CHEMICAL EQUILIBRIUM

INTRODUCTION

Whenever we hear the word Equilibrium immediately a picture arises in our mind an object under the influence of two opposing forces. For chemical reactions also this is true. A reaction also can exist in a state of equilibrium balancing forward and backward reactions.

Symbolic representation of any chemical change in terms of reactants and products is called chemical reaction.

Types of chemical reaction :

(a) On the basis of physical state

Homogeneous reactions	**Heterogeneous reaction**
All reactants and products are in same phase	Reactants and products are in two or more phase
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)$

(b) On the basis of direction

	Reversible reaction	**Irreversible reaction**
(i)	Chemical reaction in which products can be converted back into reactants $H_2 + I_2 \rightleftharpoons 2HI$	Chemical reaction in which products cannot be convert back into reactants $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
(ii)	Proceed in forward as well as backward direction	Proceed only in forward direction
(iii)	These attain equilibrium	These do not attain equilibrium
(iv)	Reactant are never completely converted into products	Reactants are nearly completely converted into products
(v)	Generally thermal dissociations are held in closed vessel $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	Generally thermal decompositions are held in open vessel $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

(c) On the basis of speed

	Fast reactions	**Slow reactions**
(i)	Generally these reactions are ionic in nature $HCl + NaOH \rightarrow NaCl + H_2O$ Acid Base Salt Water	Generally these reactions are molecular in nature $H_2 + I_2 \rightarrow 2HI$

(d) On the basis of heat

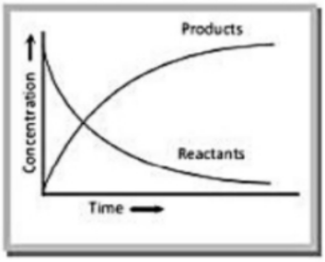
	Exothermic reaction	**Endothermic reaction**
(i)	Heat is evolved in these type of chemical reactions $R \rightarrow P + x$ kcal	Heat is absorbed in these type of chemical reactions $R \rightarrow P - x$ kcal

It is an experimental fact that most of the process 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.

EQUILIBRIUM AND ITS DYNAMIC NATURE

(1) **Definition :** "Equilibrium is the state at which the concentration of reactants and products do not change with time. i.e. concentrations of reactants and products become constant."

(2) **Characteristics :** Following are the important characteristics of equilibrium state,



(i) Equilibrium state can be recognised by the constancy of certain measurable properties such as pressure, density, colour, concentration etc. by changing these conditions of the system, we can control the extent to which a reaction proceeds.

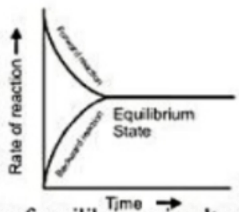
(ii) Equilibrium state can only be achieved in close vessel, but if the process is carried out in an open vessel equilibrium state cannot be attained because in an open vessel, the reverse process may not take place.

(iii) Equilibrium state is reversible in nature.

(iv) Equilibrium state is also dynamic in nature. Dynamic means moving and at a microscopic level, the system is in motion. The dynamic state of equilibrium can be compared to water tank having an inlet and outlet. Water in tank can remain at the same level if the rate of flow of water from inlet (compared to rate of forward reaction) is made equal to the rate of flow of water from outlet (compared to rate of backward reaction). Thus, the water level in the tank remains constant, though both the inlet and outlet of water are working all the time.

(v) At equilibrium state,

Rate of forward reaction = Rate of backward reaction



(3) **Types :** Equilibrium in a system implies the existence of the following types of equilibrium simultaneously,

(i) Thermal equilibrium : There is no flow of heat from one part to another i.e. T = constant.

(ii) Mechanical equilibrium : There is no flow of matter from one part to another i.e. P = constant.

(iii) Physical equilibrium : It is a state of equilibrium between the same chemical species in different phases (solid, liquid and gaseous)

(iv) Chemical equilibrium : There is no change in composition of any part of the system with time.

Physical equilibrium.

The various equilibrium which can exist in any physical system are,

Solid	$\rightleftharpoons$	Liquid
Liquid	$\rightleftharpoons$	Vapour
Solid	$\rightleftharpoons$	Gas(vapour)
Solid	$\rightleftharpoons$	Saturated solution of solid in a liquid
Gas(vapour)	$\rightleftharpoons$	Saturated solution of gas in a liquid

(1) Solid-liquid equilibrium

$$H_2O(s) \rightleftharpoons H_2O(\text{liquid})$$

Rate of transfer of molecules from ice to water = Rate of transfer of molecules from water to ice

Rate of melting of ice = Rate of freezing of water

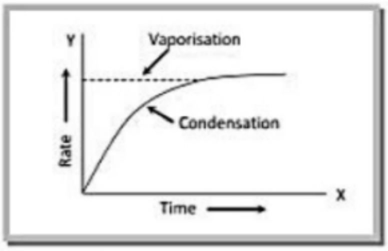
(2) Liquid-vapour equilibrium : When vapour of a liquid exists in equilibrium with the liquid, then Rate of vaporisation = Rate of condensation,

$$H_2O(\text{liquid}) \rightleftharpoons H_2O(\text{vapour})$$

Conditions necessary for a liquid-vapour equilibrium

(i) The system must be a closed system i.e., the amount of matter in the system must remain constant.

(ii) The system must be at a constant temperature.



(iii) The visible properties of the system should not change with time.

(3) Solid-vapour equilibrium : Certain solid substances on heating get converted directly into vapour without passing through the liquid phase. This process is called sublimation. The vapour when cooled, gives back the solid, it is called disposition.

$$\text{Solid} \rightleftharpoons \text{Vapour}$$

The substances which undergo sublimation are camphor, iodine, ammonium chloride etc.

For example, Ammonium chloride when heated sublimes.

$$NH_4Cl(\text{solid}) \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} NH_4Cl(\text{vapour})$$

(4) **Equilibrium between a solid and its solution :** When a saturated solution is in contact with the solid solute, there exists a dynamic equilibrium between the solid and the solution phase.

$$\text{Solid substance} \rightleftharpoons \text{Solution of the substance}$$

Example : Sugar and sugar solution. In a saturated solution, a dynamic equilibrium is established between dissolved sugar and solid sugar.

$$\text{Sugar (solid)} \rightleftharpoons \text{Sugar (aqueous)}$$

At the equilibrium state, the number of sugar molecules going into the solution from the solid sugar is equal to the number of molecules precipitating out from the solution, i.e., at equilibrium,

Rate of dissolution of solid sugar = Rate of precipitation of sugar from the solution.

(5) **Equilibrium between a gas and its solution in a liquid :** Gases dissolve in liquids. The solubility of a gas in any liquid depends upon the,

(i) Nature of the gas and liquid.

(ii) Temperature of the liquid.

(iii) Pressure of the gas over the surface of the solution.

Characteristics of chemical equilibrium :

(a) It is a dynamic equilibrium i.e. at this stage, reaction takes place in both the directions with same speed so, there is no net change.

(b) At equilibrium the reaction proceeds both the side, equally

(c) At equilibrium, both reactants and products are present and their concentration do not change with respect to time.

(d) The state of equilibrium is not effected by the presence of catalyst : It only helps to attain the equilibrium state in less or more time.

(e) Change in pressure, temperature or concentration favours one of the reactions and thus shifts the equilibrium point in one direction.

RATE OF REACTION

In a reaction , there is change in concentration of reactant or product per mole in unit time, it is known as rate of the reaction.

$$\text{Rate of reaction} = \frac{(-)\text{ change in concentration of reactant}}{\text{time}} = -\left(\frac{dc}{dt}\right)\text{reactant}$$

Here negative sign indicate that concentration of reactants decrease with time.

$$\text{Rate of reaction} = +\frac{\text{change in concentration of products}}{\text{time}} = +\left(\frac{dc}{dt}\right)\text{product}$$

Here positive sign indicate that concentration of products increase with time.

Note : The concentration change may be positive or negative but the rate of reaction is always positive.

$$\text{Unit of rate of reaction} = \frac{\text{mole/lit.}}{\text{sec}} = \frac{\text{mole}}{\text{lit.sec}} = \text{mole lit}^{-1}\ \text{sec}^{-1}$$

For example $A \rightarrow B$

For reactant $\rightarrow -\dfrac{d[A]}{dt}$ [concentration decrease with time]

For reactant $\rightarrow +\dfrac{d[B]}{dt}$ [concentration increase with time]

[d [A], d [B] are change in concentration of A & B in time dt]

At equilibrium, since there is no net change in concentration of reactant or product.

So rate of reaction is zero.

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \text{ (At equilibrium)}$$

LAW OF MASS ACTION

(a) This law was given by **Guldberg** and **Waage**.

(b) At a given temperature, the product of the concentration of products each raised to the corresponding stoichiometric coefficients in the balanced chemical equation divided by the product of the concentrations of the reactants raised to the corresponding stoichiometric coefficients has a constant value.

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

Rate of chemical reaction $\quad r \propto [A][B]$

$$r = K[A][B]$$

Mathematical Expression

(i) For unitary stoichiometeric coefficients

At the constant temperature, let us consider the following reversible reaction.

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

According to law of mass action -

Rate of forward reaction

$$r_f \propto [A][B] \quad \text{or} \quad r_f = K_f[A][B]$$

where K_f is the rate constant of the forward reaction.

