

1. 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.

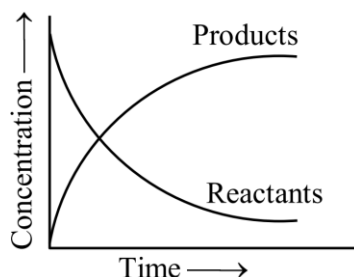
1.1 Types of chemical reaction:

(a)	On the basis of physical state Homogeneous reactions All reactants and products are in same phase $\text{N}_2(\text{g}) + 3\text{H}(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	Heterogeneous reaction Reactants and products are in two or more phase $\text{Zn}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{ZnO}(\text{s}) + \text{CO}(\text{g})$
(b)	On the basis of direction Reversible reaction (i) Chemical reaction in which products can be converted back into reactants $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$	Irreversible reaction Chemical reaction in which products cannot be convert back into reactants $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
	(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 $\text{PCl}_5 \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	Generally thermal decompositions are held in open vessel $2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$
(c)	On the basis of speed Fast reactions (i) Generally these reactions are ionic in nature $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ <div style="display: flex; justify-content: space-around; width: 100%;"> Acid Base Salt Water </div>	Slow reactions Generally these reactions are molecular in nature $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$
(d)	On the basis of heat Exothermic reaction (i) Heat is evolved in these type of chemical reactions $\text{R} \rightarrow \text{P} + x\text{kcal}$	Endothermic reaction Heat is absorbed in these type of chemical reactions $\text{R} \rightarrow \text{P} - x\text{kcal}$

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.

1.2 EQUILIBRIUM:

- **Definition:** "Equilibrium is the state at which the concentration of reactants and products don't change with time. i.e. concentrations of reactants and products become constant."
- **Characteristics:** Following are the important characteristics of equilibrium state,



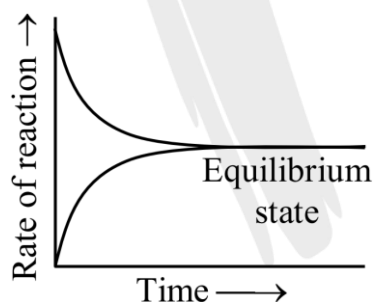
(i) Equilibrium state can be recognised by the constancy of certain measurable properties such as pressure, density, colour, concentration etc. by changing these conditions of the system, we can control the extent to which a reaction proceeds.

(ii) Equilibrium state can only be achieved in a closed 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 a water tank having an inlet and outlet. Water in the tank can remain at the same level if the rate of flow of water from the inlet (compared to rate of forward reaction) is made equal to the rate of flow of water from the 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



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. $T = \text{constant}$.

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

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

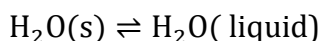
(iv) Chemical equilibrium: There is no change in composition of any part of the system with time.

2. Physical equilibrium.

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

Solid	\rightleftharpoons	liquid
Liquid	\rightleftharpoons	Vapour
Solid	\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

2.1 Solid-liquid equilibrium

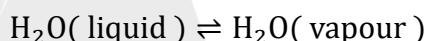


Rate of transfer of molecules from ice to water = Rate of transfer of molecules from water to ice

Rate of melting of ice = Rate of freezing of water

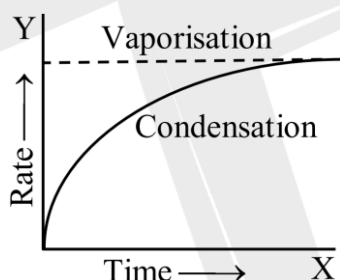
2.2 Liquid-vapour equilibrium: When vapour of a liquid exists in equilibrium with the liquid, then

Rate of vaporisation = Rate of condensation.



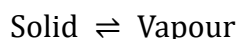
Conditions necessary for a liquid-vapour equilibrium are:

- (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.

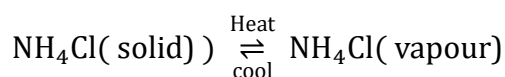


- (iii) The visible properties of the system should not change with time.

2.3 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 deposition.



The substances which undergo sublimation are camphor, iodine, ammonium chloride etc. For example, Ammonium chloride when heated sublimes.

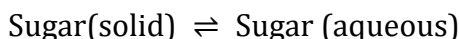


2.4 Equilibrium between a solid and its solution:

When a saturated solution is in contact with the solid solute, there exists a dynamic equilibrium between the solid and the solution phase.



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

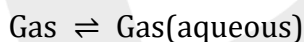


At the equilibrium state, the number of sugar molecules going into the solution from the solid sugar is equal to the number of molecules precipitating out from the solution, i.e., at equilibrium,

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

2.5 Equilibrium between a gas and its solution in a liquid:

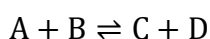
An equilibrium does exist between gas dissolved in liquid and un-dissolved gas present over the solution.

