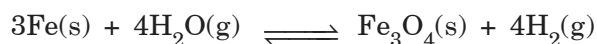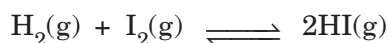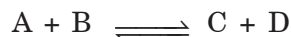# CHEMICAL EQUILIBRIUM

Reversible Reactions and Dynamic Equilibrium

A reaction is said to be reversible if the composition of the reaction mixture on the approach of equilibrium at a given temperature is the same irrespective of the initial state of the system, i.e., irrespective of the fact whether we start with the reactants or the products. Some examples of reversible reaction are listed below:

$$A + B \rightleftharpoons C + D$$

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Fe3+(aq) + Ag(s)$$

It is an experimental fact that most of the processes including chemical reactions, when carried out in a closed vessel, do not go to completion. Under these conditions, a process starts by itself or by initiation, continues for some time at diminishing rate and ultimately appears to stop. The reactants may still be present but they do not appear to change into products any more.
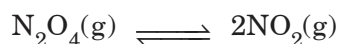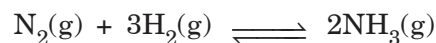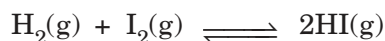
Characteristics of Chemical Equilibrium :

- Chemical equilibrium, at a given temperature, is characterised by constancy of certain observable properties such as pressure, conc., density.
- Chemical equilibrium can be approached from either side.
- Chemical equilibrium is dynamic in nature.
- A catalyst does not alter the position of equilibrium. It accelerates both the forward and reverse reactions.
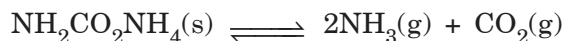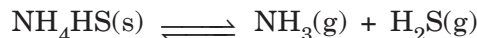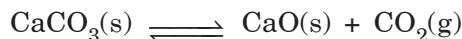
Types of Equilibria

There are mainly two types of equilibria

(a) **Homogeneous :** Equilibrium is said to be **homogeneous** if reactants and products are in same phase.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

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

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

(b) **Heterogeneous :** Equilibrium is said to be heterogeneous if reactants and products are in different phases.

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

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

$$NH_2CO_2NH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

Rate of a Reaction

The rate of a reaction is defined as the decrease in concentration per unit time of the reactants or the increase in concentration per unit time of the products.

For example, consider

$$A + 2B \rightarrow 3C$$

In the atomic reaction, according to the stoichiometric coefficients, 2 moles of B disappear for every mole of A reacting and 3 moles of C are formed for every mole of A disappears.

$$\therefore \quad -\frac{d[A]}{dt} = \frac{-1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \text{rate of reaction}$$

Here – ve sign is put before [A] and [B] because their molar concentration decrease with time.

Illustration 1

The rate of change in concentration of C in the reaction $2A + B \rightarrow 2C + 3D$ was reported as 1 mole litre^{-1} sec^{-1}. Calculate the reaction rate as well as the rate of change of concentration of A, B and D.

Solution :

$$\frac{-1}{2}\frac{d[A]}{dt} = \frac{-d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt}$$

$$= \text{rate of reaction}$$

$$\therefore \quad \frac{d[C]}{dt} = 1 \text{ mol } l^{-1} \text{ s}^{-1}$$

$$\therefore \quad \frac{-d[A]}{dt} = \frac{d[C]}{dt} = 1 \text{ mol } l^{-1} \text{ s}^{-1}$$

$$\frac{-d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = 0.5 \text{ mol } l^{-1} \text{ s}^{-1}$$

$$\frac{d[D]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = 1.5 \text{ mol } l^{-1} \text{ s}^{-1}$$

$$\text{Rate of reaction} = \frac{1}{2}\frac{d[C]}{dt} = 0.5 \text{ mol } l^{-1} \text{ s}^{-1}$$

Factors Influencing the Rate of a Reaction

(i) **Concentration of the reactant species** : Greater the concentrations of the reactants, the greater is the rate.

(ii) **Temperature :** The rate of a reaction increases with increase in temperature. In general for most reactions the rate constant doubles with every 10 rise in temperature.

(iii) **Nature of the reactants :** Reactions which do not involve considerable bond rearrangement are generally faster at room temperature than those which involve considerable bond rearrangements.

(iv) **Effect of catalyst :** A reaction proceeds much faster in the presence of a catalyst. For instance, the hydrolysis of an ester is very fast when catalyzed by H^+ ions.

(v) **Effect of radiation :** Photochemical reactions are faster than thermal ones because in the former all the energy of the photons is completely used in exciting the molecules while in the latter, the energy is distributed at random translational, rotational and vibrational modes of motion.

Law of Mass Action and Equilibrium Constant

The rate 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 reacting substance.

The reactions are generally reversible, that is, they can proceed both ways. A reaction is said to have attained equilibrium when the rate of the forward reaction equals that of the backward reaction.

Let us consider a general case of a reversible reaction,

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

Applying the law of mass action :

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

or   rate of the forward reaction $= k_1 [A]^a [B]^b$

Rate of backward reaction $\propto [M]^m [N]^n$

or   rate of backward reaction $= k_2 [M]^m [N]^n$

At equilibrium :

Rate of forward reaction = rate of backward reaction

$$k_1 [A]^a [B]^b = k_2 [M]^m [N]^n$$

$$\frac{k_1}{k_2} = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

or

$$K_C = \frac{k_1}{k_2} = \frac{[M]^m [N]^n}{[A]^a [B]^b} \qquad \text{...(1)}$$

[ ] represents concentration in moles per litre. Here, all concentrations are at equilibrium. k_1 and k_2 are known as the rate constants of the forward and backward reactions respectively.

Chemical equilibrium is dynamic in the sense that individual molecules are continually reacting, even though the overall composition of the reaction mixture does not change. The other criteria of a chemical equilibrium are the same equilibrium state can be attained from both sides of the reaction and a reaction which attains equilibrium is always incomplete.
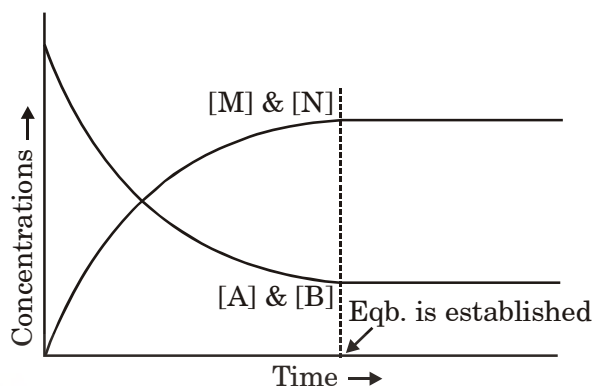
The rate constant of any reaction is defined as the rate of the reaction when the concentration of each reactant is unity. The rate constant of a reaction depends on the temperature and the catalyst.

k_c, the ratio of the rate constants, is known as the equilibrium constant. Now, if the above reaction is supposed to be a homogeneous gaseous one, the equilibrium constant may also represented as

$$K_P = \frac{p_M^m \cdot p_N^n}{p_A^a \cdot p_B^b}$$ ...(2)

where p´s* represent the partial pressures at equilibrium.

Reaction between K_p & K_c

The equilibrium constant K_p and K_c is known as pressure equilibrium constant. The magnitude of K_p and K_c is a measure of the extent to which the reaction occurs. The equilibrium constants depend only on temperature. For a given reaction K_p and K_c may be equal and may also be different depending on the stoichiometry of the reaction. K_p and K_c and are related as

$$\boxed{\mathbf{K_p = K_c (RT)^{\Delta n}}}$$ ...(3)

where, Δn = no. of moles of the gaseous product – no. of moles of the gaseous reactants (in the balanced equation and not in the reaction)

or $\Delta n = (m + n) - (a + b)$

But both the equilibrium constants for a given reaction give the same information about the state of equilibrium when the reaction at equilibrium is subjected to a change in temperature, pressure or concentration as also expressed by Le Chatelier's principle. The units of K_p and K_c are not fixed and depend on the stoichiometry of the reaction. In case the number of moles of the reactant and that of the product are same, K_p and K_c do not have any unit.

[**Note :** There is a third type of equilibrium constant, much less in use, called K_x, when concentrations are expressed in terms of mole fraction (x).]

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

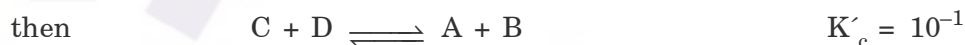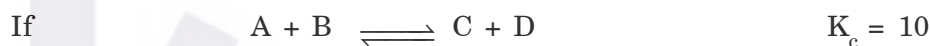Relating this expression with equations 1, 2 and 3, we get

$$K_p = K_x \cdot p^{\Delta n} = K_c (RT)^{\Delta n}$$

for
$$\Delta n = 0 : K_p = K_c = K_x$$

K_x does not have any unit. The mole fraction equilibrium constant K_x, unlike K_p and K_c, may depend on pressure and volume.
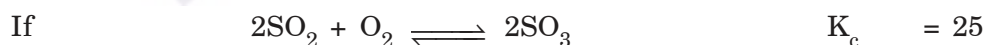
Important Relationship Involving Equilibrium Constant :

(a) If you reverse an equation, K_C or K_P is inverted i.e.

    If $A + B \rightleftharpoons C + D$ $K_c = 10$

    then $C + D \rightleftharpoons A + B$ $K_c' = 10^{-1}$

(b) If you multiply each of the coefficient in a balanced equation by a factor m, then equilibrium constant is raised to the same factor

    If $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO,$ $K_c = 5$

    then for $N_2 + O_2 \rightleftharpoons 2NO$ $K'c = K_c^2 = 5^2 = 25$

(c) If you divide each of the coefficients in a balanced equation by the factor m, then new equilibrium constant is mth root of the previous value.

    If $2SO_2 + O_2 \rightleftharpoons 2SO_3$ $K_c = 25$

    then for $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$ $K_c' = (K_c)^{\frac{1}{2}} = \sqrt{25} = 5$

(d) When you combine (i.e., add) individual equation, multiply their equilibrium constants to obtain the equilibrium constant for the reaction.
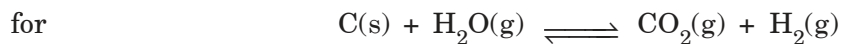
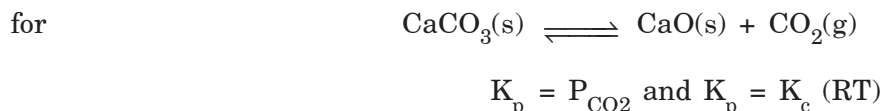   If K_1, K_2, K_3 are stepwise equilibrium constant for

                    $A \rightleftharpoons B$ ...(i)

                    $B \rightleftharpoons C$ ...(ii)

                    $C \rightleftharpoons D$ ...(iii)

    then for A $\rightleftharpoons$ D [obtained by adding (i), (ii) and (iii) net equilibrium constant is,

                    $K = K_1 K_2 K_3.$

(e) Do not include concentration terms for pure solids and pure liquids in equilibrium constant expression.

for $$C(s) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$K_c = \frac{[CO][H_2]}{[H_2O]}$$

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

$$K_p = P_{CO2} \text{ and } K_p = K_c (RT)$$

Interpretation of Equilibrium Constant

The equilibrium constant for a reaction tells about the tendency of a reaction to proceed to products.