Rate of backward reaction

$$r_b \propto [C][D] \quad \text{or} \quad r_b = K_b[C][D]$$

where K_b is the rate constant of the backward reaction.

At equilibrium :

Rate of reaction = Rate of forward reaction – Rate of backward reaction = 0

$$K_f[A][B] - K_b[C][D] = 0$$

$$\text{or} \quad \frac{K_f}{K_b} = \frac{[C][D]}{[A][B]}$$

$$\text{or} \quad \boxed{K_{eq} = \frac{[C][D]}{[A][B]}}$$

Here, k is equilibrium constant of given reversible reaction.

(ii) For non-unitary stoichiometric coefficient

$$n_1A + n_2B \rightleftharpoons m_1C + m_2D$$

$$r_f = r_b$$

$$K_{eq} = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$$

Note : [A], [B], [C], [D] are molar concentration of reactants and products, for dilute solution.

EQUILIBRIUM CONSTANTS, K_C, K_P, K_{PC} & K_X

There are various methods for measuring equilibrium constant in terms of concentration, pressure, mole fraction.

(i) **Equilibrium constant in term of concentration**

Consider an equilibrium reaction as

$$X(g) + Y(g) \rightleftharpoons Z(g)$$

For this reactions, which is in equilibrium, there exist an equilibrium constant (K_{eq}) represented as

$$K_{eq} = \frac{[Z]}{[X][Y]}$$

For the given equilibrium, irrespective of the reacting species (i.e., either X + Y or Z or X + Z or Y + Z or X + Y + Z) and their amount we start with, the ratio, $\frac{[Z]}{[X][Y]}$ is always constant at a given temperature.

The given expression involves all variable terms (variable term means the concentration of the involved species changes from the start of the reaction to the stage when equilibrium is reaches), so the ratio $\frac{[Z]}{[X][Y]}$ can also referred as K_C.

$$\therefore \qquad K_c = \frac{[Z]}{[X][Y]}$$

Thus, for the given equilibrium, it seems that K_{eq} and K_c are same but in actual practice for some other equilibrium, they are not same.

(ii) Equilibrium constant in terms of pressure

Assuming that the gases, X, Y and Z behave ideally.

$$PV = nRT$$

$$P = \frac{n}{V} RT = CRT$$

$$C = \frac{P}{RT}$$

$$\therefore \qquad [X] = \frac{P_X}{RT}; [Y] = \frac{P_Y}{RT} \text{ and } [Z] = \frac{P_Z}{RT}$$

$$\therefore \qquad K_c = \frac{\left(\frac{P_Z}{RT}\right)}{\left(\frac{P_X}{RT}\right)\left(\frac{P_Y}{RT}\right)} = \frac{P_Z \times RT}{P_X \times P_Y}$$

$$\frac{K_C}{RT} = \frac{P_Z}{P_X \times P_Y}$$

The LHS of the above expression is a constant since K_c, R and T, all are constant. This implies that RHS is also a constant, which is represented by K_p.

$$\therefore K_p = \frac{P_Z}{P_X \times P_Y}$$

Thus, expression of K_p involves partial pressures of all the involved species and represents the ratio of partial pressures of product to reactants of an equilibrium reaction.

If the phase of reactant X from gaseous to pure solid. Then the equilibrium reaction can be shown as

$$X(s) + Y(g) \rightleftharpoons Z(g)$$

Its equilibrium constant (K_{eq}) would be

$$K_{eq} = \frac{[Z]}{[X][Y]}$$

The concentration of X is the number of moles of X per unit volume of solid. As we known, the concentration of all pure solids (and pure liquids) is a constant as it is represented by d/M (where d and M represents its density and molar mass). This ratio of d/M will be a constant whether X is present initially or at equilibrium.

$$K_{eq}[X] = \frac{[Z]}{[Y]} \qquad\qquad \therefore K_c = \frac{[Z]}{[Y]}$$

Thus expression of K_c involves only those species whose concentration changes during the reaction.

The distinction between Keq and K_c is that the expression of Keq involves all the species (whether they are pure solids, pure liquids, gases, solvents or solutions) while the K_c expression involves only those species whose concentration is a variable (like gases and solutions). Thus, expression of K_c is devoid of pure components (like pure solids and pure liquids) and solvents.

$$K_c = \frac{\frac{P_Z}{RT}}{\frac{P_Y}{RT}} = \frac{P_Z}{P_Y}$$

Since, LHS of the expression is a constant, so the ratio $\frac{P_Z}{P_Y}$ would also be a constant, represented by K_P.

$$\therefore \quad K_P = \frac{P_Z}{P_Y}$$

(iii) Equilibrium constant in terms of both concentration & pressure

Consider the following equilibrium

$$X\,(sol.) + Y(g) \rightleftharpoons Z(g) + A(g)$$

$$K_c = \frac{[Z][A]}{[X][Y]}$$

If concentration of X, Y, Z and A is expressed in terms of partial pressures

$$\therefore \quad K_c = \frac{\left(\frac{P_Z}{RT}\right)\left(\frac{PA}{RT}\right)}{[X]\left(\frac{P_Y}{RT}\right)} = \frac{P_Z \times P_A}{[X]P_Y \times RT}$$

$$K_c\,(RT) = \frac{P_Z \times P_A}{[X]P_Y}$$

The LHS of the expression is an constant (as K_c, R and T all constant), which implies that the RHS will also be a constant. But RHS of the expression can neither be called K_P (as all are not partial pressure terms) nor K_c (as all are not concentration terms), so such expression that involves partial pressure and concentration terms both are reffered as K_{PC}.

$$\therefore \quad K_{PC} = \frac{P_Z \times P_A}{[X]P_Y}$$

Thus, K_P can exist only for that equilibrium which satisfies these two conditions.

(a) At least one of the reactant or product should be in gaseous phase and

(b) No component of the equilibrium should be in solution phase (Because when solution is present, the equilibrium constant would be called K_{PC})

(iv) Equilibrium constant in terms of moles fraction (K_X) :

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

Mole fraction at equilibrium $\quad X_A \quad X_B \quad X_C \quad X_D$

$$K_X = \frac{X_C \times X_D}{X_A \times X_B}$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

(i) The expression for equilibrium constant, K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.

(ii) The value of equilibrium constant is independent of initial concentration of the reactants and product.

(iii) Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.

(iv) The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.

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

$$K_p = \frac{P_{HI^2}}{P_{H_2}.P_{I_2}}$$

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

$$Kp' = \frac{P_{H_2}.P_{I_2}}{P_{HI}^2} = \frac{1}{Kp}$$

$$K_P' = \frac{1}{K_P}$$

(v) The equilibrium constant K, for a reaction is related to the equilibrium constant of the corresponding reaction whose equation is obtained by multiplying or dividing the equation.

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

$$K_p = \frac{P_{HI}^2}{P_{H_2}.P_{I_2}}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

$$K_p'' = \frac{P_{HI}}{P_{H_2}^{1/2}.P_{I_2}^{1/2}} = \sqrt{K_p}$$

(vi) If reaction is performed in multiple steps

$A \rightleftharpoons B$; overall reaction

Step-1 : $A(g) \rightleftharpoons C(g) + D(g) \qquad K_{p_1}$

Step-2 : $C(g) \rightleftharpoons E(g) \qquad K_{p_2}$

Step-3 : $D(g) + E(g) \rightleftharpoons B(g) \qquad K_{p_3}$

$A(g) \rightleftharpoons B(g) \qquad K_p \qquad$ then $K_p = K_{p_1}.K_{p_2}.K_{p_3}$

Factors which do not influence equilibrium constant :

(a) Concentration of reactants and products.

(b) Pressure and volume.

(c) Presence of catalyst.

(d) Addition of the inert gas at constant Pressure and volume.

Factors which influence the equilibrium constant :

A. Mode of representation of chemical reaction.

B. Stoichiometry of reaction.

C. Temperature.

A. Mode of representation of reaction –

If we take reaction $2HI \rightleftharpoons H_2 + I_2$

Then, we write the value of equilibrium constant K_{C_1} for the above reaction as following.

$$K_{C_1} = \frac{[H_2][I_2]}{[HI]^2} \qquad \text{....... (i)}$$

Now, if we take reaction $H_2 + I_2 \rightleftharpoons 2HI$

Then, we write the value of equilibrium constant K_{C_2} for above reaction as following

$$K_{C_2} = \frac{[HI]^2}{[H_2][I_2]} = \frac{1}{K_{C_1}} \qquad \text{...... (ii)}$$

B. Stoichiometry of the reaction –

Method of writing the equation of the reversible reaction is called as stoichiometry of the reaction.

Now, we consider the formation of HI(g) by the combination of H_2(g) and I_2(g).

$$H_2 + I_2 \overset{\Delta}{\rightleftharpoons} 2HI$$

The expression of its equilibrium constant is-

$$K_{C_1} = \frac{[HI]^2}{[H_2][I_2]}$$

If the equation of above reaction is written by following method –

$$\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \rightleftharpoons HI(g)$$

The expression for the equilibrium constant is –

$$K_{C_2} = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$$

on the basis of comparing both the equilibrium constant equation.

$$K_{C_2} = \sqrt{K_{C_1}} \quad \text{or} \quad (K_{C_1})^{1/2}$$

Note : When we divide a reaction by a factor 'n' in the equation, the value of new equilibrium constant is equal to the root of n of the previous equilibrium constant.

For Example – Suppose, the equilibrium constant for the following reaction.

