Chemical Equilibrium

Equilibrium: It is the state of a system when its properties remain unaltered with time provided the necessary variables like temperature and pressure remain constant. There are two types of equilibria

(A) Physical Equilibria
(B) Chemical Equilibria

Characteristics of chemical equilibrium:

(1) When an equilibrium is established the concentration of all the reactant and product molecules remains the same with time.

(2) The equilibrium is reversible and thereby dynamic and static in nature.

(3) The equilibrium can be approached from either side, ie. the same equilibrium state can be reached by starting the above reaction from the reactants H_2 and I_2 or the product ie HI.

Law of Mass Action:

The law states that,

"The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is directly proportional to the product of the active masses of the reacting substances."

Let us consider a general reversible chemical reaction,

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

According to the law of mass action, assuming that active masses are equivalent to molar concentrations, the rate of the forward reaction,

$$r_f \propto [A]^a[B]^b = k_f[A]^a[B]^b$$

And the rate of reverse reaction,

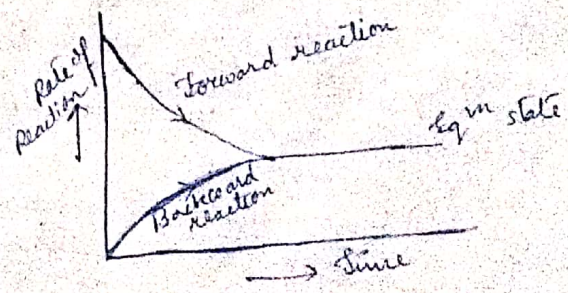
$$r_R \propto [M]^m[N]^n = k_R[M]^m[N]^n.$$

Where k_f and k_R are proportionality constants, and square bracket rep k_f is known as rate constant of the forward reaction and k_R is called rate constant of the reverse reaction.

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction

$$\text{i.e. } k_f[A]^a[B]^b = k_R[M]^m[N]^n$$

$$\therefore \frac{k_f}{k_R} = K_{eq} = \frac{[M]^m[N]^n}{[A]^a[B]^b} \longrightarrow (1)$$



The constant K_{eq} is called the eqm constant of the reaction. and eqn (1) represents the law of chemical equilibrium.

Free energy and Chemical Equilibrium:

A reaction which once properly initiated proceeds by itself is known as Spontaneous reaction.

e.g. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$, $\Delta H = -286.2 KJ$.

We know that, if the free energy change ΔG_r of a Chemical reaction is negative, the reaction can take place simultaneously, i.e. it is feasible.

If the free energy is zero, the reaction is in a state of equilibrium and if the free energy change is positive, the reaction would not proceed.

We have, $\Delta G_r = \Delta H - T\Delta S$. $\longrightarrow$ (1).

For a reaction to be spontaneous, ΔG_r must have a negative value. Hence, in eqn (1), ΔH should be negative and $T\Delta S$ should be positive. However, depending upon the relative magnitude of ΔH and ΔS and their sign following situations arise!

(1) When both energy and entropy factors are favourable, i.e. ΔH is negative and $T\Delta S$ is positive, the reaction would be highly feasible.

(2) Energy factor alone is favourable, i.e. ΔH is negative and ~~but~~ $T\Delta S$ is also negative. In this case, if the value of ΔH is more than $T\Delta S$, the reaction would be feasible. But, if the numerical value of $T\Delta S$ is greater than that of ΔH, the reaction would not be feasible.

(3) Energy factor is not favourable but entropy factor is favourable. i.e. ~~the value of~~ ΔH has a positive value and $T\Delta S$ has also a positive value. In this case, the reaction will be feasible only if $T\Delta S$ is numerically greater than ΔH.

Role of Temperature:

(1) At high temp^r, the entropy factor predominates: In case of an endothermic reaction ΔH is always positive. Hence, to make a reaction feasible, the entropy factor $T\Delta S$ is increased to a large extent by increasing temp^r. That's why endothermic reactions occur at high temp^r.

(2) At low temp^r, energy factor predominates: In case of an exothermic reaction, ΔH is always negative. When temp^r is decreased, the entropy factor $T\Delta S$ decreases to a large extent. That's why exothermic reactions remain feasible at low temp^r.