(i) If the concentration of each reactant and product in a general reaction

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

are such that,

$$\frac{[M]^m.[N]^n}{[A]^a.[B]^b} = K \text{ (equilibrium constant)}$$

the reaction is at equilibrium.

(ii) If the concentration are such that,

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

the reaction will proceed from left to right in order to attain equilibrium, or in other words, the concentration factor or the reaction quotient increases and becomes equal to K.

(iii) And, if the concentrations are such that,

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

the reaction will proceed from right to left in order to attain equilibrium, or in other words, the concentration factor or the reaction quotient decreases and becomes equal to K.

If the concentration factor, i.e.,

$$\frac{[M]^m \cdot [N]^n}{[A]^a \cdot [B]^b} \begin{matrix} \leftarrow \\ \leftarrow \end{matrix}$$ (not necessarily eqb. concentrations)

is expressed as reaction quotient, Q, we have,

1. Q > K : Reaction proceeds in backward direction until equilibrium is established.
2. Q = K : Reaction is at equilibrium.
3. Q < K : Reaction proceeds in forward direction until equilibrium is established.

Significance of the Magnitude of Equilibrium Constant

(i) A very large value of K_C or K_P signifies that the forward reaction goes to completion or very nearly so.

(ii) A very small value of K_C or K_P signifies that the forward reaction does not occur to any significant extent.

(iii) A reaction is most likely to reach a state of equilibrium in which both reactants in which both reactants and products are present if the numerical value of K_c or K_p is neither very large nor very small.

Illustration 2

The value of K_p for the reaction

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$$
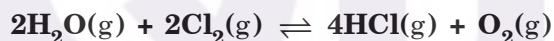
is 0.035 atm at 400 C, when the partial pressure are expressed in atmosphere.

Calculate K_c for the reaction, $\frac{1}{2}O_2(g) + 2HCl(g) \rightleftharpoons Cl_2(g) + H_2O(g)$.

Solution :

K_P = $K_C (RT)^{\Delta n}$

Δn = moles of product – moles of reactants = 5 – 4 = 1

R = 0.082 L atm/mol K

T = 400 + 273 = 673 K

$\therefore$ 0.035 = K_c (0.082 673)

K_c = 6.342 10^{-4} mol l^{-1}

$\therefore$ $K_c^{'}$ for the reverse reaction would be $\frac{1}{K_c}$

$\therefore$ $K_c^{'} = \frac{1}{6.342 \times 10^{-4}} = 1576.8 \left(mol\, l^{-1}\right)^{-1}$

When a reaction is multiplied by any number n (integer or a fraction) then K_c or K_p becomes $(K_c)^n$ or $(K_p)^n$ of the original reaction.

$$\therefore \quad K_c \text{ for } \frac{1}{2}O_2(g) + 2HCl(g) \rightleftharpoons Cl_2(g) + H_2O(g)$$

$$\text{is } \sqrt{1576.8} = 39.7 \ (\text{mol}^{-1})^{-\frac{1}{2}}$$

Calculation of K_p and K_c

From the relation $K_p = K_c (RT)^{\Delta n}$, we get two types of reaction, viz.,

(i)   when $\Delta n = 0$, i.e., those reactions in which there is no change in the number of molecules, e.g., $H_2 + I_2 \rightleftharpoons 2HI$;

       $\Delta n = 2 - 2 = 0$; for such a reaction, $K_p = K_c$

(ii)   When $\Delta n \neq 0$, i.e., those reactions in which there is a change in the number of molecules, e.g., $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta n = 2 - 4 = -2$.

For such a reaction, $K_p \neq K_c$

The calculations of K_p and K_c for the above types of reactions depend mainly on the values of molar concentration (i.e., moles/litre) and partial pressure at equilibrium, as shown in eqns. (1) and (2).

Let us now present the methods of calculating K_p and K_c by taking the following examples :

(1) Formation of HI

a	b	0	Initial moles
$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$	
$(a - x)$	$(b - x)$	$2x$	Moles at equilibrium
$\dfrac{(a-x)}{V}$	$\dfrac{(b-x)}{V}$	$\dfrac{2x}{V}$	Molar concentration at eqb.

where x is the number of moles of H_2 or I_2 converted to HI at equilibrium and V is the volume in litres of the container.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x/V)^2}{\dfrac{(a-x)}{V} \cdot \dfrac{(b-x)}{V}}$$

$$= \frac{4x^2}{(a-x)(b-x)}$$

Further, total number of moles at equilibrium

$$= (a - x) + (b - x) + 2x$$

$$= a + b$$

Let the total pressure be p.

$$p_{H_2} = \frac{(a - x)}{(a + b)} \cdot p; \ p_{I_2} = \frac{(b - x)}{(a + b)} \cdot p \ \text{ and}$$

$$p_{HI} = \frac{2x}{(a + b)} \cdot p$$

$$K_p = \frac{p_{HI}^2}{p_{H_2} p_{I_2}} = \frac{4x^2}{(a - x)(b - x)} \ \text{(substituting the value of p's)}$$

(2) Formation of NH_3

$$\begin{array}{cccc} a & b & 0 & \text{Initial moles} \\ N_2 \text{ (g)} + & 3H_2 \text{ (g)} \rightleftharpoons & 2NH_3 & \\ (a - x) & (b - 3x) & 2x & \text{Moles at equilibrium} \\ \dfrac{(a - x)}{V} & \dfrac{(b - 3x)}{V} & \dfrac{2x}{V} & \text{Molar concentration at equilibrium} \end{array}$$

where x is the number of moles of N_2 which converted to NH_3 at equilibrium.

$$\therefore \quad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{a - x}{V}\right)\left(\dfrac{b - 3x}{V}\right)^3}$$

Further, total number of moles at equilibrium

$$= a - x + b - 3x + 2x = (a + b - 2x)$$

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}} = \frac{\left\{\left(\dfrac{2x}{a + b - 2x}\right) \cdot p\right\}^2}{\left\{\dfrac{a - x}{a + b - 2x} \cdot p\right\}\left\{\dfrac{b - 3x}{a + b - 2x} \cdot p\right\}^3}$$

(3) Dissociation of PCl_5

| a | 0 | 0 | Initial moles |

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

| $(a - x)$ | x | x | Moles at equilibrium |

| $\dfrac{(a - x)}{V}$ | $\dfrac{x}{V}$ | $\dfrac{x}{V}$ | Molar concentration at eqb. |

Here, x is the number of moles of PCl_5 converted to the products at equilibrium. But if x represents degree of dissociation, i.e., fraction of the total number of molecules undergoing dissociation, the equilibrium moles and equilibrium molar concentration of each species will be as follows :

| a | 0 | 0 | Initial moles |

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

| $a(1 - x)$ | ax | ax | Moles at equilibrium |

| $\dfrac{a(1 - x)}{V}$ | $\dfrac{ax}{V}$ | $\dfrac{ax}{V}$ | Molar concentration at eqb. |

From the values of given above, equations for K_p and K_c can be derived.

(4) Dissociation of Halogen Molecules

| a | 0 | | Initial moles |

$$X_2(g) \rightleftharpoons 2X(g)$$ {If x is the number of moles of X_2 converted to X at eqb.}

| $(a - x)$ | 2x | | Moles at equilibrium |

| $\left(\dfrac{a - x}{V}\right)$ | $\left(\dfrac{2x}{V}\right)$ | | Molar concentration at equilibrium |

But if x is the degree of dissociation :

$$X_2(g) \rightleftharpoons 2X(g)$$

| $a(1 - x)$ | 2ax | | Moles at equilibrium |

| $\left(\dfrac{a(1 - x)}{V}\right)$ | $\left(\dfrac{2ax}{V}\right)$ | | Molar concentration at eqb. |

Derive K_p and K_c.

Homogeneous Equilibria and Equations for Equilibrium Constant (Equilibrium Pressure is P atm in a V L Flask)

	H_2 (g) $+$ I_2 (g) $\rightleftharpoons$ $2HI$ (g)			N_2 (g) $+$ $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)			PCl_5 (g) $\rightleftharpoons$ PCl_3 (g) $+$ Cl_2 (g)		
Initial mol	a	b	O	1	3	0	1	0	0
Equilibrium mol	$(a-x)$	$(b-x)$	$2x$	$(1-x)$	$(3-3x)$	$2x$	$(1-x)$	x	x
Total mol at eqb.	$(a+b)$			$(4-2x)$			$(1+x)$		
Active masses	$\left(\dfrac{a-x}{V}\right)$	$\left(\dfrac{b-x}{V}\right)$	$\left(\dfrac{2x}{V}\right)$	$\left(\dfrac{1-x}{V}\right)$	$3\left(\dfrac{1-x}{V}\right)$	$\left(\dfrac{2x}{V}\right)$	$\left(\dfrac{1-x}{V}\right)$	$\left(\dfrac{x}{V}\right)$	$\left(\dfrac{x}{V}\right)$
Mol fraction	$\left(\dfrac{a-x}{a+b}\right)$	$\left(\dfrac{b-x}{a+b}\right)$	$\left(\dfrac{2x}{a+b}\right)$	$\dfrac{1-x}{2(2-x)}$	$\dfrac{3}{2}\left(\dfrac{1-x}{2-x}\right)$	$\dfrac{x}{(2-x)}$	$\left(\dfrac{1-x}{1+x}\right)$	$\left(\dfrac{x}{1+x}\right)$	$\left(\dfrac{x}{1+x}\right)$
Partial pressure	$P\left(\dfrac{a-x}{a+b}\right)$	$P\left(\dfrac{b-x}{a+b}\right)$	$P\left(\dfrac{2x}{a+b}\right)$	$P\left(\dfrac{1-x}{2(2-x)}\right)$	$P\left(\dfrac{3(1-x)}{2(2-x)}\right)$	$\dfrac{Px}{(2-x)}$	$P\left(\dfrac{1-x}{1+x}\right)$	$P\left(\dfrac{x}{1+x}\right)$	$P\left(\dfrac{x}{1+x}\right)$
K_c	$\dfrac{4x^2}{(a-x)(b-x)}$			$\dfrac{4x^2V^2}{27(1-x)^4}$			$\dfrac{x^2}{(1-x)V}$		
K_p	$\dfrac{4x^2}{(a-x)(b-x)}$			$\dfrac{16x^2(2-x)^2}{27(1-x)^4 P^2}$			$\dfrac{Px^2}{(1-x)^2}$		