$A + B \rightleftharpoons C + D$ is K_1 then for the reaction

$$\frac{1}{n}A + \frac{1}{n}B \rightleftharpoons \frac{1}{n}C + \frac{1}{n}D$$

the value of the equilibrium constant K_2 is equal to $\sqrt[n]{K_1}$ or $(K_1)^{1/n}$.

$$K_2 = K_1^{1/n}$$

C Temperature –

Increase in temperature favours the endothermic reaction and decrease in temperature favours the exothermic reaction for the forward reaction so for exothermic reactions, the value of K_c and K_p decrease with rise in temperature while for endothermic reactions, the value of K_c and K_p increases with rise in temperature. This type of variation in equilibrium constant with temperature given by **Van't Hoff** equation as follows -

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

or

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

Where,

K_2 = equilibrium constant at temperature T_2

K_1 = equilibrium constant at temperature T_1

ΔH = Energy of reaction of constant temperature

R = Molar gas constant

According to the temperature, reaction are of three types.

(a) Non-thermic reaction means $\Delta H = 0$

$$\log K_2 - \log K_1 = 0$$
$$\log K_2 = \log K_1$$

There is no effect of temperature on this type of reaction.

(b) Endothermic reaction $\Rightarrow \Delta H = (+)$ ve

$\log K_2 - \log K_1 = (+)$ ve,

means $K_2 > K_1$

On increasing of temperature, equilibrium constant will also increase for this type of reaction.

(c) Exothermic reaction $\Rightarrow \Delta H = (-)$ ve

$\log K_2 - \log K_1 = (-)$ ve,

means $K_2 < K_1$

On the increase of temperature equilibrium constant will decreases for exothermic reaction.

Units of K_C and K_p

The concentration is expressed in the term of moles per litre. Therefore, units of K_c will be (moles litre^{-1})$^{\Delta n}$.

In the same way, partial pressure are measured by the unit of atmospheres and therefore units of K_p will be $(\text{Atmospheres})^{\Delta n}$.

Value of Δn	Unit of K_c	Unit of K_p
0	No unit	No unit
> 0	$(\text{Moles } l^{-1})^{\Delta n}$	$(\text{atm})^{\Delta ng}$
< 0	$(\text{Moles } l^{-1})^{\Delta n}$	$(\text{atm})^{\Delta ng}$

Relation between K_p and K_C

Let us consider the following reaction

$$n_1 A + n_2 B \rightleftharpoons m_1 C + m_2 D.$$

The value of K_c for the reaction is,

$$K_c = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$$

According to gas law $PV = n\,RT$

$$P = \left(\frac{n}{v}\right) RT \text{ .... (1)}$$

Here $\frac{n}{v} = \frac{\text{no. of moles}}{\text{lit.}} = [\ ] = \text{Active mass}$

$$\because \quad K_P = \frac{(p_C)^{m_1}\,(p_D)^{m_2}}{(p_A)^{n_1}\,(p_B)^{n_2}}$$

on putting the value of 'p' in the formula of K_P by the equation (1)

$$K_P = \frac{([C]\,RT)^{m_1}([D]RT)^{m_2}}{([A]RT)^{n_1}([B]RT)^{n_2}}$$

$$K_P = \frac{[C]^{m_1}[D]^{m_2}\ (RT)^{m_1+m_2}}{[A]^{n_1}[B]^{n_2}\ (RT)^{n_1+n_2}}$$

$$K_P = K_C\ (RT)^{(m_1+m_2)-(n_1+n_2)}$$

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

$$[\Delta n = (m_1 + m_2) - (n_1 + n_2)]$$

Δn_g = number of moles of gaseous products – number of moles of gaseous reactants.

T = Absolute temperature.

Illustration

1. At 700 K, the equilibrium constant K_P, for the reaction

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

is 1.8×10^{-3} kPa. What is the numerical value of K_C for this reaction at the same temperature–

(A) 3.09×10^{-7} mole litre^{-1} (B) 9.03×10^{-7} mole litre^{-1}

(C) 5.05×10^{-9} mole litre^{-1} (D) 5.05×10^{-5} mole litre^{-1}

Ans. A

Sol. We know the relationship

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

Here $K_P = 1.80 \times 10^{-3}$

$$K_p = \frac{1.8 \times 10^{-3}}{101.3} \text{ atm}$$

$$= 1.78 \times 10^{-5} \text{ atm}$$

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

$$\Delta n = 3 - 2 = 1$$

$$T = 700 \text{ K}$$

$$K_C = \frac{K_P}{(RT)^{\Delta n}} = \frac{1.78 \times 10^{-5}}{0.0821 \times 700}$$

$$= \mathbf{3.09 \times 10^{-7} \text{ mole litre}^{-1}}.$$

Exercise

1. Equilibrium constant K_p for the reaction

$CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$ is 8.21 atm at 727°C,

if 10 mole of $CaCO_3(s)$ is placed in a 10 L container, what is the weight (in gm) of CaO formed at equilibrium.

Ans. 0056 g

2. The value of K_C for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; is 0.50 at 400° C. What will be the value of K_P at 400°C when concentration are expressed in mole litre^{-1} and pressure in atmosphere–

(A) 1.64×10^{-4} (B) 2.80×10^{-6} (C) 2.80×10^{-4} (D) 1.64×10^{-6}

Ans A

APPLICATIONS OF EQUILIBRIUM CONSTANT

Consider some applications of equilibrium constant and use it to answer question like:

(i) predicting the extent of a reaction on the basis of its magnitude.

(ii) predicting the direction of the reaction.

(i) ***Predicting the extent of a reaction***

The magnitude of equilibrium constant is very useful especially in reactions of industrial importance. An equilibrium constant tells us whether we can expect a reaction mixture to contain a high or low concentration of product(s) at equilibrium. (It is important to note that an equilibrium constant tells us nothing about the rate at which equilibrium is reached). In the expression of K_C or K_P, product of the concentrations of products is written in numerator and the product of the concentrations of reactants is written in denominator. High value of equilibrium constant indicates that product(s) concentration is high and its low value indicates that concentration of the product(s) in equilibrium mixture is low.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

$$K_P = \frac{(P_{HBr})^2}{(P_{H_2})(P_{Br_2})} = 5.4 \times 10^{18}$$

The large value of equilibrium constant indicates that concentration of the product, HBr is very high and reaction goes nearly to completion.

Similarly, equilibrium constant for $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

is very high and reaction goes virtually to completion.

$$K_C = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.0 \times 10^{31}$$

Thus, large value of K_P or K_C (larger than about 10^3), favour the products strongly. For intermediated values of K (approximately in the range of 10^{-3} to 10^3), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than 10^{-3}), favour the reactants strongly.

At 298 K for reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = 4.8 \times 10^{-31}$$

The very small value of K_C implies that reactants N_2 and O_2 will be the predominant species in the reaction mixture at equilibrium.

(ii) ***Predicting the direction of the reaction.***

The equilibrium constant is also used to find in which direction the reaction will proceed for a given concentration of reactants and products. For this purpose, we calculate the Reaction Quotient (Q). The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_C, or with partial pressure to give Q_P) at any stage of reaction. For a general reaction:

$$n_1 A + n_2 B \rightleftharpoons m_1 C + m_2 D.$$

$$Q_C = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$$

Then, if $Q_C > K_c$, the reaction will proceed in the backward direction

if $Q_C < K_c$, the reaction will move in the forward direction

if $Q_C = K_c$, the reaction mixture is already at equilibrium.

In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, if the molar concentrations of H_2, I_2 and HI are 0.1 mol L^{-1} respectively at 783 K, then reaction quotient at this stage of the reaction is

$$Q_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_C for this reaction at 783 K is 46 and we find that $Q_C < K_C$. The reaction, therefore, will move to right i.e. more $H_2(g)$ and $I_2(g)$ will react to form more HI (g) and their concentration will decrease till $Q_C = K_C$.

DEGREE OF DISSOCIATION

Degree of dissociation is the fraction of a mole of the reactant that underwent dissociation. It is represented by 'α'

$$\alpha = \frac{\text{no. of moles of reactant dissociated}}{\text{no. of moles of reactant present initially}}$$

For example,
Let the equilibrium reaction is the dissociation equilibrium of NH_3 into N_2 and H_2.

	$NH_3(g) \rightleftharpoons$	$\frac{1}{2} N_2(g) +$	$\frac{3}{2} H_2(g)$
Moles initially	a	0	0
Moles at equilibrium	$a(1-\alpha)$	$\frac{a\alpha}{2}$	$\frac{3a\alpha}{2}$

Here, α represented the degree of dissociation.

Illustration

1. 2.56 gm of sulphur $S_8(s)$ is taken which is in equilibrium with its vapour according to reaction,
$$S_8(s) \rightleftharpoons S(g)$$
if vapours occupies 960 mℓ at 1 atm & 273 K then the degree of dissociation of $S_8(s)$ will be [Given : R = 0.08]
(A) 0.5 (B) 0.55 (C) 0.4 (D) 0.44

Ans. B

Sol. $n_{S_8} = \frac{2.56}{8\times 32} = 0.01$

$S_8(s) \rightleftharpoons 8\,S(g)$

$0.01(1-\alpha)$ $\quad$ $8 \times 0.01 \times \alpha$

$PV = nRT$

$$1 \times \frac{960}{1000} = (0.01\times 8\times\alpha)\times 0.08\times 273$$

$\alpha = 0.55$

Exercise

1. Two moles of ammonia was introduced in an evacuated vessel of 1 litre capacity. At high temperature the gas undergoes partial dissociation according to the equation :

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

At equilibrium the concentration of ammonia was found to be 1 mole. What is the value of 'K_C'?