Standard free energy change, ΔG°:

The standard free energy change of a reaction is defined as the free energy change of a reaction when the reactants and products are in their standard states.

$$\text{i.e } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where ΔH° is the standard enthalpy change of the reaction and ΔS° is the standard entropy change of the reaction at the temperature T.

Standard free energy of formation of compounds, ΔG_f°:

It is defined as the free energy change involved in the formation of one mole of the compound in its standard state (25°C and 1 atm pressure) from its elements in their standard states.

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S^\circ$$

Standard free energy change ΔG° for reactions:

The standard free energy change of formation of various substances can be used to calculate ΔG° for any reaction by the relation,

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ (products)} - \sum \Delta G_f^\circ \text{ (reactants)}$$

Free energy of mixing and spontaneity:

According to thermodynamics, the total Gibbs free energy (G) of a two component solution is given by

$$G = n_1\bar{G}_1 + n_2\bar{G}_2 \longrightarrow (1)$$

where G is the total Gibbs energy of the system, n_i is the no. of moles of component i and $\bar{G}_i$ is the partial molar Gibbs energy of component i.

The molar Gibbs energy of an ideal gas can be obtained using equation,

$$\bar{G} = \bar{G}^\circ + RT \ln \frac{P}{1\,bar} \longrightarrow (11)$$

where, $\bar{G}^\circ$ is the standard molar Gibbs energy of the gas at 1 bar, and P is the pressure of the system.

Also known as, $\bar{G}_i = \mu_i \longrightarrow (111)$.

$\therefore$ (ii) $\Rightarrow \overline{G_i} = \mu_i = \mu_i^\circ + RT \ln \frac{P_i}{1\ bar}$ ⟶ (iv)

where μ_i is the chemical potential of the i^{th} component, μ_i° is the standard chemical potential of component i of 1 bar and P_i is the partial pressure of the component i.

If we consider a system containing two gases at same temperature and pressure, then Gibbs energy of the system before mixing them is,

$$G_{initial} = n_1(\mu_1^\circ + RT \ln P) + n_2(\mu_2^\circ + RT \ln P) \longrightarrow (v)$$

When the gases are mixed together, each will exert a partial pressure on the total system, P_1 and P_2 such that total pressure, $P = P_1 + P_2$.

$\therefore$ Gibbs energy of the mixture,

$$G_{final} = n_1(\mu_1^\circ + RT \ln P_1) + n_2(\mu_2^\circ + RT \ln P_2) \longrightarrow (vi)$$

$\therefore$ Gibbs energy of mixing.

~~$\Delta_{mix} G = G_{fin} - G_{final}$~~

$$\Delta_{mix} G = G_{final} - G_{initial}$$

$$= n_1 RT \ln \frac{P_1}{P} + n_2 RT \ln \frac{P_2}{P}$$

$$= n_1 RT \ln x_1 + n_2 RT \ln x_2 \longrightarrow (vii)$$

where, $P_i = x_i P$ ⟶ (viii)

x_i is the mole fraction of gas i.

We know, $x_i = \frac{n_i}{n}$ ⟶ (viii)

$\therefore$ (viii) $\Rightarrow$

$$\boxed{\Delta_{mix} G = nRT(x_1 \ln x_1 + x_2 \ln x_2)} \longrightarrow (ix)$$

Eq^n (ix) ~~is the mixing of~~ shows the effect of mixing on the Gibbs energy of sth^n.

$\therefore$ x_1 and $x_2 < 1$.

$\therefore$ $\Delta_{mix} G$ will always be negative.

Hence, gases mix spontaneously at constant P and T.

Thermodynamic derivation between Gibbs free energy of reaction and reaction quotient:

Let us consider a general reversible reaction.

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

where the reactants and products are considered as ideal gases.

We know,

$$G_{reactant} = a\mu_A + b\mu_B.$$

where μ_A and μ_B are the chemical potentials of the species A and B respectively.