**3. CHEMICAL EQUILIBRIUM :****3.1 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.

3.2 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.



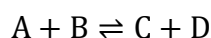
$$\text{Rate of chemical reaction } r \propto [A][B]$$

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

Mathematical Expression

(i) For unitary stoichiometric coefficients

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



According to law of mass action -

Rate of forward reaction

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

where K_f is the rate constant of the forward reaction.

Rate of backward reaction

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

where K_b is the rate constant of the backward reaction.

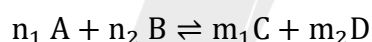
At equilibrium :

Rate of reaction = Rate of forward reaction - Rate of backward reaction = 0

$$\begin{aligned} K_f[A][B] - K_b[C][D] &= 0 \\ \text{or } \frac{K_f}{K_b} &= \frac{[C][D]}{[A][B]} \\ \text{or } K_{eq.} &= \frac{[C][D]}{[A][B]} \end{aligned}$$

Here, k is equilibrium constant of given reversible reaction.

(ii) For non-unitary stoichiometric coefficient



$$r_f = r_b$$

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

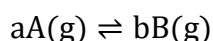
Note: $[A]$, $[B]$, $[C]$, $[D]$ are molar concentration of reactants and products, for dilute solution.

3.3 TYPES OF EQUILIBRIUM CONSTANTS:

There are various methods for measuring equilibrium constant :

(I) K_C : If equilibrium constant is written in term of concentration.

Consider the following equilibrium reaction



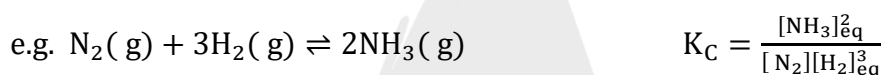
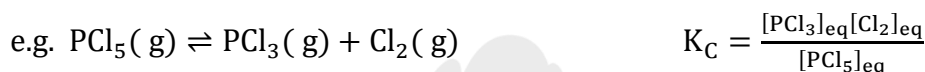
for this reactions, equilibrium constant (K_C) is represented as

$$K_C = \frac{[B]^b}{[A]^a}$$

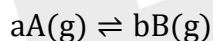
for the given equilibrium, irrespective of the reacting species (i.e., either A or B) and their amount we start with, the ratio, $\frac{[B]^b}{[A]^a}$ is always constant at a given temperature. The given expression involves all variable terms (variable term means the concentration of the involved species changes from the start of the reaction to the stage when equilibrium is reached), so the ratio $\frac{[B]^b}{[A]^a}$ can also be referred to as K_C .

Unit of K_C : (Moles l^{-1}) $^{\Delta n}$

So, K_C is a constant and is called the equilibrium constant in terms of concentration. where all the concentrations are at equilibrium and are expressed in moles/litre.



(II) K_P : If equilibrium constant is written in terms of partial pressure.



$$K_P = \frac{P_B^b}{P_A^a}$$

P_B = Partial pressure $B(g)$ at equilibrium

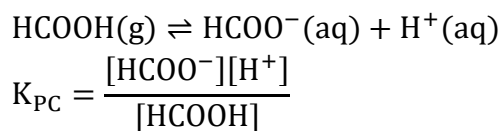
P_A = Partial pressure $A(g)$ at equilibrium

Thus, K_P can only be written for that equilibrium which contains at least one of the reactant or product should be in gaseous phase and

Unit of K_P : (atm) $^{\Delta n_g}$

(III) K_{PC} : If equilibrium constant is written in terms of concentrations of aqueous species & in terms of partial pressure of gaseous species.

Consider the following equilibrium



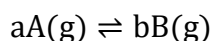
(III) K_P^0 : $aA(g) \rightleftharpoons bB(g)$

$$K_P^0 = \frac{\{P_B/1\text{bar}\}^b}{\{P_A/1\text{bar}\}^a} \text{ Unitless}$$

(IV) K_C^0 : $aA(g) \rightleftharpoons bB(g)$

$$K_C^0 = \frac{\{[B]/1M\}^b}{\{[A]/1M\}^a} \text{ Unitless}$$

3.3.1 Relation between K_P & K_C :



$$K_P = \frac{p_B^b}{p_A^a}$$

$P = CRT$ (C = Concentration of gaseous species)

$$K_P = \frac{[B]RT^b}{[A]RT^a} = \frac{[B]^b}{[A]^a} (RT)^{b-a}$$

$$K_P = K_C (RT)^{\Delta n_g} \quad R = 0.0821 \text{ Latm mol}^{-1} \text{ K}^{-1}$$

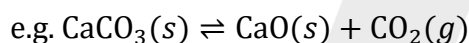
$$\text{If, } \Delta n_g = 0 \quad K_P = K_C \quad [\text{If, } RT > 1]$$

$$\Delta n_g > 0 \quad K_P = K_C$$

$$\Delta n_g < 0 \quad K_P < K_C$$

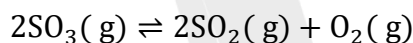
For the given reaction K_{eq} depends only on temp and independent on amount of reactant and product (initial)

Δn_g = sum of the number of moles of gaseous products - sum of the number of moles of gaseous reactants. Δn_g can be positive, negative, zero or even fraction.