Ans. 1.7 $mol^2\ \ell^{-2}$

Calculation of K_P & K_C

(a) Homogeneous equilibrium in gaseous phase

(b) Homogeneous equilibrium in solution phase

(c) Equilibrium constant for various heterogeneous equilibrium

(a) Homogeneous equilibrium in gaseous phase

Formation of Nitric Oxide : ($\Delta n = 0$)

A. Calculation of K_C : –

Suppose the initial concentration of N_2 and O_2 is a and b respectively. x is the degree of dissociation.

	N_2	+	O_2	$\rightleftharpoons$	2NO
Initial moles	a		b		0
moles at equilibrium	(a–x)		(b–x)		2x
Active mass (mol l^{-1})	$\frac{(a-x)}{V}$		$\frac{(b-x)}{V}$		$\frac{2x}{V}$

Here, V is the volume of container in litre.

According to the law of mass action

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

Substituting the values in the above equation $$K_C = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

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

K_c for this reaction is independent of V of the reaction container.

B. Calculation of K_P :

All the things being same as above, except pressure. Let P atmosphere is the pressure at equilibrium.

	N_2	+	O_2	$\rightleftharpoons$	2 NO
Initial moles	a		b		0
moles at equilibrium	(a–x)		(b–x)		2x

Total no. of moles = (a–x) + (b–x) + 2x = (a+b)

The partial pressure of the above three species can be calculated as below-

$$P_{N_2} = \frac{(a-x)P}{(a+b)}$$

$$P_{O_2} = \frac{(b-x)P}{(a+b)}$$

$$P_{NO} = \frac{(2x)P}{(a+b)}$$

According to the law of mass action

$$K_P = \frac{[P_{NO}]^2}{[P_{N_2}][P_{O_2}]}$$

substituting the value of P_{NO}, P_{N_2}, P_{O_2} in the above equation of K_P -

$$K_P = \frac{\left[\frac{(2x)P}{(a+b)}\right]^2}{\left[\frac{(a-x)P}{(a+b)}\right]\left[\frac{(b-x)P}{(a+b)}\right]}$$

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

Thermal Dissociation of Phosphorus pentachloride- ($\Delta n > 0$)

A. Calculation of K_C - Suppose one mole of PCl_5 is take in a closed container of V litre. Further at equilibrium x mol of PCl_5 dissociated

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
Initial moles	1	0	0
moles at equilibrium	(1–x)	x	x
Concentration (mol l^{-1})	$\frac{1-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

According to law of mass action

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Substituting the values in the above equation.

$$K_C = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{1-x}{v}\right)}$$

$$\boxed{K_C = \frac{x^2}{(1-x)\,v}}$$

The formula of K_C has V in the denominator, hence the equilibrium will be affected by V of the reaction container for the given reaction.

If $x << 1$ then $1 - x \approx 1$

So, $K_C = \frac{x^2}{v}$

$x^2 = K_C.v$

$x^2 \propto v$

$\boxed{x \propto \sqrt{v}}$

If we increase the volume, the dissociation x is also increased.

B. Calculation of K_P -

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
initial moles	1		0		0
moles at equilibrium	1–x		x		x

Total no. of moles at equilibrium,

$$(1 - x) + x + x = (1 + x) \text{ moles}$$

According to law of mass action

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

At equilibrium $P_{PCl_3} = \frac{x \times P}{(1+x)}$

$$P_{Cl_2} = \frac{x \times P}{(1+x)}$$

$$P_{PCl_5} = \frac{(1-x)P}{(1+x)}$$

Substituting the values in the above equation of K_P -

$$K_P = \frac{\left(\frac{x \times P}{1+x}\right)\left(\frac{x \times P}{1+x}\right)}{\frac{(1-x) \times P}{(1+x)}}$$

$$K_P = \frac{x^2 P}{1-x^2}$$

The equation of K_P is not independent of pressure.

suppose, $x << 1$ then $1 - x^2 \approx 1$

$$K_P = x^2 P$$

$$x^2 = \frac{K_P}{P}$$

$$x^2 \propto \frac{1}{P}$$

$$\boxed{x \propto \frac{1}{\sqrt{P}}}$$

The degree of dissociation of PCl_5 is inversely proportional to the square root of pressure so, decrease of pressure increases dissociation of PCl_5.

Formation of Ammonia – ($\Delta n < 0$)

A. Calculation of K_C : –

	N_2	+	$3H_2 \rightleftharpoons$	$2NH_3$
Initial moles	1		3	0
moles at equilibrium	(1–x)		(3–3x)	2x
Active mass (mol l^{-1})	$\left(\frac{1-x}{v}\right)$		$\left(\frac{3-3x}{v}\right)$	$\left(\frac{2x}{v}\right)$

According to law of mass action

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting the values in the above equation-

$$K_C = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{1-x}{v}\right)\left(\frac{3-3x}{v}\right)^3}$$

$$K_C = \frac{4x^2v^2}{(1-x)(3-3x)^3}$$

$$\boxed{K_C = \frac{4x^2v^2}{27(1-x)^4}}$$

The formula of K_C has V in the numerator, hence the equilibrium will be affected by V of the reaction container.

Dependence If, $x << 1$ then, $(1-x)^4 = 1$

$$K_C = \frac{4x^2v^2}{27}$$

$$x^2 = \frac{27K_C}{4V^2}$$

$$x^2 \propto \frac{1}{V^2} \qquad \boxed{x \propto \frac{1}{V}}$$

If we increase the volume of the container the degree of dissociation x is decreased.

B. Calculation of K_P :

	N_2	+	$3H_2 \rightleftharpoons$	$2NH_3$
Initial concentration	1		3	0
moles at equilibrium	$(1-x)$		$(3-3x)$	$2x$

Total number of moles at equilibrium

$= (1-x) + (3-3x) + 2x = (4-2x)$

According to the law of mass action

$$K_P = \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3}$$

At equilibrium $$P_{NH_3} = \frac{(2x).P}{(4-2x)}$$

$$P_{N_2} = \frac{(1-x).P}{(4-2x)}$$

$$P_{H_2} = \frac{(3-3x).P}{(4-2x)}$$

Substituting the values in the above equation of K_P.

$$K_P = \frac{\left(\frac{2x}{4-2x}.P\right)^2}{\left(\frac{1-x}{4-2x}.P\right)\left(\frac{3-3x}{4-2x}.P\right)^3}$$

$$K_P = \frac{4x^2(4-2x)^2}{(1-x)(3-3x)^3 p^2}$$

$$\boxed{K_P = \frac{16x^2(2-x)^2}{27(1-x)^4 P^2}}$$

The equation of K_P is not independent of pressure

suppose, $x << 1$ then,

$(1-x)^4 = 1$

and $(2-x)^2 = 4$

$$K_P = \frac{64x^2}{27P^2}$$

$$x^2 \propto P^2$$

$$\boxed{x \propto P}$$

If we increase the pressure the degree of dissociation x is also increased.

Illustration

1. At a certain temperature (T), the equilibrium constant (K_C) is 1 for the reaction
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
If 2 moles of N_2, 4 moles of H_2, 6 moles of NH_3 & 3 moles of inert gas are introduced into a two litre rigid vessel at constant temperature T. It has been found that equilibrium concentration of H_2 & NH_3 are equal then what is the equilibrium concentration of N_2 (in M)?

Sol. $$Q_C = \frac{\left(\frac{6}{2}\right)^2}{\left(\frac{2}{2}\right)\left(\frac{4}{2}\right)^3} \Rightarrow 1.125$$

$\because Q_C > K_C$ so reaction will proceed in backward direction.

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3$;
at equilibrium :	$2+x$		$4+3x$		$6-2x$

$\because$ At equilibrium $[H_2(g)] = [NH_3(g)]$

$$\frac{4+3x}{2} = \frac{6-2x}{2} \Rightarrow x = 0.4$$

$\therefore [N_2(g)]$ at equilibrium $= \dfrac{2+x}{2} \Rightarrow 1.2$ M

Exercise

1. At certain temperature pure PCl_5 (g) is found to be 25% dissociated at total pressure of 50 atm. At what total pressure it is 50% dissociated at same temperature.
(A) 10 atm (B) 20 atm (C) 15 atm (D) 30 atm

Ans. A

(b) Homogeneous equilibrium in solution phase

Formation of ethyl acetate

Equilibrium is represented as

	$C_2H_5(OH)(l)$ +	$CH_3COOH(l)$ $\rightleftharpoons$	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
Initial moles	1	1	0	0
Moles at equilibrium	1–x	1–x	x	x
Active mass (mol l^{-1})	$\frac{1-x}{V}$	$\frac{1-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]} \qquad K_C = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(1-x)}{V} \times \frac{(1-x)}{V}} = \frac{x^2}{(1-x)(1-x)}$$

Illustration

1. Determine the amount of ester present under equilibrium when 3 moles of ethyl alcohol react with 1 mole of acetic acid, when equilibrium constant of the reaction is 4.

