----------(6)

For the reaction in equation (1), assume that the reactants and products are ideal gases.

For one mole of an ideal gas,

$$PV = RT$$

Therefore, $V = \frac{RT}{P}$ --(7)

Substituting (7) in equation (6) we get,

$dG = \frac{RT.dP}{P}$ ---(8)

Integrating equation (8) we get,

$$\int dG = RT \int \frac{1}{P}.dP$$

$G = RT\ln P + c$ ---(9)

Where c is the constant of integration.

To evaluate c, we apply the condition of standard state. In standard state, P = 1 atm

$$G^0 = RT\ln(1) + c$$

ie. $G^0 = c$ --(10)

Substituting (10) in equation (9) we get,

$G = G^0 + RT\ln P$ --(11)

For reaction in equation (1) , the free energy change ΔG is given by,

$$\Delta G = \sum G_{Products} - \sum G_{reactant}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \text{ -----------------------(12)}$$

Expressing free energies of reactants and products in the form of equation (11) we get,

$$\left.\begin{aligned} aG_A &= aG_A + aRT\ln P_A \\ bG_B &= bG_B + bRT\ln P_B \\ cG_C &= cG_C + cRT\ln P_C \\ dG_D &= dG_D + dRT\ln P_D \end{aligned}\right\} \text{ ----------------------------------(13)}$$

Substituting equation (13) in equation (12) we get

$\Delta G = [(cG^0_C + cRT\ln P_C)+(dG^0_D + dRT\ln P_D)] - [(aG^0_A + aRT\ln P_A)+(bG^0_B + bRT\ln P_B)]$ --(14)

On rearranging equation (14) we get,

$\Delta G = [(cG^0_C + dG^0_D) - (aG^0_A + bG^0_B)] + (RT\ln P^c_C + RT\ln P^d_D) - (RT\ln P^a_A)+(RT\ln P^b_B)$

$$\Delta G = \Delta G^0 + RT ln \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$$

$\Delta G = \Delta G^0 + RT\ln k_p$ (from equation (2))

At equilibrium $\Delta G = 0$

Therefore, $\Delta G^0 = - RT\ln k_p$

Or $\boldsymbol{\Delta G^0 = - 2.303RT\log_{10}k_p}$ --(15)

Equation (15) is known as vant Hoff reaction isotherm. This is considered as a thermodynamic derivation of a law of chemical equilibrium.

Variation of equilibrium constant with temperature (derivation of Vant Hoff reaction isochore equation)

The equilibrium constant of a reaction depend upon temperature and it changes with change in temperature. The variation of equilibrium constant with temperature is given by vant Hoff reaction isochore, which is derived as follows:

Consider a gaseous chemical reaction at equilibrium assuming the reactants and products as ideal gases.

$$aA_{(g)} + bB_{(g)} \rightleftarrows cC_{(g)} + dD_{(g)}$$

The equilibrium constant K_p for this reaction is given by

$$\boldsymbol{K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}}$$

The standard free energy change ΔG^0 is related to the equilibrium constant k_p by the relation,

$$\Delta G^0 = - RT\mathit{l}nk_p \text{ --------------------------(1)}$$

Differentiating equation (1) w.r.t. temperature at constant pressure, we get,

$$\left(\frac{d(\Delta G^0)}{dT}\right)_P = - R\mathit{l}nk_p - RT\frac{dln\,k_p}{dT} \text{ ------------------------(2)}$$

Multiplying equation (2) throughout by T, we get

$$T\left(\frac{d(\Delta G^0)}{dT}\right)_P = - RT\mathit{l}nk_p - RT^2\,\frac{dln\,k_p}{dT} \text{ ----------------(3)}$$

But , $\Delta G^0 = - RT\mathit{l}nk_p$

Therefore, $T\left(\frac{d(\Delta G^0)}{dT}\right)_P = +\Delta G^0 - RT^2\,\frac{dln\,k_p}{dT}$ -----------------(4)

From Gibbs_Helmholtz equation in standard conditions,

$$\Delta G^0 = \Delta H^0 + T\left(\frac{d(\Delta G^0)}{dT}\right)_P$$

Therefore, $T\left(\frac{d(\Delta G^0)}{dT}\right)_P = \Delta G^0 - \Delta H^0$ -----------------------------(5)

Comparing equation (5) with (4) we get,

$$\Delta H^0 = - RT^2\,\frac{dln\,k_p}{dT} \text{ --------------------------------------(6)}$$

or $$\frac{dln\,k_p}{dT} = \frac{\Delta H^0}{RT^2} \text{--(7)}$$

Equation (7) is referred as van't Hoff reaction isochore because it was first developed by Vant Hoff for a system at constant volume. In practice, it is observed that for a chemical reaction, the difference between ΔH and ΔH^0 is almost negligible. Hence replacing ΔH^0 by ΔH in equation (7) we get,

$$\frac{dln\,k_p}{dT} = \frac{\Delta H}{RT^2} \text{--(8)}$$

If K_{p_1} and K_{p_2} are equilibrium constants of a reaction at temperature T_1 and T_2 respectively ($T_2 > T_1$) , then integrating equation (8) we get,

$$\int_{K_{p_1}}^{K_{p_2}} \frac{dlnk_p}{dT} = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} - - - - - - (9)$$

On rearranging equation (8) and assuming ΔH to remain constant obe the temperature range T_1 and T_2 , we get,

$$\int_{K_{p_1}}^{Kp\,2} dlnk_p = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{1}{T^2}.dT$$

$$[lnk_p]_{k_{p_1}}^{k_{p_2}} = \frac{\Delta H}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2} \qquad - - - - - - (10)$$

$$lnk_{p_2} - lnk_{p_1} = \frac{\Delta H}{R}\left[-\frac{1}{T_2} + \frac{1}{T_1}\right]$$

$$\therefore ln\frac{k_{p_2}}{k_{p_1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$2.303log\frac{k_{p_2}}{k_{p_1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] - - - - - - -(11)$$

Equation (11) is the integrated form of Vant Hoff equation.

Applications of Vant Hoff reaction isochore equation:

1) It helps to calculate ΔH if k_{p_1} and k_{p_2}, T_1 and T_2 are known.

2) It helps to calculate equilibrium constant value at any temperature provided ΔH is known for the reaction.