Similarly, $G_{product} = m\mu_M + n\mu_N$.

$$\therefore (\Delta G)_{reaction} = G_{product} - G_{reactant}$$

$$= (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) \longrightarrow (I)$$

The chemical potential of the i^{th} species in the gaseous state is given by. $\mu_i = \mu_i^\circ + RT\ln p_i$. $\longrightarrow (II)$.

where, p_i is the partial pressure of the i^{th} component and μ_i° is its standard chemical potential.

$$\therefore (I) \Rightarrow (\Delta G)_{reaction} = \left[m\left(\mu_M^\circ + RT\ln p_M\right) + n\left(\mu_N^\circ + RT\ln p_N\right)\right] - \left[a\left(\mu_A^\circ + RT\ln p_A\right) + b\left(\mu_B^\circ + RT\ln p_B\right)\right].$$

$$= \left[\left(m\mu_M^\circ + n\mu_N^\circ\right) - \left(a\mu_A^\circ + b\mu_B^\circ\right)\right] + RT\ln\left(\frac{p_M^m\, p_N^n}{p_A^a\, p_B^b}\right).$$

$$\Rightarrow (\Delta G)_{reaction} = (\Delta G^\circ)_{reaction} + RT\ln\left(\frac{p_M^m\, p_N^n}{p_A^a\, p_B^b}\right).$$

The factor $\frac{p_M^m\, p_N^n}{p_A^a\, p_B^b}$ is called pressure coefficient or reaction coefficient or reaction quotient and is represented as Q_p.

$$\therefore \boxed{\Delta G = \Delta G^\circ + RT \ln Q_p} \longrightarrow (iii)$$

Now, if $\Delta G = 0$, i.e. when equilibrium is established

$$(iii) \Rightarrow 0 = \Delta G^\circ + RT \ln (Q_p)_{equilib}$$

$$\Rightarrow \Delta G^\circ = -RT \ln (Q_p)_{equilib}$$

$$\Rightarrow \boxed{\Delta G^\circ = -RT \ln \left(\frac{P_M^m P_N^n}{P_A^a P_B^b} \right)_{equilib}}$$

Relationship of standard free energy change and equilibrium constant : Van't Hoff reaction isotherm :

We have,

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

Here, R = gas constant.

T = Temp$^{\text{r}}$ which is constant.

~~P_M^*~~ P_M, P_N, P_A, P_B are definite values corresponding to equilibrium state.

a, b, m, n are stoichiometric coefficients of the reactant and product molecules A, B, C and D respectively.

$\therefore\ \Delta G^\circ = -RT \ln \left(\frac{P_M^m P_N^n}{P_A^a P_B^b} \right)$ is constant.

But, $K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b}$

$$\therefore\ \Delta G^\circ = -RT \ln K_p \longrightarrow (i)$$

$$\therefore \boxed{\Delta G = -RT \ln K_p + RT \ln Q_p} \longrightarrow (ii)$$

Eqn (ii) was first given by van't Hoff

Eqn (i) $\Rightarrow \boxed{K_p = e^{-\Delta G^\circ / RT}}$

Degree of Advancement of Reaction; De Donder's Treatment of Chemical Equilibria:

For a general reaction,

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

the Gibbs free energy, $G = f(T, P, n)$.

Hence, Gibbs free energy change is given by.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{P,T} dn.$$

$$= -SdT + Vdp + \mu_A dn_A + \mu_B dn_B + \mu_M dn_M + \mu_N dn_N \longrightarrow (I).$$

If the reaction is carried out at constant T and P.

Then, $dT = 0$ and $dP = 0$

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

If, in a balanced equation for the reaction, all the moles of the reactants get converted into products, the progress of the reaction is said to be 100%. But if all the moles of the reactants do not get converted into products, the reaction would be less than 100%. Thus, to express the progress or advancement of the reaction, a variable ξ is introduced - called the degree of advancement of a chemical reaction.

If the reaction advances by ξ units, then.

$$\left.\begin{aligned} n_A &= n_A^\circ - a\xi, & n_B &= n_B^\circ - b\xi, \\ n_M &= n_M^\circ + m\xi, & n_N &= n_N^\circ + n\xi. \end{aligned}\right\} \longrightarrow (III).$$

differentiating eq^n (III).

$$dn_A = -a\,d\xi, \quad dn_B = -b\,d\xi, \qquad \left[\because n_i^\circ s \text{ are constants}\right]$$

$$dn_M = +m\,d\xi, \quad dn_N = n\,d\xi$$

$$\therefore d\xi = -\frac{dn_A}{a}, \quad d\xi = \frac{-dn_B}{b} = \frac{dn_B}{b},$$

$$d\xi = \frac{+dn_M}{m}, \quad d\xi = \frac{dn_N}{n}.$$

The quantity $d\xi$ is called the differential advancement or the increment of the degree of advancement of the reaction.