Sol. $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

$$\frac{1-x}{V} \qquad \frac{3-x}{V} \qquad \frac{x}{V} \qquad \frac{x}{V}$$

$$K_c = 4 = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{3-x}{V}\right)}$$

$3x^2 - 16x + 12 = 0$

$x = 0.903$

Amount of ester at equilibrium = 0.903 mole

(c) Equilibrium constant for various heterogeneous equilibrium

Heterogenous equilibrium results from a reversible reaction involving reactants and product that are in different phases. The law of mass action is applicable to a homogeneous equilibrium and is also applicable to a heterogeneous system.

(a) Decomposition of solid $CaCO_3$ into solid CaO and gaseous CO_2

Let 'a' moles of $CaCO_3$ are taken in a vessels of volumer 'V' litre at temperature 'T' K.

	$CaCO_3(s) \rightleftharpoons$	$CaO(s)$ +	$CO_2(g)$
Moles initially	a	0	0
Moles at equilibrium	a–x	x	x

$$K_{eq} = \frac{[CaO][CO_2]}{[CaCO_3]}$$

As $CaCO_3$ and CaO(s) are pure solids, so their concentration is unity

$\therefore K_C = [CO_2] = \frac{x}{V}$ ....(1)

Assuming CO_2 gas to behave ideally at the temperature & pressure of the reaction, the molar concentration of CO_2 can be written using ideal gas equation as $\frac{P_{CO_2}}{RT}$

$$\therefore K_C = \frac{P_{CO_2}}{RT}$$

$$K_C(RT) = P_{CO_2}$$

Since K_C, R and T are constant, their product will also be a constant referred as K_P.

$$\therefore K_P = P_{CO_2} = \frac{xRT}{V} \qquad \text{....................(2)}$$

Illustration

1. At 87°C, the following equilibrium is established:

$$H_2(g) + S(s) \rightleftharpoons H_2S(g),\ K_c = 8 \times 10^{-2}$$

If 0.3 mole hydrogen and 2 mole sulphur are heated to 87°C in a 2 L vessel, what will be the partial pressure of H_2S approximately at equilibrium. [Use R = 0.08 atm.L / mol. K]

(A) 0.32 atm (B) 0.43 atm (C) 0.62 atm (D) 4.0 atm

Ans. A

Sol. $K_C = \frac{[H_2S(g)]}{[H_2(g)]} \Rightarrow 8 \times 10^{-2} = \frac{x}{0.3-x}$

$0.024 - 0.08 = x$

$0.024 = 1.08\ x$

$x = 0.022$ $\qquad P_{H_2S} = \frac{0.022 \times 0.08 \times 360}{2} \Rightarrow \approx 0.32$ atm

Exercise

1. Equilibrium constant k_p for the reaction

$$CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2\ (g) \text{ is } 0.821 \text{ atm at } 727°C,$$

if one mole of $CaCO_3(s)$ is placed in a 10 L container, what is the weight of CaO formed at equilibrium.

(A) 56 gm (B) 5.6 gm (C) 0.56 gm (D) 0.056 gm

Ans. B

MULTIPLE EQUILIBRIUM

In multiple equilibrium the product molecules (s) in one equilibrium system are involved in a second equilibrium process.

$$A(g) + B(g) \rightleftharpoons C(g) + D(g) \qquad K_{C_1} = \frac{[C][B]}{[A][B]}$$

$$C(g) + E(g) \rightleftharpoons F(g) + G(g) \qquad K_{C_2} = \frac{[F][G]}{[C][E]}$$

Overall reaction : $A(g) + B(g) + E(g) \rightleftharpoons D(g) + F(g) + G(g) \qquad K_{C_3} = \frac{[D][F][G]}{[A][B][E]}$

In this case, one of the product molecule, C(g) of the first equilibrium reaction combines with E(g) to give F(g) and G(g) in another equilibrium reaction, so in the overall, C(g) will not appear on either side.

The equilibrium constant (K_{C_3}) of the overall reaction can be obtained if we take the product of the expression of (K_{C_1}) and (K_{C_2}).

$$K_{C_1} \times K_{C_2} = \frac{[C][D]}{[A][B]} \times \frac{[F][G]}{[C][E]} = \frac{[D][F][G]}{[A][B][E]}$$

$$\therefore \quad K_{C_1} \times K_{C_2} = K_{C_3}$$

If a equilibrium reaction can be expressed as the sum of two or more equilibrium reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constant of the individual reactions.

SIMULTANEOUS EQUILIBRIUM

In simultaneous equilibrium more than one equilibrium are established in a vessel at the same time and any one of the reactant or product is common in more than one equilibrium, then the equilibrium concentration of the common species in all the equilibrium would be same.

For example, if we take $CaCO_3$(s) and C(s) together in a vessel of capacity 'V' litre and heat it at temperature 'T' K, then $CaCO_3$ decomposes to CaO(s) and CO_2(g). Further, evolved CO_2 combines with the C(s) to give carbon monoxide. Let the moles of $CaCO_3$ and carbon taken initially be 'a' and 'b' respectively.

	$CaCO_3(s)$	$\rightleftharpoons CaO(s) +$	$CO_2(g)$
Moles at equilibrium	a-x	x	(x–y)
	$CO_2(g) +$	$C(s) \rightleftharpoons$	$2CO(g)$
Moles at equilibrium	(x–y)	(b–y)	2y

Thus, as CO_2 is common in both the equilibrium so its concentration is same in both the equilibrium constant expression.

Equilibrium constant for first equilibrium, $K_{C_1} = [CO_2] = \frac{x-y}{V}$

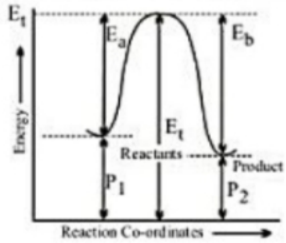
Equilibrium constant for second equilibrium, $K_{C_2} = \frac{[CO]^2}{[CO_2]} = \frac{(2y)^2 V}{V^2(x-y)} = \frac{4y^2}{V(x-y)}$

EQUILIBRIUM CONSTANT AS PER KINETICS

According to the kinetic theory of gases, in any gaseous system, different gas molecules travel with different speeds. The molecular collision with low energy can never cause bond cleavage and hence can not result the product formation. Only those molecular collision result the formation of product in which the molecules collides with a certain minimum energy.

Threshold energy -The minimum amount of energy, which the colliding molecules must posses in order to make the chemical reaction to occur, is known as Threshold energy, E_T.
Activation energy -The minimum amount of energy required to make active participated of almost all molecules in a reaction is called Activation energy, E_a. The activation energy is equal to $E_t - E_R$, where E_R is the average energy level of reactant molecules.
Activation energy for forward reaction = Threshold energy – Potential energy of reactants

The activation energy of reaction depends on the nature of reactant and temperature. It decreases with increase in temperature but the decrease is so small that it is normally considered temperature independent.



E_t = Threshold energy
E_a = Activation energy of forward reaction
E_b = activation energy of backward reaction
P_1 = Potential energy of reactants
P_2 = Potential energy of products

$$A(g) \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B(g) + C(g)$$

$$\frac{-d[A]}{dt} = K_f[A] - K_b[B][C]$$

At equilibrium $\frac{-d[A]}{dt} = 0$

$$\frac{K_f}{K_b} = \frac{[B][C]}{[A]} = K_c$$

According to Arrhenius equation

where $k = A \cdot e^{-E_a/RT}$; A : pre-exponential factor

$k_f = A_f \cdot e^{-E_{a(f)}/RT}$ E_a : activation energy

$k_b = A_b \cdot e^{-E_{a(b)}/RT}$

$$K = \frac{k_f}{k_b} = \frac{A_f e^{-E_{a(f)}/RT}}{A_b e^{-E_{a(b)}/RT}}$$

$$k = A \cdot e^{-\Delta H/RT} \qquad \left[A = \frac{A_f}{A_b}\right]$$

where $\Delta H = E_{a(f)} - E_{a(b)}$

$$\ln K_1 = \ln A - \frac{\Delta H}{RT_1} \qquad \text{(at temp } T_1, K = K_1)$$

$$\ln K_2 = \ln A - \frac{\Delta H}{RT_2} \qquad \text{(at temp } T_2, K = K_2)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

CALCULATION OF DEGREE OF DISSOCIATION BY VAPOUR DENSITY MEASUREMENT

Reactions in which there is a change in the number of moles after dissociation, the extent of dissociation can be determined by vapour density measurement.

Consider the following reaction -

	$PCl_5 \rightleftharpoons$	PCl_3	$+ Cl_2$
Initially	1	0	0
moles at equilibrium	$(1 - \alpha)$	α	α

('α' is the degree of dissociation)

Total number of moles at equilibrium = $(1 - \alpha) + \alpha + \alpha = (1 + \alpha)$

V is the volume occupied by 1 mol of $PCl_5(s)$ which have vapour density is 'D' before dissociation and after dissociation is 'd'. Under the same conditions, the volume occupied by $(1 + \alpha)$ moles at equilibrium would be $(1 + \alpha)$ V litre.

$$\text{Density} \propto \frac{1}{\text{Volume}}$$

$$D \propto \frac{1}{V} \qquad d \propto \frac{1}{(1+\alpha)V}$$

or $$\frac{D}{d} = \frac{\frac{1}{V}}{\frac{1}{(1+\alpha)V}} = (1 + \alpha)$$ or $$\alpha = \frac{D}{d} - 1 = \frac{D-d}{d}$$

Molecular mass = 2 × Vapour density

$$\text{so } \alpha = \frac{M_t - M_o}{M_o}$$

where M_t = calculate molecular mass

M_o = observed molecular mass

Note : When one mole of reactant on dissociation gives 'n' moles of gaseous products.