Heterogeneouos Equilibria and Equation for Equilibrium Constant (Equilibrium Pressure is P atm)

	$NH_4HS(s) \rightleftharpoons NH_3(g)+H_2S(g)$			$C(s)+CO_2(g) \rightleftharpoons 2CO(g)$			$NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g)+ CO_2(g)$		
Initial mol	1	0	0	1	1	0	1	0	0
Eqn. mol	$(1-x)$	x	x	$(1-x)$	$(1-x)$	$2x$	$(1-x)$	$2x$	x
Total mol. at eqn. (solidnotincluded)	$2x$			$(1+x)$			$3x$		
molfraction	$\dfrac{x}{2x}=\dfrac{1}{2}$	$\dfrac{1}{2}$		$\left(\dfrac{1-x}{1+x}\right)$	$\left(\dfrac{2x}{1+x}\right)$		$\dfrac{2}{3}$	$\dfrac{1}{3}$	
Partial pressure	$\dfrac{P}{2}$	$\dfrac{P}{2}$		$P\left(\dfrac{1-x}{1+x}\right)$	$P\left(\dfrac{2x}{1+x}\right)$		$\dfrac{2P}{3}$	$\dfrac{P}{3}$	
K_p	$\dfrac{P^2}{4}$			$\dfrac{4P^2x^2}{(1-x^2)}$			$\dfrac{4P^3}{27}$		

Relation Between Vapour Density and Degree of Dissociation

Let equilibrium reaction be with x as degree of dissociation

$$A \rightleftharpoons yB.$$
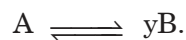
given by

$$x = \frac{D - d}{(y - 1)d}$$

where D is the vapour density of A before dissociation, d the vapour density of the reaction mixture consisting of A and B, and y the no. of products.

$$D \quad 2 = \text{mol. wt of A}$$

$$d \quad 2 = \text{mol. wt of mixture (also called abnormal mol. wt. of A)}$$

Thus $x = \dfrac{D - d}{d}$ for $(PCl_5 \rightleftharpoons PCl_3 + Cl_2)$ with $y = 2$

Example 1

Write equilibrium constants for each :

(a) $$KClO_{3(s)} \rightleftharpoons KCl_{(s)} + \frac{3}{2} O_2$$

(b) $$H_{2(s)} + 3FeO_{3(s)} \rightleftharpoons H_2O_{(g)} + 2Fe_3O_{4(s)}$$

(c) $$CaC_{2(s)} + 5O_{2(g)} \rightleftharpoons 2CaCO_{3(s)} + 2CO_{2(s)}$$

(d) $$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

(e) $$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

(f) $$CH_3COOH_{(l)} + CH_3OH_{(l)} \rightleftharpoons CH_3COOCH_{3(l)} + H_2O_{(l)}$$

Solution :

Note : 1. Write K_p for heterogeneous systems if gaseous phase is present.

2. Write K_C for homogeneous solution phase.

3. Write K_p or K_c for homogeneous gaseous phase.

(a) $$K_p = \left[P'_{O_2} \right]^{3/2}$$

(b) $$K_p = \frac{\left[P'_{H_2O} \right]}{P'_{H_2}} = \frac{n_{H_2O}}{n_{H_2}} \times \left[\frac{P}{\sum N} \right]^0$$

(c) $$K_p = \frac{\left[P'_{CO_2} \right]^2}{\left[P'_{O_2} \right]^5} = \frac{\left[n_{CO_2} \right]^2}{\left[n_{O_2} \right]^5} \cdot \left[\frac{P}{\sum N} \right]^{-3}$$

(d) $\quad K_p = \dfrac{\left[P'_{HI}\right]^2}{P'_{H_2} \times P'_{I_2}}$ $\qquad$ or $\qquad$ $K_C = \dfrac{[HI]^2}{[H_2][I_2]}$

(e) $\quad K_p = \dfrac{\left[P'_{NH_3}\right]^2}{\left[P'_{N_2}\right]\left[P'_{H_2}\right]^3}$ $\qquad$ or $\qquad$ $K_C = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(f) $\quad K_C = \dfrac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$

Example 2

If a mixture of 3 mole of H_2 and one mole of N_2 is completely converted into NH_3, what would be the ratio of the initial and final volume at same temperature and pressure ?
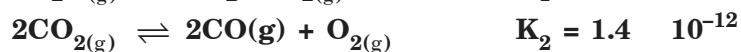
Solution :

$$N_2 \quad + \quad 3H_2 \quad \rightleftharpoons \quad 2NH_3$$

Initial mole	1	3	0
Final mole	0	0	2	$(\therefore$ complete conversion$)$
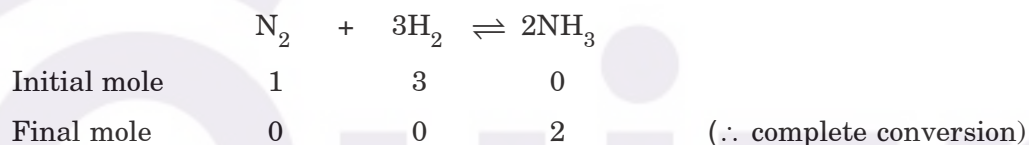
$\therefore \quad$ Ratio of initial and final volumes $\quad = \dfrac{\text{Initial mole}}{\text{Final mole}}$

$(\therefore$ V $\propto$ n if P and T are constant$) \qquad = \dfrac{4}{2} = 2$
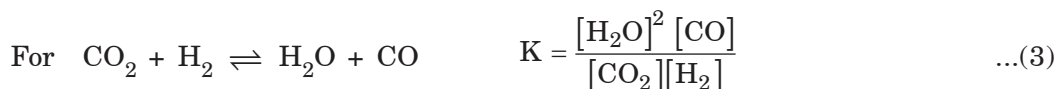

Example 3

Calculate the equilibrium constant for the reaction $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$ at 1395 K, if the equilibrium constants at 1395 K for the following are :

$$2H_2O_{(g)} \rightleftharpoons 2H_2 + O_{2(g)} \qquad K_1 = 2.1 \quad 10^{-13}$$
$$2CO_{2(g)} \rightleftharpoons 2CO(g) + O_{2(g)} \qquad K_2 = 1.4 \quad 10^{-12}$$

Solution :

For $2H_2O \rightleftharpoons 2H_2 + O_2$ $\qquad K_1 = \dfrac{[H_2]^2[O_2]}{[H_2O]^2}$ $\qquad$ ...(1)

For $2CO_2 \rightleftharpoons 2CO + O_2$ $\qquad K_2 = \dfrac{[CO]^2[O_2]}{[CO_2]^2}$ $\qquad$ ...(2)

For $CO_2 + H_2 \rightleftharpoons H_2O + CO$ $K = \dfrac{[H_2O]^2\,[CO]}{[CO_2][H_2]}$ ...(3)

Thus, by Eqs. $\dfrac{(2)}{(1)}$

$$\dfrac{K_2}{K_1} = \dfrac{[CO]^2\,[O_2]}{[CO_2]^2} \times \dfrac{[H_2O]^2}{[H_2]^2[O_2]}$$

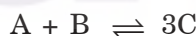$$\dfrac{K_2}{K_1} = \dfrac{[CO]^2\,[H_2O]^2}{[CO_2]^2[H_2]^2} = K^2$$

$$K = \sqrt{\left(\dfrac{K_2}{K_1}\right)} = \sqrt{\left(\dfrac{1.4 \times 10^{-12}}{2.1 \times 10^{-13}}\right)} = 2.58$$

Example 4

For the reaction A + B $\rightleftharpoons$ 3C at 25 C , a 3 litre vessel contains 1, 2, 4 mole of A, B and C respectively. Predict the direction of reaction if :

    (a) K_C **for the reaction is 10.**

    (b) K_C **for the reaction is 15.**

    (c) K_C **for the reaction is 10.66.**

Solution :

$$A + B \rightleftharpoons 3C$$

Before reaction $[A] = 1/3$

$[B] = 2/3$

$[C] = 4/3$

Thus, $Q = \dfrac{[C]^3}{[A][B]} = \dfrac{4^3 \times 3 \times 3}{3^3 \times 1 \times 2} = \dfrac{64}{6} = 10.66$

    (a)   Since $K_C = 10$, thus Q must decrease to attain K_C value and thus, [C] must decrease or [A] and [B] should increase. Thus, reaction will occur in backward direction.

    (b)   Since $K_C = 15$, thus Q must increase to attain K_C value and thus, [C] must increase or [A] and [B] should decrease. Thus, direction will occur in forward direction.

    (c) $Q = K_C$; thus, reaction is in equilibrium.

Example 5

At temperature T, a compound $AB_2(g)$ dissociates according to the reaction : $2AB_{2(g)} \rightleftharpoons 2AB_{(g)} + B_{2(g)}$ with a degree of dissociation 'x' which is small compared to unity. Deduce the expression for 'x' in terms of the equilibrium constant K_p and the total pressure P.

[IIT 1994]

Solution :

$$2AB_{2(g)} \rightleftharpoons 2AB_{(g)} + B_{2(g)}$$

Mole before dissociation   1   0   0

Mole after dissociation $(1-x)$ x $\dfrac{x}{2}$

Total mole at equilibrium $\left(\sum n\right) = 1 - x + x + \dfrac{x}{2} = 1 + \dfrac{x}{2}$

Now,

$$K_p = \frac{n_{B_2} \times \left(n_{AB}\right)^2}{\left(n_{AB_2}\right)^2} \times \left[\frac{P}{\sum n}\right]^{\Delta n}$$

$$K_p = \frac{\dfrac{x}{2}.(x)^2}{(1-x)^2} \times \left[\frac{P}{1 + \dfrac{x}{2}}\right]^1$$

$$K_p = \frac{x^3 P}{2} \qquad \left[\because x \text{ is small}, \therefore 1 - x \approx 1 \text{ and } 1 + \frac{x}{2} \approx 1\right]$$

or

$$x = \sqrt[3]{\frac{2K_p}{P}}$$

Example 6

For a gaseous phase reaction, $A + 2B \rightleftharpoons AB_2$, $K_C = 0.3475$ litre^2 mol^{-2} at 200 C. When 2 mole of B are mixed with one mole of A, what total pressure is required to convert 60% of A in AB_2?