Other forms of Equilibrium constants:

If the chemical potentials of various species are expressed in terms of mole fractions (x_i), then

$$\mu_i = \mu_i^\circ + RT \ln x_i \longrightarrow (1).$$

We know,

$$K_p = \left(\frac{P_M^m P_N^n}{P_A^a P_B^b} \right)_{equilib.}$$

$$\therefore K_x = \frac{x_M^m x_N^n}{x_A^a x_B^b}.$$

Again,

If, the chemical potentials are expressed in terms of molar concentrations (c_i), Then,

$$\mu_i = \mu_i^\circ + RT \ln c_i.$$

$$\therefore K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}.$$

Hence,

Case I: When concentrations of the reactants and products are given in terms of partial pressures,

$$K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b}.$$

Case II: When concentrations of reactants and products are in terms of mole fractions.

$$K_x = \frac{x_M^m x_N^n}{x_A^a x_B^b}.$$

Case III: When concentrations of reactants and products are in terms of molar concentrations.

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}.$$

Q. Calculate K_p for the reaction: $\frac{3}{2} O_2(g) \rightleftharpoons O_3(g)$ at 298 K, ΔG° for the reaction is 163.43 KJ mol^{-1}.

Soln:- $\Delta G^\circ = -RT \ln K_p$

$\Rightarrow \ln K_p = \frac{-\Delta G^\circ}{RT}$

$= \frac{163.43 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{mol}^{-1}) \times 298 \text{ K}}$

$= -65.964$

$\Rightarrow \log K_p \times 2.303 = -65.964$

$\Rightarrow \log K_p = \frac{-65.964}{2.303} = -28.64$

$\Rightarrow K_p = \text{antilog}(-28.64)$

$\Rightarrow K_p = \text{antilog}(\overline{29}.3576)$

$\Rightarrow K_p = 2.23 \times 10^{-29}$

Coupling of Exoergic and Endoergic reactions:

The free energy change for any reaction ΔG° is given by.

$\Delta G^\circ = \Sigma \Delta G_f^\circ \text{(products)} - \Sigma \Delta G_f^\circ \text{(reactants)}$.

where, ΔG_f° is the free energy of formation.

The chemical reactions in which ΔG neg is negative are called exoergic (exo- exoergonic (exo = out, ergo = work). and ΔG when ΔG is positive the reaction is called endoergonic.

In exoergonic reactions the ΔG_f° values of products are less than those of reactants, and in endoergonic reactions ΔG_f° (reactants) are less than ΔG_f° (products).

e.g. Glucose + H_3PO_4 $\longrightarrow$ G-6-P + H_2O, $\Delta G^\circ = 12.5$ KJ mol^{-1}.

Glucose-6-phosphate

This is an endoergonic reaction.

$ATP + H_2O \longrightarrow ADP + H_3PO_4$, $\Delta G^\circ = -34.1$ KJ/mol

This is an exoergonic reaction.

Imp: Relations between K_p, K_c and K_x:

Case I: Relation between K_p and K_x:

In an ideal gaseous mixture, each component obeys Dalton's law of partial pressures, i.e. $p_i = x_i P$, where P is the total pressure and p_i is the partial pressure of the ith component with mole fraction x_i in the mixture.

For the reaction

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

we have,

$$p_A = x_A P.$$
$$p_B = x_B P.$$
$$p_M = x_M P$$
$$p_N = x_N P,$$

$$\therefore K_p = \frac{p_M^m p_N^n}{p_A^a p_B^b} = \frac{(x_M P)^m (x_N P)^n}{(x_A P)^a (x_B P)^b}$$

$$= \frac{x_M^m x_N^n}{x_A^a x_B^b} P^{(m+n)-(a+b)}.$$

$$\Rightarrow K_p = K_x (P)^{\Delta n_g} \longrightarrow (1),$$

where, Δn_g = sum of no. of moles of gaseous products − sum of no. of moles of gaseous reactants.

$$= (m+n) - (a+b).$$

Case II: Relation between K_p and K_c:

For an ideal gas mixture,

$$p_i V = n_i RT.$$

$$\Rightarrow p_i = \left(\frac{n_i}{V}\right) RT = c_i RT.$$

where, $c_i = \frac{n_i}{V}$ is the molar concentration of the ith component in the mixture of total volume V.