	A $\rightleftharpoons$	nB
Initial moles	1	0
Moles after dissociation	$1-\alpha$	$n\alpha$

Total moles of equilibrium $1 - \alpha + n\alpha = 1 + \alpha(n-1)$

$$\frac{D}{d} = 1(n-1)\alpha, \qquad \frac{D-d}{d} = (n-1)\alpha \text{ or } \alpha = \frac{1}{(n-1)}\frac{(D-d)}{d}$$

Illustration

1. N_2O_3 on decomposition gives NO and NO_2, they are found to be in equilibrium at 300 K. If the vapour density of such an equilibrium mixture is 23.75, calculate percentage by mass of N_2O_3 in the equilibrium mixture?

(A) 80 % (B) 60 % (C) 40 % (D) 20 %

Ans. C

Sol. $N_2O_3 \rightleftharpoons NO + NO_2$

$1-\alpha \quad \alpha \quad \alpha$

$$\because \alpha = \frac{D-d}{d(n-1)} = \frac{38-23.75}{23.75(2-1)} = 0.6$$

$$\text{Mass \% of } N_2O_3 \text{ in the equilibrium mixture} = \frac{\text{wt. of } N_2O_3}{\text{Total wt.}} \times 100$$

$$= \frac{0.4\times 76}{0.6\times 30 + 0.6\times 46 + 0.4\times 76}\times 100 = 40\,\%$$

Exercise

1. If PCl_5 is 80% dissociated at 250° C then its vapour density at room temperature will be

(A) 56.5 (B) 104.25 (C) 101.2 (D) 52.7

Ans. B

GIBB'S FREE ENERGY AND EQUILIBRIUM CONSTANT

Gibb's free energy (G) of a system is defined as the thermodynamic quantity of the system, the decrease in whose value during a process is equal to useful work done by the system.
Standard free energy change is defined as the free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted to products in their standard state. It is denoted as ΔG^o.

Note : *Standard free energy change (ΔG^o) is not the free energy change at equilibrium.*
ΔG^o is related to K (equilibrium constant) by the relation

$\Delta G^o = -RT\ln K.$
$\Delta G^o = -2.303\ RT \log K.$
K may either be K_C or K_P.
The units of ΔG^o depends only on RT. T is always in Kelvin, and if R is in Joules, ΔG^o will be in joules and if R is calories then ΔG^o will be in calories.

Illustration

1. NO and Br_2 at initial partial pressures of 98.4 and 41.3 torr, respectively, were allowed to react at 300K. At equilibrium the total pressure was 110.5 torr. Calculate the value of the equilibrium constant and the standard free energy change at 300 K for the reaction $2NO(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g)$.

Sol.

	$2NO(g)$	+	$Br_2(g) \rightleftharpoons$	$2NOBr(g)$
Initial pressure	98.4		41.3	0
At equilibrium	98.4-x		$41.3-\frac{x}{2}$	x

Total pressure at equilibrium is 110.5 torr

$$\therefore\ 98.4-x+41.3-\frac{x}{2}+x=110.5$$

$x = 58.4$ torr

Now, 1 atm = 760 torr; $\therefore\ x = 7.68 \times 10^{-2}$ atm

$P_{NOBr} = 7.68 \times 10^{-2}$ atm; $\qquad p_{NO} = 98.4 - x = 40$ torr $= 5.26 \times 10^{-2}$ atm

$$P_{Br_2} = 41.3 - \frac{x}{2} = 12.1 \text{ torr} = 1.59 \times 10^{-2} \text{ atm}$$

$$K_p = \frac{[p_{(NOBr)}]^2}{[p(NO)]^2\,[p_{(Br_2)}]} = \frac{(7.68\times10^{-2})^2}{(5.26\times10^{-2})^2\,(1.59\times10^{-2})} = 134\ \text{atm}^{-1}$$

$\Delta G^o = -2.303\ RT \log K = -2.303\ (1.99) \times 10^{-3}\ (300)\ (\log 134)$
$= -2.92$ k cal $= 12.2$ k J.

[If R is used as 1.99 cal/mol K, then ΔG^o will be in cal. If R is used as 8.314 J/mol K, then ΔG^o will be in joules. But K_p must be in $(atm)^{\Delta n}$]

Exercise

1. For the reaction takes place at certain temperature $NH_4HS\,(s) \rightleftharpoons NH_3(g) + H_2S\,(g)$, if equilibrium pressure is X bar, then $\Delta_r G^\circ$ would be
(A) $-2\,RT \ln X$ (B) $-RT \ln (X - \ln 2)$ (C) $-2\,RT (\ln X - \ln 2)$ (D) None of these

Ans. C

LE CHATELIER PRINCIPLE

Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in concentration, pressure, volume and temperature may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. There is a general rule (named Le Chaterlier principle) that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume or temperature occurs. Le Chatelier's principle state that if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset.

The word "stress" here implies a change in concentration, pressure, volume, addition of an inert gas or temperature that removes a system from the equilibrium state.

Le Chatelier principle can be explained using the following equilibrium reaction

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

Let the moles of PCl_5, PCl_3 and Cl_2 at equilibrium be a, b and c respectively, Also let the volume of the container in which equilibrium is established be 'V' litre and the total pressure of the system at equilibrium be P_T atm.

$$K_P = \frac{\left(P_{PCl_3}\right)\left(P_{Cl_2}\right)}{\left(P_{PCl_5}\right)} = \frac{\left(\frac{b}{a+b+c} \times P_T\right)\left(\frac{c}{a+b+c} \times P_T\right)}{\left(\frac{a}{a+b+c} \times P_T\right)}$$

$$\therefore \quad K_P = \frac{bc \times P_T}{a(a+b+c)} \qquad \text{.............(1)}$$

The total pressure of the system (P_T) can be given as (assuming all gases at equilibrium behave ideally under the given conditions)

$$P_T = \frac{(a+b+c)\,RT}{V}$$

$$\therefore \quad \frac{P_T}{(a+b+c)} = \frac{RT}{V}$$

Inserting the value of $\frac{P_T}{(a+b+c)}$ in equation (i), we get

$$K_P = \frac{bc \times RT}{a \times V} \qquad \text{..............(2)}$$

Let us examine the effect of change of certain parameters like moles of reactant, moles of product, volume, temperature, addition of inert gas and addition of catalyst on the given equilibrium.

(a) Change in number of moles of reactant

If we add 'd' moles of PCl_5 to the equilibrium mixture, the equilibrium would be disturbed and the expression $\frac{bc \times RT}{(a+d)V}$ becomes Q_P. As $Q_P < K_P$, so the net reaction moves in the forward direction till Q_P becomes equal to K_P.

Thus for any equilibrium, when more reactant is added to (or some product is removed from) an equilibrium mixture, the net reaction moves in the forward direction (as Q < K) to establish a new equilibrium state.

(b) Change in number of moles of product

Let 'd' moles of PCl_3 (or Cl_2) are added to the equilibrium. The equilibrium would be under stress and thus the expression $\frac{(b+d)c \times RT}{a \times V}$ would become Q_P. Since $Q_P > K_P$, so the net reaction moves in the reverse direction till Q_P becomes same as K_P.

Thus for any equilibrium, when product is added to (or some reactant is removed from) an equilibrium mixture, *the net reaction moves in the reverse (backward) direction (as Q > K) to establish a new equilibrium state.*

(c) Change in volume

Let the volume of the container be increased from V to V' litre. The equilibrium would be disturbed and the expression $\frac{bc \times RT}{a \times V'}$ becomes Q_P. The value of Q_P is less than K_P, so the net reaction moves in the forward direction to establish new equilibrium. But when the volume of the container is decreased, the reaction moves in the backward direction to again attain the equilibrium state.

Thus for any equilibrium, on increasing the volume of the container, the net reaction shifts in the direction of more moles of the gases while on decreasing the volume of the vessel, the reaction goes in the direction of fewer moles of the gases.

(d) Addition of an inert gas

The effect of addition of an inert gas can be studied under two conditions (i), at constant volume (ii) at constant pressure.

(i) At constant volume

Let 'd' moles of an inert gas are added to the equilibrium mixture at constant volume. The total number of moles of the system increases so is the pressure of the system but the partial pressure of all the species would still be same. Let the total pressure becomes P_T' then $\frac{P_T^{'}}{(a+b+c+d)} = \frac{RT}{V}$. As R, T and V are constant, so the expression $\frac{bc \times RT}{a \times V}$ would still be equal to K_P. As, $Q_P = K_P$, *then net reaction does not move at all.*

Thus for any equilibrium when an inert gas is added at constant volume, the equilibrium remains unaffected whether the equilibrium reactions have Δn equal to zero or non-zero.

(ii) At constant pressure

Now, let 'd' moles of an inert gas are added to the equilibrium mixture at constant pressure to keep the pressure constant, volume of the vessel should increases. Let the volume of the vessel increases from V to V' litre. So, the expression $\frac{bc \times RT}{a \times V'}$ becomes Q_P. As the value of $Q_P < K_P$, so the net reaction moves in the forward direction to establish new equilibrium state. Thus, *addition of an inert gas at constant pressure has the same effect as produced by the increased volume of the container.*

Thus, for equilibrium having $\Delta n = 0$, when an inert gas is added at constant pressure, the equilibrium remains unaffected (since V does not appear in the expression of K_p) while for equilibrium having $\Delta n \neq 0$, the addition of an inert gas at constant pressure causes reaction to move in the direction of more moles of the gases.