Solution :

$$A + 2B \rightleftharpoons AB_2$$

Initial mole   1   2   0

Mole at equilibrium $(1-x)$ $(2-2x)$ x

Total mole at equilibrium $= 1 - x + 2 - 2x + x = 3 - 2x$

Let pressure at equilibrium be P;

Now, $P'_{AB_2} = \left[\dfrac{x}{3-2x}\right]P;$ $P'_A = \left[\dfrac{1-x}{3-2x}\right]P;$ $P'_B = \left[\dfrac{2-2x}{3-2x}\right]P$

$\therefore$ $K_p = \dfrac{x.P}{(3-2x).P\dfrac{(1-x)}{(3-2x)}P^2\dfrac{(2-2x)^2}{(3-2x)^2}}$

$K_p = \dfrac{x(3-2x)^2}{P^2(1-x)(2-2x)^2}$ ...(1)

Alternate to derive K_p or Eq. (1),

$K_p = \dfrac{n_{AB_2}}{n_A \times (n_B)^2} \times \left(\dfrac{P}{\sum n}\right)^{\Delta n}$

$\therefore$ $K_p = \dfrac{x}{(1-x)(2-2x)^2} \times \left[\dfrac{P}{(3-2x)}\right]^{-2}$

$= \dfrac{x(3-2x)^2}{(1-x)(2-2x)^2.P^2}$ ...(1)

Given that x = 0.6   and $\Delta n = -2$

$\therefore$ $K_p = K_c(RT)^{\Delta n} = 0.3475 \quad (0.0821 \quad 473)^{-2}$ ...(2)

By Eqs. (1) and (2),

$\therefore$ $0.3475 \quad (0.0821 \quad 473)^{-2} = \dfrac{0.6(3-1.2)^2}{P^2(1-0.6)(2-1.2)^2}$

$= \dfrac{0.6 \times (1.8)^2}{P^2(0.4)(0.8)^2}$
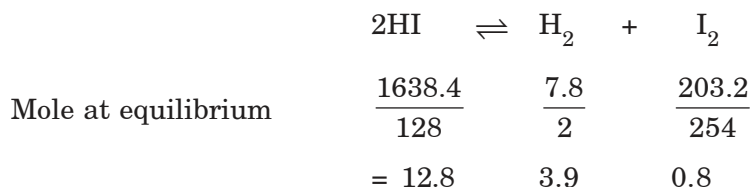
P = 181.5 atm

Example 7

For a gaseous phase reaction, $2HI \rightleftharpoons H_2 + I_2$, at equilibrium 7.8 g, 203.2 g and 1638.4 g of H_2, I_2 and HI respectively were found in 5 litre vessel. Calculate K_c. If all the reactants and products are transferred to a 2 litre vessel, what will be the amount of reactants and products at equilibrium ?

Solution :

$$2HI \quad \rightleftharpoons \quad H_2 \quad + \quad I_2$$

Mole at equilibrium $\quad \dfrac{1638.4}{128} \qquad \dfrac{7.8}{2} \qquad \dfrac{203.2}{254}$

$$= 12.8 \qquad 3.9 \qquad 0.8$$

Let volume of container be V litre

$$[H_2] = \dfrac{3.9}{V}; \quad [HI] = \dfrac{12.8}{V}; \quad [I_2] = \dfrac{0.8}{V}$$

$$\therefore \qquad K_C = \dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{3.9 \times 0.8}{V \times V \times \left(\dfrac{12.8}{V}\right)^2} = 0.019$$
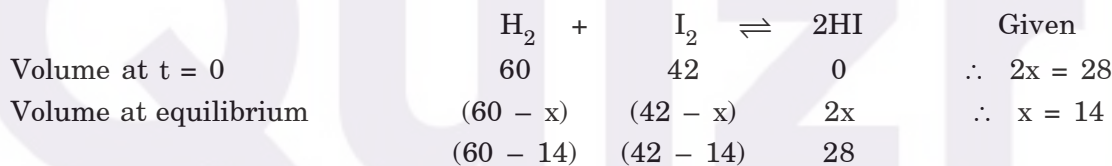
$$\therefore \qquad K_C = 0.019$$

For the given reaction $\Delta n = 0$ and thus there will be no effect on equilibrium concentration of reactants and products if the matter is transferred to attain equilibrium in 2 litre vessel.
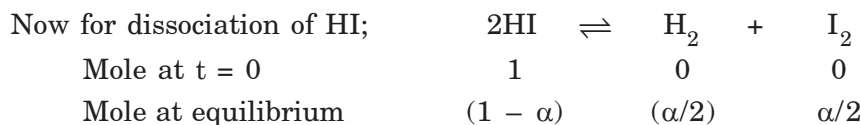

Example 8

60 mL of H_2 and 42 mL of I_2 are heated in a closed vessel. At equilibrium the vessel contains 28 mL HI. Calculate degree of dissociation of HI.

Solution :

	H_2	+	I_2	$\rightleftharpoons$	2HI	Given
Volume at t = 0	60		42		0	$\therefore$ 2x = 28
Volume at equilibrium	(60 − x)		(42 − x)		2x	$\therefore$ x = 14
	(60 − 14)		(42 − 14)		28	

Since at constant P and T, mole $\propto$ volume of gas (By PV = nRT). Thus, volume of gases given can be directly used as concentration. This can be done only for reactions having $\Delta n = 0$.

$$\therefore \qquad K_C = \dfrac{28 \times 28}{46 \times 28} = \dfrac{28}{46}$$

Now for dissociation of HI; $\qquad 2HI \quad \rightleftharpoons \quad H_2 \quad + \quad I_2$

Mole at t = 0	1	0	0
Mole at equilibrium	(1 − α)	(α/2)	α/2

where α is degree of dissociation

$$K_{C1} = \dfrac{\alpha^2}{4(1-\alpha)^2} = \dfrac{1}{K_C}$$

$$\therefore \qquad \dfrac{\alpha}{2(1-\alpha)} = \sqrt{\left(\dfrac{46}{28}\right)}$$

$$\therefore \qquad \alpha = 0.719 \qquad \text{or} \qquad 71.9\%$$

Example 9

K_C for $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ at 986 C is 0.63. A mixture of 1 mole $H_2O_{(g)}$ and 3 mole $CO_{(g)}$ is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm.

    (1)   How many mole of H_2 are present at equilibrium ?

    (2)   Calculate partial pressure of each gas at equilibrium.

Solution :

$$CO_{(g)} + \quad H_2O_{(g)} \quad \rightleftharpoons \quad CO_{2(g)} + \quad H_{2(g)}$$

Initial mole	3	1	0	0
Mole at equilibrium	$(3-x)$	$(1-x)$	x	x

Total mole at equilibrium $= 3 - x + 1 - x + x + x = 4$

Now $\qquad K_C = \dfrac{x^2}{(3-x)(1-x)}$

$\therefore \qquad \dfrac{x^2}{3 + x^2 - 4x} = 0.63 \qquad\qquad (\therefore K_C = 0.63)$

$\therefore \qquad x = 0.681$

$\therefore \qquad$ Mole of H_2 formed $= 0.681$

Total pressure at equilibrium $= 2$ atm

Total mole at equilibrium $= 4$

$$P_g' = P_M \quad \text{mole fraction of that gas}$$

$\therefore \qquad P_{CO_2}' = P_{H_2} = \dfrac{x.P}{4} = \dfrac{0.681 \times 2}{4} = 0.34$ atm

$$P_{CO}' = \dfrac{(3-x).P}{4} = 1.16 \text{ atm}$$

$$P_{H_2O}' = \dfrac{(1-x).P}{4} = 0.16 \text{ atm}$$

Example 10

An equilibrium mixture of $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_2(g)$ present in a vessel of one litre capacity at 815 C was found by analysis to contain 0.4 mole of CO, 0.3 mole of H_2O, 0.2 mole of CO_2 and 0.6 mole of H_2.

(a) Calculate K_C.

(b) If it is derived to increase the concentration of CO to 0.6 mole by adding CO_2 to the vessel, how many mole must be added into equilibrium mixture at constant temperature in order to get this change ?
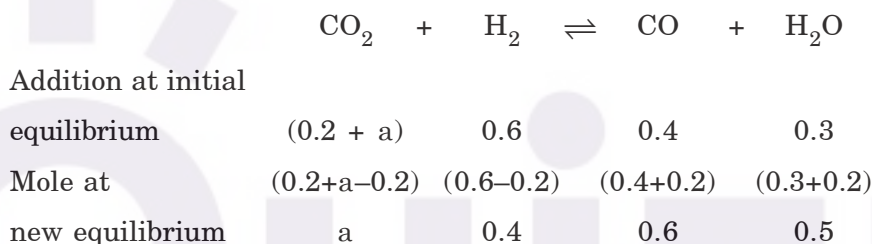
Solution :

$$CO_{(g)} \quad + \quad H_2O_{(g)} \quad \rightleftharpoons \quad CO_{2(g)} \quad + \quad H_{2(g)}$$

Mole at equilibrium   0.4   0.3   0.2   0.6
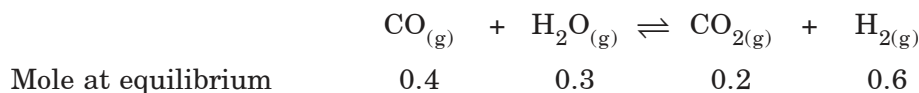
(a) $\therefore$ $K_C = \dfrac{[CO_2][H_2]}{[CO][H_2O]} = \dfrac{0.2 \times 0.6}{0.4 \times 0.3} = 1$

($\therefore \Delta n = 0$, $\therefore$ Volume terms are not needed.)

(b) Now it is desired to increase the conc. of CO by 0.2 at equilibrium by forcing CO_2 into equilibrium mixture. Suppose a mole of CO_2 are forced in vessel at equilibrium by doing so reaction proceeds in backward direction, i.e.,
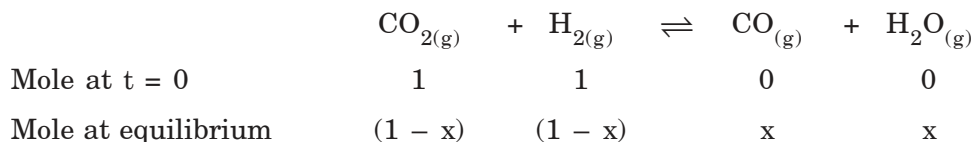
$$CO_2 \quad + \quad H_2 \quad \rightleftharpoons \quad CO \quad + \quad H_2O$$

Addition at initial

equilibrium   (0.2 + a)   0.6   0.4   0.3

Mole at   (0.2+a–0.2)   (0.6–0.2)   (0.4+0.2)   (0.3+0.2)

new equilibrium   a   0.4   0.6   0.5

$\therefore$ $\dfrac{1}{K_C} = \dfrac{[CO][H_2O]}{[CO_2][H_2]} = \dfrac{0.6 \times 0.5}{a \times 0.4}$

a = 0.75 mole

Example 11

A mixture of one mole of CO_2 and one mole of H_2 attains equilibrium at a temperature of 250 C and a total pressure of 0.1 atm for the change $CO_{2(g)} + H_{2(g)} + H_2O_{(g)}$. Calculate K_p if the analysis of final reaction mixture shows 0.16 volume per cent of CO.