Hence,

$P_A = C_A RT$, $P_B = C_B RT$

$P_M = C_M RT$; $P_N = C_N RT$.

$$\therefore K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b} = \left(\frac{C_M^m C_N^n}{C_A^a C_B^b}\right)(RT)^{(m+n)-(a+b)}$$

$$\Rightarrow K_p = K_C (RT)^{\Delta ng} \longrightarrow (2)$$

Eq^{n}s (1) and (2) $\Rightarrow K_p = K_x (P)^{\Delta ng} = K_C (RT)^{\Delta ng} \longrightarrow (3)$.

If $\Delta ng = 0$,

$m + n = a + b$.

Then, $\boxed{K_p = K_x = K_C}$

Q. Calculate K_C for the reaction :

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

for which $K_p = 3.5 \times 10^{-23}$ atm at 27°C.

Soln :- For the reaction,

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g),$$

$$\Delta ng = (2+1) - 2 = 1.$$

$\therefore K_C = \frac{K_p}{}$

we know, $K_p = K_C (RT)^{\Delta ng}$

$$\Rightarrow K_C = \frac{K_p}{(RT)^{\Delta ng}}$$

$T = 27°C$
$= (27 + 273)$
$= 300K$

$$= \frac{3.5 \times 10^{-23} \text{ atm}}{0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 300K}$$

$\times 300K$

$$= 1.42 \times 10^{-24} \text{ mol dm}^{-3}.$$

Home assignment:

Q. Calculate K_c and K_x for the reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$ for which

$K_p = 0.157$ atm at 27°C and 1 atm pressure.

Temperature – Dependence of the equilibrium constant; The Van't Hoff equation or Van't Hoff Isochore:

We know,

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

$$\Rightarrow \frac{\Delta G^\circ}{T} = -R \ln K_p \quad \longrightarrow (1)$$

Differentiating both sides w.r.t. temperature T at constant P.

$$\left[\frac{\partial (\Delta G^\circ/T)}{\partial T}\right]_P = -R \frac{d \ln K_P}{dT} \quad \longrightarrow (II)$$

But as per the Gibbs - Helmholtz equation,

$$\left[\frac{\partial (\Delta G^\circ/T)}{\partial T}\right] = -\frac{\Delta H^\circ}{T^2} \quad \longrightarrow (III)$$

$\therefore$ (II) and (III) $\Rightarrow$ $$\boxed{\frac{d \ln K_P}{dT} = \frac{\Delta H^\circ}{RT^2}} \quad \longrightarrow (IV)$$

where ΔH° is the standard enthalpy of the reaction.

Eqn (IV) is known as Van't Hoff equation or Van't Hoff isochore.

Integrated form of the Van't Hoff equation:

We know,

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \quad \longrightarrow (1)$$

If over a short temperature range, ΔH° is assumed to be temp^r independent, then integration of eqn (1) gives,

$$\int \frac{d \ln K_p}{dT} = \int \frac{\Delta H^\circ}{RT^2} dT = \frac{\Delta H^\circ}{R} \int \frac{dT}{T^2} \quad \longrightarrow (II)$$

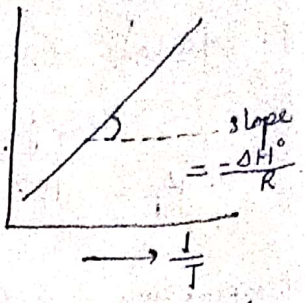
$$\Rightarrow \ln K_p = -\frac{\Delta H^\circ}{R} + I \quad \longrightarrow (III)$$

where I is the constant of integration.

If eqn (II) is plotted in a graph with $\ln K_P$ in y-axis and $1/T$ in x-axis then, a straight line is obtained

with slope $= -\Delta H^\circ/R$.