(e) Addition of a catalyst

A catalyst enhances the rate of a reaction by lowering the reactions' activation energy. Actually a catalyst lowers the activation energy of the forward reaction and the reverse reaction to the same extent, *so the presence of a catalyst does not alter the equilibrium constant nor does it shift the position of an equilibrium system.* Adding a catalyst to a reaction mixture that is not at equilibrium will simply cause the mixture to reach equilibrium faster.

(f) Change in temperature

If K_p increases, the net reaction moves forward while if K_p decreases, the net reaction moves backward.

The variation of K_p with temperature is given by Van't Hoff equation as

$$\log \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \text{ where } T_2 > T_1$$

All reactions are either endothermic or exothermic in nature. For an endothermic reactions, ΔH is positive and with an increase in temperature of the system to T_2 K from T_1 K, the RHS of the expression becomes positive. Thus, equilibrium constant at higher temperature (K_{T_2}) would be more than the equilibrium constant at lower temperature (K_{T_1})

But for an exothermic reaction, ΔH is negative and on increasing the temperature of the system from T_1 K to T_2 K, the RHS of the expression becomes negative. So the equilibrium constant at higher temperature would be less than equilibrium constant at lower temperature.

The give equilibrium, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is endothermic in nature. So, with the increase of temperature from T_1 K to T_2 K, K_p and Q_P both increases. Therefore, equilibrium shifts in the forward direction.

Thus, for an endothermic reaction (ΔH = positive), with the increase of temperature, net reaction moves in the forward direction and the decreases in temperature favours backward reaction while for an exothermic reaction (ΔH = negative), net reaction moves in the backward direction with the increase of temperature and in forward direction with the decrease temperature.

In general, *with the increases of temperature, net reaction moves in that direction where the heat is absorbed and the effect of increasing temperature is nullified.*

(g) Change in more than one parameter

For the given equilibrium, if the number of moles of PCl_3 is increased four folds and the volume of the vessel is doubled, then the equilibrium would be disturbed. The expression $\frac{4b \times c \times RT}{a \times 2V}$ would becomes Q_p. Since $Q_p > K_p$, so the net reaction moves in reverse direction till Q_p becomes equal to K_p.

Thus, *when two or more parameters are simultaneously changed for any equilibrium, find the changed value of Q and K and compare them.* If Q = K, there will be no effect on the reaction, if Q > K, the net reaction moves in the backward direction. While if Q < K, net reaction moves in the forward direction.

Application of Le chatelier principle on physical equilibrium

A. Melting of Ice :

$$H_2O(s) \rightleftharpoons H_2O(\ell)$$

Ice	water
more volume	less volume

If we increase the pressure, the equilibrium will in the direction of less volume. Hence, the rise of pressure, more ice will melt into water i.e. melting point of ice is decreased by rise of pressure.

B. Vaporization of liquid -

$$H_2O(\ell) \rightleftharpoons H_2O(g)$$

water	vapour
less volume	more volume

Vaporization of a liquid is endothermic process in the nature i.e. the evaporation of a liquid into its vapour is completed by absorption of heat, so the rise of temperature will favour vaporization. On the other hand in this process, on increase of pressure the equilibrium will shift in the direction of less volume means water cannot be converted into vapour and boiling point increases.

C. Melting of Sulphur :

$$\text{Sulphur}(s) \rightleftharpoons \text{Sulphur}(\ell)$$

less volume	more volume

On increase in pressure, the equilibrium will shift towards less volume means solid is not converted into liquid and thus, melting point of sulphur increases.

Illustration

1. Following two equilibrium is simultaneously established in a container

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

If some Ni(s) is introduced in the container forming Ni $(CO)_4$ (g) then at new equilibrium

(A) PCl_3 concentration will increase
(B) PCl_3 concentration will decrease
(C) Cl_2 concentration will remain same
(D) CO concentration will remain same

Ans. B

Exercise

1. For the gas phase exothermic reaction, $A_2 + B_2 \rightleftharpoons C_2$, carried out in a closed vessel, the equilibrium moles of A_2 can be increased by

(A) increasing the temperature
(B) decreasing the pressure
(C) adding inert gas at constant pressure
(D) removing some C_2

Ans. A, B, C

K_p & K_C for different reactions

S No	Reaction	Δn	Relation between K_p and K_C		Values of K_C	Values of K_P	Unit of K_C	Unit of K_P	ΔH	Condition for obtaining more product
1.	$H_2 + I_2 \rightleftharpoons 2HI$	0	$K_P=K_C(RT)^0$	$K_P=K_C$	$\frac{4x^2}{(a-x)(b-x)}$	$\frac{4x^2}{(a-x)(b-x)}$	None	None	-ve (exothermic)	Low temperature No pressure High concentration of reactant
2	$2HI \rightleftharpoons H_2 + I_2$	0	$K_P=K_C(RT)^0$	$K_P=K_C$	$\frac{x^2}{4(1-x)^2}$	$\frac{x^2}{4(1-x)^2}$	None	None	+ve (endothermic)	High temperature No pressure High concentration of reactant
3.	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	+1	$K_P=K_C(RT)^1$	$K_P>K_C$	$\frac{x^2}{(1-x)v}$	$\frac{x^2p}{1-x^2}$	$mol\ L^{-1}$	atm	+ve (endothermic)	High temperature Low pressure High concentration of reactant
4.	$N_2O_4 \rightleftharpoons 2NO_2$	+1	$K_P=K_C(RT)^1$	$K.K_C$	$\frac{4x^2}{(1-x)v}$	$\frac{4x^2p}{1-x^2}$	$mol\ L^{-1}$	atm	+ve (endothermic)	High temperature Low pressure High concentration of reactant
5.	$2NH_3 \rightleftharpoons N_2 + 3H_2$	+2	$K_P=K_C(RT)^2$	$K_P>K_C$	$\frac{27x^4}{4(1-x)^2v^2}$	$\frac{27x^4p^2}{16(1-x)^2(1-x)^2}$	$mol^2\ L^{-2}$	atm^2	+ve (endothermic)	High temperature Low pressure High concentration of reactant
6.	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	-2	$K_P=K_C(RT)^{-2}$	$K_P<K_C$	$\frac{4x^4v^2}{27(1-x)^4}$	$\frac{16x^2(2-x)^2}{27(1-x)^4p^2}$	$L^2\ mol^{-2}$	atm^{-2}	-ve (exothermic)	Low temperature Low pressure High concentration of reactant
7.	$PCl_3 + Cl_2 \rightleftharpoons PCl_5$	-1	$K_P=K_C(RT)^{-1}$	$K_P<K_C$	$\frac{xv}{(1-x)^2}$	$\frac{x(2-x)}{(1-x)^2p}$	$L\ mol^{-1}$	atm^{-1}	-ve (exothermic)	Low temperature Low pressure High concentration of reactant
8.	$2SO_3 + O_2 \rightleftharpoons 2SO_3$	-1	$K_P=K_C(RT)^{-1}$	$K_P<K_C$	$\frac{x^2v}{(1-x)^3}$	$\frac{x^2(3-x)}{(1-x)^3p}$	$L\ mol^{-1}$	atm^{-1}	-ve (exothermic)	Low temperature Low pressure High concentration of reactant

SOLVED EXAMPLES

Q.1 For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$,
The moles of each component PCl_5, PCl_3 and Cl_2 at equilibrium were found to be 2. If the total pressure is 3 atm. The K_P will be –

(A) 1 atm. (B) 2 atm. (C) 3 atm. (D) 1.5 atm.

Ans. A

Sol. Total Moles = 2 + 2+ 2 = 6

$$P_{PCl_3} = \frac{2}{6} \times 3,\ P_{PCl_5} = \frac{2}{6}\times 3,\ P_{Cl_2} = \frac{2}{6}\times 3$$

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{1\times 1}{1} = 1 \text{ atmosphere.}$$

Q.2 For the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

The value of equilibrium constant is 9.0. The degree of dissociation of HI will be –

(A) 2 (B) 2/5 (C) 5/2 (D) 1/2

Ans. B

Sol. Equilibrium constant of the reaction

$$H_2 + I_2 \rightleftharpoons 2HI \text{ is } 9.0$$

So the equilibrium constant for the dissociation of HI i.e. $2HI \rightleftharpoons H_2 + I_2$ will be 1/9.

$$\begin{array}{cccc} 2HI & \rightleftharpoons H_2 & + & I_2 \\ 1 & 0 & & 0 \\ 1-x & \frac{x}{2} & & \frac{x}{2} \end{array}$$

$$K_C = \frac{x}{2}\times\frac{x}{2}\ \frac{1}{(1-x)}\times\frac{1}{(1-x)}$$

$$\frac{1}{9} = \frac{x^2}{2\times 2(1-x)^2};$$

$$\frac{1}{3} = \frac{x}{2(1-x)}$$

or $2 - 2x = 3x$

$5x = 2$

$x = 2/5$

Q.3 For the reaction $N_2 \rightleftharpoons 2NH_3$, $N_2 : H_2$ were taken in the ratio of 1 : 3 . Up to the point of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. The partial pressure of ammonia would be –

(A) P/3 (B) P/6 (C) P/4 (D) P/8

Ans. A

Sol.