Solution :

$$CO_{2(g)} \quad + \quad H_{2(g)} \quad \rightleftharpoons \quad CO_{(g)} \quad + \quad H_2O_{(g)}$$

Mole at t = 0   1   1   0   0

Mole at equilibrium   (1 – x)   (1 – x)   x   x

Given that Vol. % of CO = 0.16

$\therefore$ Mole of CO = x

Total mole at equilibrium = 1 – x + 1 – x + x + x = 2

$$\therefore \qquad \frac{x}{2} = \frac{0.16}{100}$$

$$\therefore \qquad x = 0.0032$$

Now, $\qquad K_C = K_p = \dfrac{x^2}{(1-x)^2} \qquad (\therefore \Delta n = 0,$ volume terms are not needed)

$$K_p = \frac{(0.0032)^2}{(1-0.0032)^2} = 1.03 \times 10^{-5}$$

Le Chatelier's Principal and Equilibrium Constant

Le Chatelier's principle states that if a chemical reaction at equilibrium is subjected to a change in temperature, pressure or concentration, the equilibrium shifts to that direction by which the effect of the change is minimised.

One should note that the change in either pressure or concentration at equilibrium may shift the equilibrium or more clearly, change the state of equilibrium, but it cannot change the equilibrium constant K_p or K_c which depends only on temperature.

However, when a reaction (except those for which $\Delta H = 0$) is subjected to a change in temperature, the equilibrium shifts to another equilibrium position at the new temperature and the equilibrium constant also changes.

In general, for an exothermic reaction (ΔH is negative), increase in temperature results in shifting the equilibrium from right to left, thereby decreasing the value of the equilibrium constant. For an endothermic reaction (ΔH is positive), the value of equilibrium constant increases as the temperature increases.

Effect of Temperature on Equilibrium Constant

The quantitative effect of temperature on the equilibrium constant can be determined by the following thermodynamically derived equation, known as Van't Hoff equation,

$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 . T_2}\right]$$

where K_{p_1} and K_{p_2} are the equilibrium constants at temperatures T_1 and T_2 respectively, ΔH is standard heat of the reaction at constant pressure.

Here, it has been assumed that ΔH is constant in the temperature range between T_2 and T_1 ($T_2 > T_1$). We readily see that $K_{p_2} > K_{p_1}$, if ΔH is positive, (endothermic) and $K_{p_2} < K_{p_1}$, if ΔH is negative (exothermic).
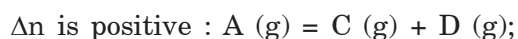
Factors Influencing the Equilibrium State

The effects of various factors on the equilibrium state for the different types of reactions may be clearly understood by using the following expressions of K_p.

Type I reaction

$$\Delta n = 0 : A\ (g) + B\ (g) = C\ (g) + D\ (g);$$

$$K_p = \frac{\text{moles of C} \times \text{moles of D}}{\text{moles of A} \times \text{moles of B}}$$

Type II reaction

Δn is positive : $A\ (g) = C\ (g) + D\ (g);$

$$K_p = \frac{\text{moles of C} \times \text{moles of D}}{\text{moles of A}} \times \frac{\text{total pressure}}{\text{total moles}}$$

Δn is negative : $A\ (g) + B\ (g) = D\ (g);$

$$K_p = \frac{\text{moles of D}}{\text{moles of A} \times \text{moles of B}} \times \frac{\text{total moles}}{\text{total pressure}}$$

1. Effect of Pressure (or volume)

Type of reaction	Effect of Pressure (or volume)
Type I : $\Delta n = 0$	Eqb. is not affected
Type II : $\Delta n = +ve$	Increase in p (or decrease in V) shifts the eqb. to the left
$\Delta n = -ve$	Increase in p (or decrease in V) shifts the eqb. to the right.

2. Effect of Addition of Inert Gas

Type of reaction	Effect of addition of inert gas
Type I : $\Delta n = 0$	Eqb. is not affected either at constant pressure or at constant volume
Type II : $\Delta n = +ve$	At constant volume : eqb. is not affected At constant pressure : eqb. shifts to the right
$\Delta n = -ve$	At constant volume : eqb. is not affected At constant pressure : eqb. shifts to the left

3. Effect of Addition of Catalyst

Adding a catalyst to a reaction changes its rate but this cannot shift the equilibrium in favour of either products or reactants. Because a catalyst affects the activation energy of both forward and backward reactions equally, it changes both rate constants by the same factor, so their ratio K_c, does not change. Thus, adding a catalyst to a reaction at equilibrium has no effect; it changes neither the reaction quotient, Q, nor the equilibrium constant K, but only the time required to established equilibrium is altered.

4. Effect of Addition or Removal of any of the Reactants or Products

If any of the reactants or products is added or removed from a system at equilibrium the equilibrium shifts in the direction that consumes or produces the added or removed substance respectively. This is only true if the volume of the system is kept constant. But under the constant pressure condition, shifting of equilibrium may be in the reverse direction depending upon the value and sign of Δn and number of molecules of the added or removed substance involved in the reaction.

THERMODYNAMICS OF CHEMICAL EQUILIBRIUM

Spontaneity

A **spontaneous** or natural process is a process that occurs in a system left to itself once started; no action from outside the system (external action) is necessary to make the process continue. On the other hand, a **nonspontaneous** process will not occur unless some external action is continuously applied. We say that the rusting of iron is spontaneous.

$$2Fe_{(s)} + 3O_{2(g)} \rightarrow Fe_2O_{3(s)}$$
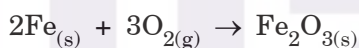
Reverse reaction is not impossible, but it is certainly non spontaneous.

Gibbs Free Energy* Change and Spontaneity :

The Gibbs free energy 'G' for system is defined as

$$G = H - TS$$

and, for a change at constant T,

$$\Delta G = \Delta H - T\Delta S$$

where ΔG = change in Gibbs free energy G

ΔH = change in enthalpy H

ΔS = change in entropy S

Sign of ΔG is taken as the true **criterion** for spontaneity.

For a process occuring at constant T and P, if

(i) $\Delta G < 0$ (negative) the process is spontaneous

(ii) $\Delta G > 0$ (positive) the process is nonspontaneous

(iii) $\Delta G = 0$ (zero) the process is at equilibrium

Sign of ΔG, based on eqn. ($\Delta G = \Delta H - T \Delta S$) can be decided depending on sign of ΔH and ΔS, and magnitude of T, and is explained in Table below.

Case	ΔH	ΔS	ΔG	Result	Example
1	–	+	–	spontaneous at all temp.	$2N_2O_{(g)} \rightarrow 2N_{2(g)} + O_{2(g)}$
2	–	–	–	spontaneous at low temp.	$H_2O(l) \rightarrow H_2O_{(g)}$
			+	nonspontaneous at high temp.	
3	+	+	+	nonspontaneous at low temp.	$2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)}$
			–	spontaneous at high temp	
4	+	–	+	nonspontaneous at all temp	$3O_{2(g)} \rightarrow 2O_{3(g)}$
5	$T\Delta S = \Delta H$		0	equilibrium	$A \rightleftharpoons B$

Relationship of ΔG to the Equilibrium Constant K :

ΔG for a reaction under any set of conditions is related to its value for standard conditions, that is ΔG by eqn.

$$\Delta G = \Delta G + 2.303 \, RT \log Q$$

under equilibrium condition $Q = K_p = K_c = K$

$$\Delta G = 0$$

$$\Delta G = -2.303 \, RT \log K$$

We have replaced K_p or K_c by K called thermodynamic equilibrium constant. For a general reaction

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

$$K = \frac{(aC)^c \, (aD)^4}{(aA)^a \, (aB)^b}$$

the symbol a represents the activity of the reactants and products. It is actually a ratio of the equilibrium activity of a substance to its activity in its standard state. Thus thermodynamic equilibrium constant is unitless quantity, a being also unitless.

– For pure solids and liquids :   a = 1
– For gases : ideal behaviour is considered and the activity of a gas is equal to its pressure in atm.
– For components in solution :   a = molar concentration

Variation of K with Temperature : The van't Hoff Equation :

Equilibrium constant K varies with temperature T as given by van't Hoff eqn.

$$\log K = \frac{\Delta H°}{2.303 \, RT} + \frac{\Delta S°}{R}$$

where ΔH and ΔS, heat of reaction and entropy change respectively in standard state are temperature independent. If K_1 and K_2 are equilibrium constants at T_1 and T_2 respectively, then

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

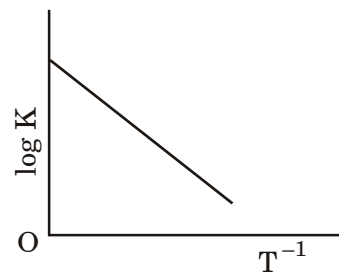This equation can be used to compute ΔH

also $\quad \dfrac{d \log K}{dT} = \dfrac{\Delta H^\circ}{2.303 RT^2}$

A graph between $\log K$ and T^{-1} is a straight line of

slope $= -\dfrac{\Delta H^\circ}{2.303\,R}$

$\Delta H = -2.303\ R \quad$ slope

MISCELLANEOUS

Example 1

At 46 C, K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.66. Compute the percent dissociation of N_2O_4 at 46 C and a total pressure of 0.5 atm. Also calculate partial pressure of N_2O and NO_2 at equilibrium.

Solution :

Let x = fraction of N_2O_4 dissociated at 0.5 atm

$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2$	
1	0		mol at start
$-x$	2x		change by reaction
$1-x$	2x		mol at equilibrium
$\dfrac{1-x}{1+x}$	$\dfrac{2x}{1+x}$		mol fraction
$P_{N_2O_4} = 0.5\left(\dfrac{1-x}{1+x}\right)$	$P_{NO_2} = 0.5\left(\dfrac{2x}{1+x}\right)$		partial pressure

thus

$$K_p = 0.66 = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{\left(\dfrac{2x \times 0.5}{1+x}\right)^2}{\dfrac{(1-x)}{(1+x)}0.5}$$

this give   x = 0.5 i.e. 50% dissociation

hence partial pressure of N_2O_4 = 0.167 atm

and that of NO_2 = 0.333 atm

Alternate method :

let P_{NO_2} = P atm

hence $P_{N_2O_4}$ = (0.5 − P) atm

hence $K_p = \dfrac{P^2_{NO_2}}{P_{N_2O_4}} = \dfrac{P^2}{(0.5-P)} = 0.66$ atm

$$P^2 + 0.66\ P - 0.33 = 0$$

this gives P_{NO_2} = 0.333 atm, $P_{N_2O_4}$ = 0.167 atm

CHEMICAL EQUILIBRIUM

Example 2

What will be the effect on the equilibrium constant for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -22.4$ kcal, when (a) pressure is increased (b) concentration of N_2 is increased, and (c) temperature is raised at equilibrium ?