$\therefore \Delta H^\circ = -R \times$ slope.



Now, if the integration is carried out between two temperatures T_1 and T_2 when the equilibrium constants are $K_{p,1}$ and $K_{p,2}$ respectively, then, assuming that ΔH° is constant over this temp^{re} range, we get.

$$\int_{K_{p,1}}^{K_{p,2}} d\ln K_p = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \longrightarrow (iv).$$

$$\Rightarrow \ln \frac{K_{p,2}}{K_{p,1}} = \frac{\Delta H^\circ}{R} \left[-\frac{1}{T_2} - \left(-\frac{1}{T_1}\right) \right]$$

$$\Rightarrow \boxed{\ln \frac{K_{p,2}}{K_{p,1}} = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]} \longrightarrow (v)$$

Eqn (v) is the integrated Vant Hoff equation.

Q. The eqm constant K_p for the reaction.

$H_2(g) + S(g) \rightleftharpoons H_2S(g)$ is $20.2\ atm^{-1}$ at 945°C and $9.1\ atm^{-1}$ at 1065°C. Calculate ΔH°.

Soln:

Given, $K_{p,2} = 9.1\ atm^{-1}$,

$K_{p,1} = 20.2\ atm^{-1}$.

$T_1 = 945°C = 945 + 273 = 1218\ K$.

$T_2 = 1065°C = 1338\ K$.

We know,

$$\ln\left(\frac{K_{p,2}}{K_{p,1}}\right) = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right].$$

$$\Rightarrow \ln\left(\frac{9.1}{20.2}\right) = \frac{\Delta H^\circ}{R} \left[\frac{1338 - 1218}{1338 \times 1218} \right].$$

$$\Rightarrow \Delta H^\circ = \left(8.314\ J K^{-1} mol^{-1}\right) \ln\left(\frac{9.1}{20.2}\right) \left(\frac{1338 \times 1218}{1338 - 1218}\right)$$

$$\Rightarrow \Delta H^\circ = -88679.5\ J\,mol^{-1}$$

$$\Rightarrow \Delta H = -88.7\ kJ\,mol^{-1}\ //.$$

Pressure - dependence of equilibrium constants:

① Pressure dependence of K_p:

We know,

$$\Delta G = -RT\ln K_p .$$

Since ΔG° depends upon temp^r alone, hence K_p also depends on temp^r alone and is independent of pressure.

Hence,

$$\left(\frac{\partial \ln K_p}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left(\frac{\Delta G^\circ}{RT}\right)_T = 0 .$$

② Pressure - dependence of K_c:

$$\because \quad K_p = K_c (RT)^{\Delta ng}$$

$$\Rightarrow K_c = K_p (RT)^{-\Delta ng}$$

$$\Rightarrow \ln K_c = \ln K_p - \Delta ng \ln RT .$$

$$\Rightarrow \left(\frac{d \ln K_c}{dP}\right)_T = \left(\frac{d \ln K_p}{dP}\right)_T - \Delta ng \left(\frac{d \ln RT}{dP}\right)_T .$$

$\because \left(\frac{d \ln K_p}{dP}\right)_T$ and $\Delta ng \left(\frac{d \ln RT}{dP}\right)_T$ are equal to 0.

$$\therefore \left(\frac{d \ln K_c}{dP}\right)_T = 0 .$$

i.e. K_c is also independent of pressure.

③ Pressure - dependence on K_x:

We know $K_p = K_x P^{\Delta ng}$

$$\Rightarrow K_x = K_p \cdot P^{-\Delta ng}$$

$$\Rightarrow \ln K_x = \ln K_p - \Delta ng \ln P .$$

$$\Rightarrow \left(\frac{d \ln K_x}{dP}\right)_T = \left(\frac{d \ln K_p}{dP}\right)_T - \Delta ng \left(\frac{d \ln P}{dP}\right)_T$$

$$= \left(\frac{d \ln K_p}{dP}\right) - \frac{\Delta ng}{P} .$$

$$= -\frac{\Delta ng}{P} \quad \left[\because \frac{d \ln K_p}{dP} = 0\right] .$$

$$= -\frac{\Delta V}{RT} \longrightarrow (1) .$$

where, $\Delta V = \Sigma V_{products} - \Sigma V_{reactants}$.