	N_2 +	$3H_2$	$\rightleftharpoons 2NH_3$
Initially	1	3	0
At equilibrium	1-0.5	3-1.5	2×0.5

Total moles $= (1 - 0.5) + (3 - 1.5) + 1 = 3$

$; P_{NH_3} = \frac{1}{3}P$

Q.4 In a reaction vessel of 2 litre capacity 3 moles of N_2 reacts with 2 moles of O_2 to produce 1 mole of NO. What is the molar concentration of N_2 at equilibrium ?

(A) 1.25 (B) 1.50 (C) 0.75 (D) 2.0

Ans. A

Sol.

N_2 +	O_2	$\rightleftharpoons 2NO$
3	2	0
3-x	2-x	2x

$\because \quad 2x = 1 ; x = 0.5$

$[N_2] = \frac{3-0.5}{2} = 1.25$

Q.5 HI was heated in a sealed tube at 440°C till the equilibrium was established. The dissociation of HI was found to be 22%. The equilibrium constant for dissociation is –

(A) 0.282 (B) 0.0786 (C) 0.0199 (D) 1.99

Ans. C

Sol. The equilibrium of the dissociation of

$2HI \rightleftharpoons$	H_2 +	I_2
1	0	0
$1-\frac{22}{100}$	$\frac{22}{100 \times 2}$	$\frac{22}{100 \times 2}$
0.78	0.11	0.11

$K_C = \frac{0.11 \times 0.11}{0.78 \times 0.78} \approx 0.0199$

Q.6 At 87°C, the following equilibrium is established

$H_2(g) + S(s) \rightleftharpoons H_2S\ (g) \qquad K_p = 7 \times 10^{-2}$

If 0.50 mole of hydrogen and 1.0 mole of sulphur are heated to 87°C in 1.0 L vessel, what will be the partial pressure of H_2S at equilibrium?

(A) 0.966 atm (B) 1.38 atm (C) 0.0327 atm (D) 9.66 atm

Ans. A

Sol.

	$H_2(g)$	$+ S(s) \rightleftharpoons$	$H_2S(g)$
Concentration at equilibrium	$0.5-x$	–	x

$$K_c = \frac{[H_2S]}{[H_2]} \Rightarrow 7 \times 10^{-2} = \frac{x}{0.5-x}$$

$x = 0.0327$

$$P_{H_2S} = \left(\frac{n_{H_2S}}{V}\right)RT \Rightarrow 0.0327 \times 0.0821 \times 360 \Rightarrow 0.966 \text{ atm. Ans.}$$

Q.7 At some temperature N_2O_4 is dissociated to 40% & 50% into NO_2 at total pressure P_1 & P_2 atm respectively, then the ratio of P_1 & P_2 is

(A) $\frac{4}{5}$ (B) $\frac{7}{4}$ (C) $\frac{4}{7}$ (D) None of these

Ans. B

Sol.

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
at P_1 (t=Eq)	$1-0.4$	$2(0.4)$
	$= 0.6$	$= 0.8$
at P_2 (t=Eq)	$1-0.5$	$2(0.5)$
	$= 0.5$	$=1$

$\because$ temperature is same, $\therefore K_p$ is same

$$\frac{\left(\frac{0.8}{1.4}P_1\right)^2}{\frac{0.6}{1.4}P_1} = \frac{\left(\frac{1}{1.5}P_2\right)^2}{\left(\frac{0.5}{1.5}P_2\right)} \Rightarrow \frac{P_1}{P_2} = \frac{1.4 \times 0.6}{(0.8)^2 \times 1.5 \times 0.5} = \frac{7}{4}$$

Q.8 $\Delta G°$ for the dissociation of the dimer ($A_2 \rightleftharpoons 2A$) in benzene solution at 27°C is 6.909 kcal/mol. If 8 moles of A is dissolved in 10 dm^3 of benzene at 27°C. What is the ratio of equilibrium concentration of monomer to dimer $([A]/[A_2])$? **Given** : R = 2 Cal/ mol. K

(A) 1 : 200 (B) 1 : 100 (C) 200 : 1 (D) 800 : 1

Ans. A

Sol. $\Delta G° = -RT \ln K_{eq}$

$6.909 \times 1000 = -2 \times 300 \times 2.303 \log K_C$

$-5 = \log K_C$ or $K_C = 10^{-5}$

$K_C' = 1/K_C = 10^5$

$2A \rightleftharpoons A_2$

$0.8-2x \qquad x$

$\because K_C'$ is very high $\qquad$ so $2x \simeq 0.8 \quad \Rightarrow x \approx 0.4$

$\therefore 0.8-2x \simeq y$

$10^5 = \dfrac{0.4}{(y)^2} \quad ; \qquad y = (0.4 \times 10^{-5})^{1/2} \quad \Rightarrow 2 \times 10^{-3}$

$\dfrac{[A]}{[A_2]} = \dfrac{y}{x} = \dfrac{2\times10^{-3}}{0.4} = \dfrac{5}{1000} = \dfrac{1}{200}$ **Ans.**

Q.9 For the equilibrium at 27°C.
$LiCl.3NH_3(s) \rightleftharpoons LiCl.NH_3(s) + 2NH_3(g)$; $K_p = 9$ atm^2
A 24.63 litre flask contain 1 mol $LiCl.NH_3$. How many moles of NH_3 should be added to flask at this temperature to drive the backward reaction for compleletion.

Sol. $K_p = 9$ atm^2

$p^2_{NH_3} = 9$ atm^2

$p_{NH_3} = 3$ atm

$3 \times 24.63 = n_{NH_3} \times R \times 300$

$n_{NH_3} = 3$ (at equilibrium)

$LiCl.3NH_3(s) \rightleftharpoons LiCl.NH_3(s) + 2NH_3(g)$

$\qquad\qquad 1 \qquad\qquad n$

$\qquad\qquad 0 \qquad\qquad n-2$

$n-2=3$

$n = 5$ moles

Q.10 In a system, the equilibrium reaction :

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

was studied starting with NH_3 and Ne(inert gas). It is found that at 10 atm and 700 K, the equilibrium gaseous mixture contains 10 mole % each of $NH_3(g)$ and Ne(g). Calculate K_p (in atm^2)

Sol. $X_{N_2} + X_{H_2} = 1 - 0.1 - 01 = 0.8$

$X_{N_2} = \dfrac{1}{4} \times 0.8 \qquad \Rightarrow 0.2$

$X_{H_2} = \dfrac{3}{4} \times 0.8 \qquad \Rightarrow 0.6$

$P_{NH_3} = 0.1 \times 10 = 1$ atm

$P_{N_2} = 0.2 \times 10 = 2$ atm

$P_{H_2} = 0.6 \times 10 \qquad \Rightarrow 6$ atm

$K_p = 2 \times 216$

$K_p = 432$ (atm)^2 **Ans.**

Q.11 At a certain temperature the equilibrium constant K_c is 0.25 for the reaction

$$A_2(g) + B_2(g) \rightleftharpoons C_2(g) + D_2(g)$$

If we take 1 mole of each of the four gases in a 10 litre container, what would be equilibrium concentration of $A_2(g)$.

Sol. $Q = \frac{1\times1}{1\times1} \Rightarrow 1$

$\because Q > K_c$ so reaction will proceed in backward direction

$$\begin{array}{lcccc} & A_2(g) + & B_2(g) \rightleftharpoons & C_2(g) + & D_2(g) \\ \text{concentration at equilibrium} & \frac{1.0+x}{10} & \frac{1.0+x}{10} & \frac{1.0-x}{10} & \frac{1.0-x}{10} \end{array}$$

$$0.25 = \frac{\left(\frac{1-x}{10}\right)^2}{\left(\frac{1+x}{10}\right)^2} \qquad \Rightarrow 0.5 = \frac{1-x}{1+x} \Rightarrow 0.5 + 0.5\,x = 1 - x$$

$1.5\,x = 0.5 \quad \Rightarrow \quad x = 0.333 \qquad [A_2(g)] = \frac{1+x}{10} \Rightarrow \frac{1.333}{10} \Rightarrow$ **0.13 Ans.**

Q.12 At a certain temperature, equilibrium constant $K_C = 4 \times 10^{-2}$ for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

If we take 1.5 mole of NO and 2 mole each of N_2 & O_2 in 5 litre vessel, what would be the equilibrium concentration of NO (in mole/litre)?

Sol. $Q_C = \frac{(1.5/5)^2}{(2/5)^2} \Rightarrow 0.5625 \quad ; \quad \therefore Q > K_C$

reaction will proceed in backward direction

$$\begin{array}{llll} & N_2(g) + & O_2(g) \rightleftharpoons & 2NO(g) \\ \text{Initial moles} & 2 & 2 & 1.5 \\ \text{moles at eq}^m & 2+x & 2+x & 1.5-2x \\ \text{con}^n \text{ at eq}^m & \frac{2+x}{5} & \frac{2+x}{5} & \frac{1.5-2x}{5} \end{array}$$

$$K_C = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]} = \frac{\left(\frac{1.5-2x}{5}\right)^2}{\left(\frac{2+x}{5}\right)^2}$$

$$\frac{1.5-2x}{2+x} \Rightarrow \sqrt{0.04} \Rightarrow 0.2$$

$1.5 - 2x = 0.4 + 0.2\,x \qquad x = 0.5$

$\therefore$ Equilibrium concentration of NO $= \frac{1.5-2x}{5} \Rightarrow 0.1$ M **Ans.**