Solution :

(a)   No effect $\Big\}$ As K does not depend on

(b)   No effect   pressure and concentration

(c)   Equilibrium constant will decrease as the temperature is increased.

Example 3

K_c for the reaction $SO_2 + \dfrac{1}{2}O_2 \rightleftharpoons SO_3$ at 600 C is 61.7. Calculate K_p. What is the unit of Kp for the above equilibrium ? (R = 0.0821 lit. atm per deg. per mole)

Solution :

$$\Delta n = \text{moles of product} - \text{moles of reactant}$$

$$= 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$$
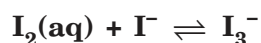
$$K_p = K_c \, (RT)^{\Delta n}$$

$$K_p = 61.7\{0.0821 \times (600 + 273)\}^{-\frac{1}{2}} = 7.29$$

$$K_p = \frac{p_{SO_3}}{p_{SO_2} \cdot p_{O_2}^{\frac{1}{2}}} = \frac{\text{atm}}{\text{atm.atm}^{\frac{1}{2}}}$$

Unit of K_p is atmosphere$^{-\frac{1}{2}}$

Example 4

A saturated solution of iodine in water contains 0.330 g I_2/L. More than this can dissolve in a KI solution because of the following equilibrium :

$$I_2(aq) + I^- \rightleftharpoons I_3^-$$

A 0.100 M I^- solution dissolves 12.5 g I_2/L, most of which is converted to I_3^-. Assuming that the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant for the above reaction.

Solution :

$$0.330 \text{ g } I_2 = \frac{0.330}{254} = 1.30 \quad 10^{-3} \text{ mol } I_2$$

$$12.5 \text{ g } I_2 = \frac{12.5}{254} = 0.0492 \text{ mol } I_2$$

at equilibrium, $[I_2] = 1.30 \quad 10^{-3} \text{ M},$

$$\left[I_3^-\right] = (0.0492 - 1.30 \quad 10{-3}) = 0.0479 \text{ M}$$

$$[I^-] = (0.100 - 0.0479) = 0.0521 \text{ M}$$

$$K = \frac{\left[I_3^-\right]}{[I_2]\left[I^-\right]} = \frac{0.0479}{\left(1.30 \times 10^{-3}\right)(0.0521)} = 707$$

Example 5

The degree of dissociation of I_2 molecule at 1000 C and under atmospheric pressure is 40% by volume. Find the total pressure on the gas at equilibrium so that the dissociation is reduced to 20% at the same temperature.

Solution :

	$I_2(g)$	$\rightleftharpoons$	$2I(g)$
initial mol	1		0
at equilibrium	$(1 - x)$	$2x$	$x = 0.40$, $P_1 = 1$ atm in case I
	$(1 - y)$	$2y$	$y = 0.20$, $P_2 = ?$ in case II
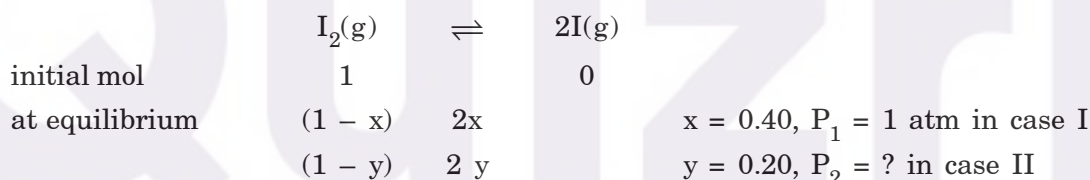
$$K_p = \frac{P_1^2}{P_{I_2}} = \frac{4x^2 P_1}{(1 - x^2)} = \frac{4y^2 P_2}{(1 - y^2)}$$

$\therefore$

$$\frac{4 \times 0.16 \times 1}{(1 - 0.16)} = \frac{4 \times 0.04 \times P_2}{(1 - 0.04)}$$

this gives $P_2 = 4.57$ atm.

Example 6

Solid ammonium carbonate, $NH_4CO_2NH_2$ dissociates completely into ammonia and carbon dioxide when it evaporates as shown by $NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$ At 25 C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium constant of the reaction? If 0.1 atm of CO_2 is introduced after equilibrium is reached, will the final pressure of CO_2 be greater or less than 0.1 atm? Will the pressure of NH_3 increase or decrease?

Solution :

$$NH_4CO_2NH_2(s) \quad \rightleftharpoons \quad 2NH_3(g) \quad + \quad CO_2(g)$$

initially :	1	0	0
at equilibrium	$(1 - x)$	$2x$	x

total mol of gaseous substance at equilibrium = $2x + x = 3x$

$$ NH_3 \qquad CO_2$$

$$\therefore \quad \text{mol fraction} \quad : \quad \frac{2}{3} \qquad \frac{1}{3}$$

$$\text{partial pressure} \quad : \quad \frac{2}{3}P \qquad \frac{1}{3}P$$

$$K_p = P_{NH_3}^2 \cdot P_{CO_2} = \left(\frac{2}{3}P\right)^2 \left(\frac{P}{3}\right) = \frac{4P^3}{27}$$

$$= \frac{4}{27} \times (0.116)^3 = 2.31 \times 10^{-4} \text{ atm}^3$$

If CO_2 is introduced after equilibrium is reached, then its final pressure will increase. But final pressure of NH_3 will decrease to keep K_p constant.

Example 7

The oxidation of sulphur dioxide is a reversible process : $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. Calculate the value of the equilibrium constant K_p at 1000 K from the following equilibrium partial pressure.

P_{SO_2}	P_{O_2}	P_{SO_3}
0.273 atm	**0.402 atm**	**0.325 atm**

If the above equilibrium was obtained by starting with a mixture of sulphur dioxide and oxygen in a sealed vessel at 1000 K, what were the initial pressures of these two gases ?

Solution :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
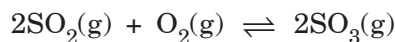
$$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{(0.325)^2}{(0.273)^2 (0.402)} = 3.53 \, \text{atm}^{-1}$$

Initially there is no SO_3, hence at equilibrium 0.325 atm pressure of SO_3 would have been due to 0.325 atm of SO_2 and $(0.325/2)$ atm of O_2.

hence initial pressure of SO_2 = 0.273 + 0.325

= 0.598 atm

and initial pressure of O_2 = $0.402 + \dfrac{0.325}{2}$

= 0.565 atm.

Example 8

From the given data of equilibrium constants of the following reactions,
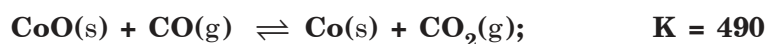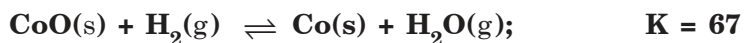
$$CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g); \qquad K = 67$$

$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g); \qquad K = 490$$

Calculate the equilibrium constant of the reaction,

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Solution :

$$CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g) \quad K_1 = 67 \qquad \qquad ...(1)$$
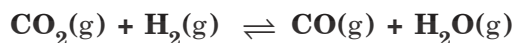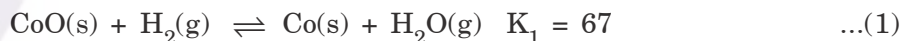
Now reversing the second reaction

$$Co(s) + CO_2(g) \rightleftharpoons CoO(s) + CO(g) \quad K_2 = \frac{1}{490} \qquad \qquad ...(2)$$
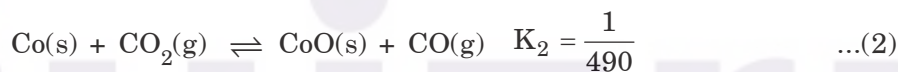
Adding the two reactions, we get,

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$
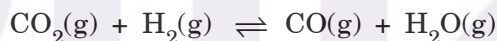
for which $\qquad \qquad K = K_1.K_2 = 67 \times \dfrac{1}{490} = 0.137$

Example 9

Given that at 1000 K $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad K = 261$

Calculate K for the following equations :

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

(ii) $\quad SO_3(g) \rightleftharpoons SO2(g) + \dfrac{1}{2}O_2(g)$

(iii) $\quad SO_2(g) + \dfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$
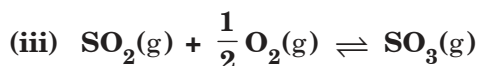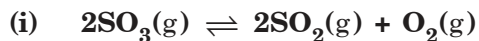
Solution : Equation (i) is the reverse of the given equation

$\therefore \qquad K = \dfrac{1}{261} = 0.0038$ (for (i)).

As the equation (ii) has been obtained by dividing the equation (i) by 2,

K for the equation (ii) will be $(0.0038)^{\frac{1}{2}} = 0.0619$.

Reversing the equation (ii) we get the equation (iii), K for which will be

$$\frac{1}{0.0619} = 16.155$$

Example 10

Calculate the volume per cent of chlorine of equilibrium in PCl_5 under a total pressure of 1.5 atm (K_p = 0.202).

Solution :

$$\qquad\qquad 1 \qquad\qquad 0 \qquad\quad 0 \qquad\qquad \text{Initial moles}$$

$$PCl_5 \quad \rightleftharpoons \quad PCl_3 + Cl_2$$

$$(1 - x) \qquad x \qquad\quad x \qquad\qquad \text{Moles at equilibrium}$$

Total moles at equilibrium = $1 - x + x + x = (1 + x)$
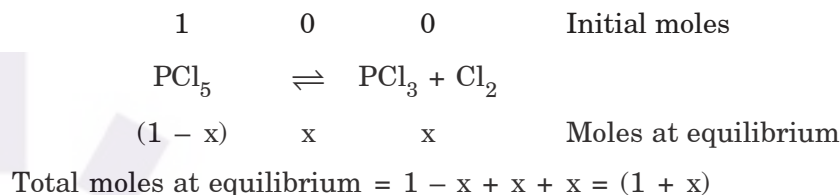
$$K_p = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}} = \frac{\left(\dfrac{x}{1+x} \cdot p\right)\left(\dfrac{x}{1+x} \cdot p\right)}{\left(\dfrac{1-x}{1+x} \cdot p\right)}$$

$$\{\text{partial pressure of a species} = \frac{\text{moles of species}}{\text{total moles}} \times \text{total pressure}\}$$

$$K_p = \frac{x^2}{1 - x^2} \cdot p$$

Substituting the values of K_p and p

$$0.202 = \frac{x^2}{1 - x^2} \times 1.5; \; x = 0.343$$

$\therefore \qquad$ moles of Cl_2 at equilibrium = 0.343

and total moles at equilibrium = 1 + x

$$= 1 + 0.343$$

$$= 1.343$$

$\therefore$ volume percentage of chlorine = mole percent of chlorine

$$= \frac{\text{moles of } Cl_2}{\text{total moles}} \times 100$$

$$= \frac{0.343}{1.343} \times 100$$

$$= 25.5\%$$

Example 11

$COCl_2$ gas dissociates according to the equation $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ when heated to 724 K, density of the gas mixture at 101.325 kPa and at equilibrium is 1.162 dm^{-3}. Calculate (a) the degree of dissociation, (b) K_p, (c) ΔG for the reaction at 724 K.