From eqⁿ ①, following conclusions are obtained:

① When $\Delta n_g = 0$, the reaction involves no change in the total no. of moles of gaseous species in the system so that $\Delta V = 0$, K_x is independent of pressure.

② When $\Delta n_g \neq 0$, K_x is pressure dependent.

ⓐ $\Delta n_g > 0$, i.e. there is an increase in the no. of moles of so that $\Delta V > 0$. Hence, K_x decreases with increasing of pressure in eqⁿ ①.

ⓑ $\Delta n_g < 0$, i.e. there is a decrease in the no. of moles so that $\Delta V < 0$. Hence, K_x increases with increasing pressure.

Equilibria between Ideal gases and pure condensed gases

If the substances participating in the chemical equilibrium are in more than one phase, the equilibrium is said to be heterogeneous.

If the substances are all present in a single phase, the equilibrium is homogeneous.

Let us consider the dissociation of solid calcium carbonate in a closed vessel.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g).$$

If ξ is the extent of the reaction, then.

$$d\xi = -dn_{CaCO_3} = dn_{CaO} + dn_{CO_2}.$$

and $dG = (\mu_{CaO} + \mu_{CO_2} - \mu_{CaCO_3})\, d\xi$.

$$\therefore \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_{CaO} + \mu_{CO_2} - \mu_{CaCO_3} = \Delta G$$

at equilibrium, $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$.

$$\therefore \mu_{CaO} + \mu_{CO_2} - \mu_{CaCO_3} = 0.$$

Under ordinary conditions,

$$\mu_{CaO} = \mu^\circ_{CaO} \quad \text{and} \quad \mu_{CaCO_3} = \mu^\circ_{CaCO_3}.$$

Also, $\mu_{CO_2} = \mu^\circ_{CO_2} + RT \ln p_{CO_2}$.

$\therefore$ At equilibrium,

$$\mu_{CaCO_3} (= \mu^\circ_{CaCO_3}) = \mu_{CaO} + \mu_{CO_2} = \mu^\circ_{CaO} + \mu^\circ_{CO_2} + RT \ln p_{CO_2}.$$

$$\Rightarrow RT \ln P_{CO_2} = -\left[\mu^\circ_{CaO} + \mu^\circ_{CO_2} - \mu^\circ_{CaCO_3}\right] = -\Delta G^\circ$$

But, $-\Delta G^\circ = RT \ln K_p$.

$\therefore \quad K_p = P_{CO_2}$

Thus, it is found that whereas ΔG° of a reaction involves ΔG°_f values of the reactants and the products, the equilibrium constant involves only the partial pressures of the gaseous state species.

Factors that alter the state of equilibrium ; Le Chatelier's principle :

There are three main factors which alter the state of equilibrium

① Concentration
② Temperature
③ Pressure

≠ Le Chatelier, a French Chemist, studied the effect of concentration, temperature and pressure on a large no. of chemical equilibria. He summed up his conclusions in the form of a generalisation known as Le Chatelier's principle, which states as follows :

"If an equilibrium is subjected to a stress, the equilibrium shifts in such a way as to reduce the stress."

According to this principle, if a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.

Application of Le Chatelier's principle to Chemical ~~eh~~ equilibria :

① Effect of change of concentration : Increasing the concentrations of the reactants results in shifting the equilibrium in favour of the products while increasing the concentrations of the products results in shifting the equilibrium in favour of the reactants.

② Effect of change of Temperature : Let us consider the equilibrium,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g),$$

Here, the forward reaction is endothermic. Therefore, the backward reaction must be exothermic. Now, let the system is heated and allowed to rise the temperature.

According to Le Chatelier's principle, the equilibrium will shift in the direction which tends to produce cooling. Therefore, the eqm will shift in favour of NO_2. i.e. the dissociation of N_2O_4 into NO_2 will increase.

③ Effect of change of pressure :-

The volume of a gas enclosed in a vessel at some constant temperature decreases with increase of pressure. So, for gaseous reactions under equilibrium, when pressure is increased, the equilibrium will shift in the direction in which volume decreases.