Solution :

$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	$+$	$Cl_2(g)$	
1		0		0	...initially
$(1-x)$		x		x	...at equilibrium
$\left(\dfrac{1-x}{1+x}\right)$		$\dfrac{x}{(1+x)}$		$\dfrac{x}{(1+x)}$	...mole fraction
$P\left(\dfrac{1-x}{1+x}\right)$		$\dfrac{Px}{(1+x)}$		$\dfrac{Px}{(1+x)}$	...partial pressure
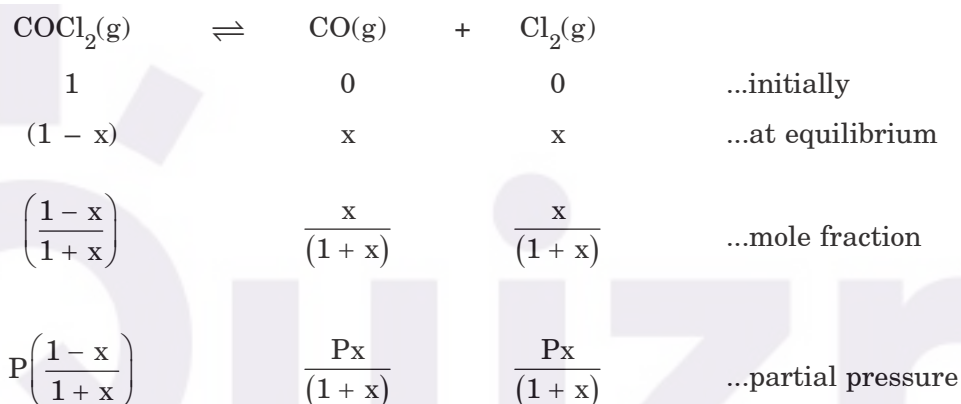
Thus

$$K_p = \frac{P_{CO} \cdot P_{Cl_2}}{P_{COCl_2}} = \frac{Px^2}{\left(1-x^2\right)}$$

Also

$$P = \frac{\rho RT}{m(\text{observed})} \quad (\rho = \text{density})$$

This gives observed molecular wt of $COCl_2 = \dfrac{\rho RT}{P}$

$$= \frac{1.162 \times 8.314 \times 724}{101.325} = 69 \text{ g mol}^{-1}$$

Note : ρ density) g/dm^3 = kg/m^3

(a)

$$x = \frac{D-d}{d} = \frac{99-69}{69} = 0.435$$

---

where $\quad$ D = vapour density of $COCl_2$ before dissociation = $\dfrac{M}{2} = \dfrac{99}{2}$

$\quad$ d = vapour density of $COCl_2$ after dissociation = $\dfrac{69}{2}$

This can also be explained in terms of van't Hoff factor.

$$i = 1 + (y - 1)\, x = 1 + x = \dfrac{m\,(\text{theoretical})}{m\,(\text{observed})}$$

$$(1 + x) = \dfrac{99}{69}$$

(b) $\quad$ P = 101.325 kPa = 1 atm

hence from (1) $\;\; K_p = \dfrac{Px^2}{\left(1 - x^2\right)} = \dfrac{1\,(0.435)^2}{[1 - (0.435)^2]} = 0.233$ atm

(c) $\quad \Delta G \;\; = -\,2.303\; RT \log K_p = -\,2.303 \quad 8.314 \quad 724 \log 0.233$

$\quad\quad\quad = 8770$ J mol

Alternatively we can compute value of x as

total mol of gaseous substances at equilibrium = (1 + x)

hence $\quad$ P = $\dfrac{nRT(1+x)}{V} = \dfrac{w}{mV} RT(1 + x) = \dfrac{\rho RT(1 + x)}{m}$

$\therefore \quad$ (1 + x) = $\dfrac{Pm}{\rho RT} = \dfrac{101.325 \times 99}{1.162 \times 8.314 \times 724} = 1.435$

$\quad\quad$ x = 0.435

Example 12

25 mL of hydrogen and 18 mL of iodine when heated in a closed container, produced 30.8 mL of HI at equilibrium. Calculate the degree of dissociation of HI at the same temperature.

Solution :

In this problem, volume of the species is proportional to their concentration. Thus
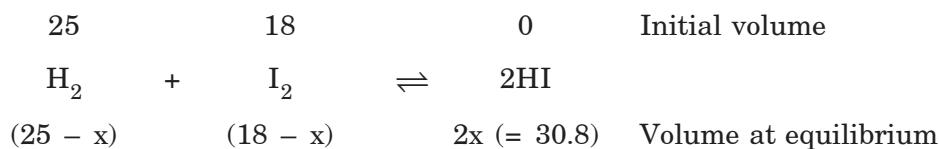
	25		18		0	Initial volume
	H_2	+	I_2	$\rightleftharpoons$	2HI	
	(25 − x)		(18 − x)		2x (= 30.8)	Volume at equilibrium
or	(25 − 15.4)		(18 − 15.4)		30.8	$\left(x = \dfrac{30.8}{2} = 15.4 \right)$
	= 9.6		= 2.6			

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{30.8^2}{9.6 \times 2.6} = 38.01$$

Now, if the dissociation of HI is carried out at the same temperature then for the reaction having the degree of dissociation, x´, we have,

1	0	0	Initial moles
2HI $\rightleftharpoons$	H_2	$+$ I_2	
$(1 - x´)$	$\dfrac{x´}{2}$	$\dfrac{x´}{2}$	Moles at equilibrium
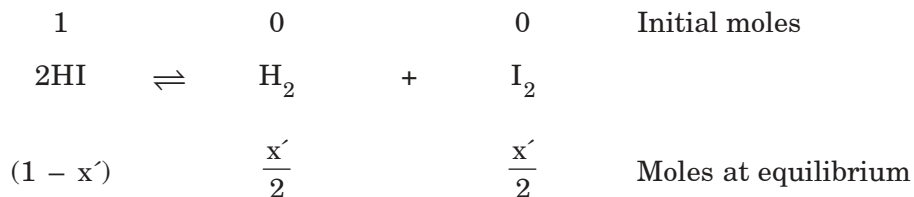
Equilibrium constant

$$K´_c = \frac{1}{K_c} = \frac{1}{38.01} \qquad ...(Eqn.\ 5)$$

$$K´_c = \frac{\left(\dfrac{x´}{2}\right)\left(\dfrac{x´}{2}\right)}{(1 - x´)^2} = \frac{1}{38.01}$$

$$x´ = 0.245$$

Example 13

Variation of equilibrium constant K with temperature T is given by van't Hoff eqn. log K = log A − $\dfrac{\Delta H°}{2.303\ RT}$. A graph between log K and T^{-1} was a straight line as shown (Fig.) and having θ = tan^{-1} (0.5) and OP =10. Calculate

    (a)   **ΔH (standard heat of reaction) when T = 298 K**

    (b)   **A (pre-exponential factor)**

    (c)   **equilibrium constant K, at 298 K**

    (d)   **K at 798 K if ΔH is independent of temp.**
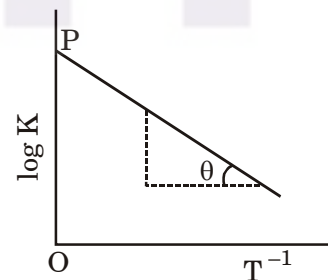
Solution :

    (a)   Above eqn. represents a straight line of

$$slope = -\frac{\Delta H°}{2.303\,R} = -\tan\theta = -0.5$$

$$\therefore \qquad \Delta H = 2.303 \quad 8.314 \quad 0.5 = 9.574 \text{ J mol}^{-1}$$

(b)   also intercept, $\log A = OP = 10$

∴ $A = 10^{10}$

(c)
$$\log K = \log A - \frac{\Delta H°}{2.303\ RT}$$

$$= 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

$$= 10 - 1.68 \quad 10^{-3}$$

$$K = 9.96 \quad 10^9$$

(d)   Putting values calculated in (a) and (c) into eqn.

$$\Delta H = \frac{2.303\ RT_1 T_2}{T_2 - T_1} \log \frac{K_2}{K_1}$$

we have $9.574 = \dfrac{2.303 \times 8.314 \times 298 \times 798}{(798 - 298)} \log \dfrac{K_2}{\left(9.96 \times 10^9\right)}$

∴ K_2 (equilibrium constant at 798 K) = **9.98**   **10^9**

Example 14

In the preparation of MgO, the reaction is

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$

Experiments carried out between 850 C and 950 C led to a set of K_p values fitting an empirical equation

$$\log K_p = 7.310 - \frac{8500}{T}$$

if the reaction is carried out in quiet air, what temperature would be predicted from the equation for the complete decomposition of the $MgCO_3$?

Solution :

If $MgCO_3$ can decompose to yield CO_2 at 1.00 atm (to push back the air), it will do so.

$$K_p = P_{CO2} = 1\ atm$$

∴ $\log K_p = \log 1 = 0.00 = 7.310 - \dfrac{8500}{T}$

∴ $T = \dfrac{8500}{7.310} = 1163\ K = 890\ C$

Example 15

For the reaction at 298 K A(g) + B(g) $\rightleftharpoons$ C(g) + D(g)

ΔH = – 29.8 kcal, ΔS = – 0.100 kcal K^{-1}

Calculate ΔG and equilibrium constant.

Solution :

We know $\hspace{3cm} \Delta G = \Delta H - T\,\Delta S$

$\hspace{5cm} = -\,29.8 - 298 \quad 0.1 = 0$

since $\hspace{3cm} \Delta G = 2.303\ RT\ \log K$
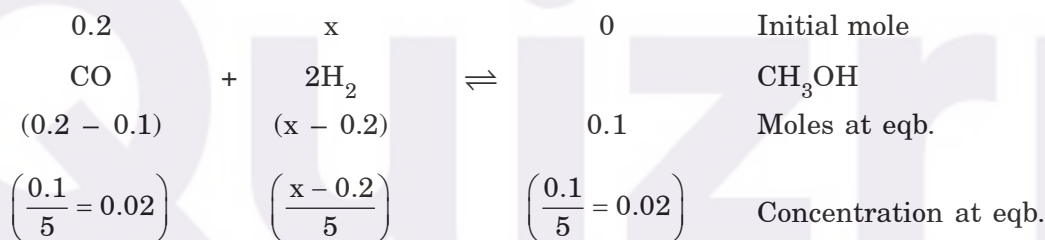
hence log K = 0 which gives $\hspace{1cm}$ K = 1

Example 16

For the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, hydrogen gas is introduced into a five-litre flask at 327 C, containing 0.2 mole of CO (g) and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of CH_3OH is formed. Calculate the equilibrium constants K_p and K_c.

(IIT 1990)

Solution :

Suppose x moles of H_2 are introduced into the flask

$\hspace{2cm}$ 0.2 $\hspace{3cm}$ x $\hspace{4cm}$ 0 $\hspace{2cm}$ Initial mole

$\hspace{2cm}$ CO $\hspace{1.5cm} + \hspace{1cm} 2H_2 \hspace{2cm} \rightleftharpoons \hspace{2cm} CH_3OH$

$\hspace{2cm}$ (0.2 – 0.1) $\hspace{1.5cm}$ (x – 0.2) $\hspace{3cm}$ 0.1 $\hspace{1.5cm}$ Moles at eqb.

$\hspace{1.5cm} \left(\dfrac{0.1}{5} = 0.02\right) \hspace{1cm} \left(\dfrac{x-0.2}{5}\right) \hspace{1.5cm} \left(\dfrac{0.1}{5} = 0.02\right) \hspace{1cm}$ Concentration at eqb.

Total moles = 0.1 + x – 0.2 + 0.1 = x

$$\therefore \hspace{1cm} K_p = \frac{P_{CH_3OH}}{P_{CO} \times P_{H_2}^2} = \frac{\left(\dfrac{0.1}{x} \times 4.92\right)}{\left(\dfrac{0.1}{x} \times 4.92\right)\left(\dfrac{x-0.2}{x} \times 4.9\right)^2}$$

or $\hspace{1cm} K_p = \left[\dfrac{x}{(x-0.2)4.9}\right]^2 \hspace{3cm}$ ...(1)

Further,

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.02}{0.02 \times \left(\dfrac{x-0.2}{5}\right)^2} = \left(\frac{5}{x-0.2}\right)^2 \hspace{2cm} ...(2)$$

Applying $\quad\quad K_p = K_c \, (RT)^{\Delta n}$

$$\frac{K_p}{K_c} = (RT)^{\Delta n} = (0.0821 \quad 600)^{-2} \quad\quad\quad ...(3)$$

From (1) and (2), we have,

$$\frac{K_p}{K_c} = \left(\frac{x}{(x-0.2)4.92}\right)^2 \left(\frac{x-0.2}{5}\right)^2 = \left(\frac{x}{4.92 \times 5}\right)^2 \quad\quad ...(4)$$

From (3) and (4), we have

$$\left(\frac{x}{4.92 \times 5}\right) = \left(0.821 \times 600\right)^{-2} ; \, x = 0.5$$

Substituting x in (1) and (2), we get

$$K_p = 0.1147 \text{ atm}^{-2}$$
$$K_c = 277.78 \text{ (moles/litre)}^{-2}$$

Example 17

For the equilibrium $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ the standard enthalpy and entropy changes at 300 K and 1200 K for the forward reaction are as follows :

$\quad\quad \Delta H_{300K} = -41.16 \text{ kJ mol}^{-1} \quad\quad\quad \Delta S_{300K} = -0.0424 \text{ kJ mol}^{-1}$

$\quad\quad \Delta H_{1200K} = -32.93 \text{ kJ mol}^{-1} \quad\quad\quad \Delta S_{1200K} = -0.0296 \text{ kJ mol}^{-1}$

In which direction will the reaction be spontaneous ?

(a) at 300 K and (b) at 1200 K, when $P_{CO} = P_{CO_2} = P_{H_2} = P_{H_2O} = 1$ atm

Also calculate Kp for the reaction at each temperature.

Solution :
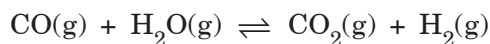
Using the relationship, $\quad\quad \Delta G = \Delta H - T \Delta S$, we have

$$\Delta G_{300K} = \Delta H_{300K} - T \Delta S_{300K}$$
$$= -41.16 - 300 \, (-0.0424) = -28.44 \text{ kJ mol}^{-1}$$

and $\quad\quad\quad\quad \Delta G_{1200K} = \Delta H_{1200K} - T \Delta S_{1200K}$
$$= -32.93 - 1200 \, (-0.0296) = 2.59 \text{ kJ mol}^{-1}$$

we know that a process is spontaneous if $\Delta G = -ve$, therefore, the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

is spontaneous at 300 K, whereas the reverse reaction is spontaneous at 1200 K.

also $\quad\quad\quad\quad\quad\quad \Delta G = -2.303 \, RT \log K_p$

hence at 300 K

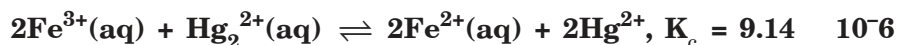$$- 28.44 = - 2.303 \quad 8.314 \quad 10^{-3} \quad 300 \log K_p$$

this gives $\qquad K_p = 8.8 \quad 10^4$

similarly $\qquad K_p \ (1200 \ K) \ = 0.77$

Example 18

A solution is prepared having these initial concentration : $[Fe3+] = [Hg_2^{2+}] = 0.50$ M; $[Fe^{2+}]$ = $Hg^{2+}] = 0.03$ M. The following reaction occurs among these ions at 25 C.

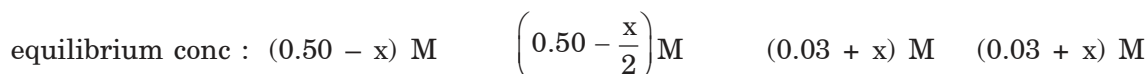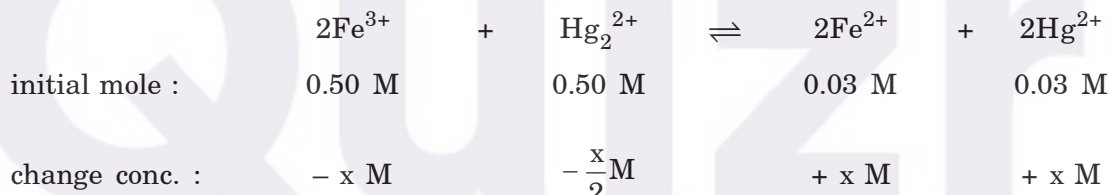$$2Fe^{3+}(aq) + Hg_2^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + 2Hg^{2+}, \ K_c = 9.14 \quad 10^{-6}$$

What will be the ionic concentration when equilibrium is established ?

Solution :

Since all reactants and products are present initially, we do not know whether a net reaction will occur 'to the right' or 'to the left'. This is where the reaction quotient Q can help us :

$$Q = \frac{\left[Fe^{2+}\right]^2\left[Hg^{2+}\right]^2}{\left[Fe^{3+}\right]^2\left[Hg_2^{2+}\right]} = \frac{(0.03)^2(0.03)^2}{(0.50)^2(0.50)} = 6.48 \times 10^{-6}$$

Since Q ($6.48 \quad 10^{-6}$) is smaller than K_c ($9.14 \quad 10^{-6}$), a net reaction must proceed to the right.

	$2Fe^{3+}$	+	Hg_2^{2+}	$\rightleftharpoons$	$2Fe^{2+}$	+	$2Hg^{2+}$
initial mole :	0.50 M		0.50 M		0.03 M		0.03 M
change conc. :	– x M		$-\frac{x}{2}M$		+ x M		+ x M
equilibrium conc :	(0.50 – x) M		$\left(0.50 - \frac{x}{2}\right)M$		(0.03 + x) M	(0.03 + x) M

$$\therefore \qquad K_c = \frac{(0.03 + x)^2 \ (0.03 + x)^2}{(0.50 - x)^2 \left(0.50 - \frac{x}{2}\right)^2} = 9.14 \times 10^{-6}$$

Since K_c is very small, x would be <<< 1

hence $\qquad (0.50 - x) \approx 0.50, \ \left(0.50 - \frac{x}{2}\right) \approx 0.50$

hence

$$K_c = \frac{(0.03 + x)^2 (0.03 + x)^2}{(0.50)^2 (0.50)} = 9.14 \times 10^{-6}$$

$$(0.03 + x)^4 = 1.1425 \quad 10^{-6}$$

$\therefore \qquad (0.03 + x)^2 = 1.07 \quad 10^{-3}$

$(0.03 + x) = 3.27 \quad 10^{-2}$

$\therefore \qquad x = 2.7 \quad 10^{-3}$

hence ionic concentrations of

$[Fe^{2+}] = 0.03 + x = 0.03 + 2.7 \quad 10^{-3} = 3.27 \quad 10^{-2}$ M

$[Hg^{2+}] = 0.03 + x = 0.03 + 2.7 \quad 10^{-3} = 3.27 \quad 10^{-2}$ M

$[Fe^{3+}] = 0.50 - x = 0.50 - 2.7 \quad 10^{-3} = 4.973 \quad 10^{-1}$ M

$[Fe_2^{2+}] = 0.50 - \dfrac{x}{2} = 0.50 - 1.4 \quad 10^{-3} = 4.986 \quad 10^{-1}$ M

Example 19

For the equilibrium :

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

$\Delta H_f^0 (CaCO_3) = -1207.1$ **kJ/mole,** $\Delta H_f^0 (CaO) = -635.5$ **kJ/mole**

$\Delta H_f^0 (CO_2) = -393.5$ **kJ/mole**

(i) **How would K_p depend on temperature ?**

(ii) **The equilibrium constant for this reaction is much less than 1. Why, then, does heating $CaCO_3(s)$ in an open container lead to a complete concentration to the products ?**

Solution :

(a) $\Delta H^0 = [\Delta H_f^0 (CaO) + \Delta H_f^0 (CO_2)] - \Delta H_f^0 (CaCO_3)$

$\qquad = [-635.5 + (-393.5)] - (-1207.1)$

$\qquad = +178.1$ kJ.

Because the given reaction is endothermic, the equilibrium constant will increase with increasing temperature.

(b) On heating $CaCO_3$, K_p increases which favours the dissociation of $CaCO_3$. Also, in an open container, CO_2 gas escapes and more $CaCO_3$ dissociates to replace it until no more $CaCO_3$ remains.