$\Delta n_g = 1$ (because there is only one gas component in the products and no gas component in the reaction), so: $K_P = K_C \cdot (RT)$

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



is $1.8 \times 10^{-3} \text{ kPa}$. What is the numerical value of K_C for this reaction at the same temperature

(A) $3.09 \times 10^{-7} \text{ mole litre}^{-1}$

(B) $9.03 \times 10^{-7} \text{ mole litre}^{-1}$

(C) $5.05 \times 10^{-9} \text{ mole litre}^{-1}$

(D) $5.05 \times 10^{-5} \text{ mole litre}^{-1}$

Ans. (A)

Sol. We know the relationship

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

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

$$K_P = \frac{18 \times 10^{-3}}{101.3} \text{ atm}$$

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

$$R = 0.0821 \text{ litre atm K}$$

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

$$T = 700 \text{ K m}^{-1}$$

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

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

3.4 Factors which influence the equilibrium constant:

3.4.1 Mode or representation or reaction -

If we take reaction $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$; then, we write the value of equilibrium constant K_{C_1} for the above reaction as following.

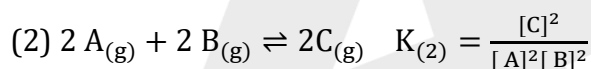
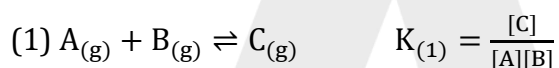
$$K_{C_1} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \dots (i)$$

Now, if we take reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$; then, we write the value of equilibrium constant K_{C_2} for above reaction as following

$$K_{C_2} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1}{K_{C_1}} \dots (ii)$$

3.4.2 Stoichiometry of the reaction:

The value of K for a given chemical reaction at a particular temperature depends on how the chemical equation is balanced. For example, the reaction in which $\text{A}_{(\text{g})}$ reacts with $\text{B}_{(\text{g})}$ to produce $\text{C}_{(\text{g})}$ can be balanced in lots of ways using different stoichiometric coefficients (mole ratios):



- There is a relationship between these different values for the equilibrium constant for the same reaction under the same conditions.

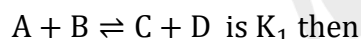
For the example given above:

$$K_1 = \sqrt{K_2}$$

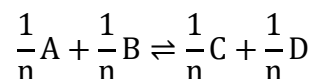
$$K_2 = K_1^2$$

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.



for the reaction



the value of the equilibrium constant K_2 is equal to $n\sqrt{k_1}$ or $(K_1)^{1/n}$.

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

3.4.2 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 will 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 –

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

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

Where, K_2 = equilibrium constant at temperature T_2

K_1 = equilibrium constant at temperature T_1

ΔH = Enthalpy of reaction (Assuming that independent from temperature)

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

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

$$\text{means } K_2 > K_1$$

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

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

$$\log K_2 - \log K_1 = (-) \text{ ve,}$$

$$\text{means } K_2 < K_1$$

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

Factors which do not influence equilibrium constant :

(a) Concentration of reactants and products.

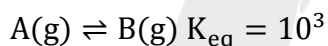
(b) Pressure and volume.

(c) Presence of catalyst.

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

3.5 APPLICATION OF EQUILIBRIUM CONSTANT:

3.5.1 To predict the extent of progress of reaction:



Case-I: If K is large ($K > 10^3$) then product concentration is very very larger than the reactant ($[Product] \gg \gg [Reactant]$) Hence concentration of reactant can be neglected with respect to the product. In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.

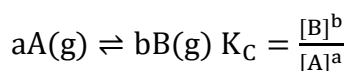
Case-II : If K is very small ($K < 10^{-3}$)

$$[Product] \ll [Reactant]$$

Hence concentration of Product can be neglected as compared to the reactant.

In this case, the reaction is reactant favourable.

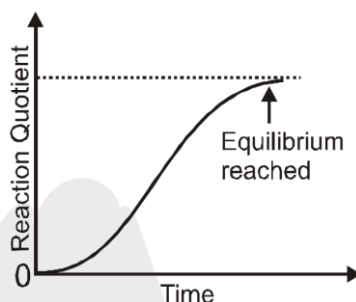
3.5.2 To determine the net direction of reaction:



Reaction Quotient (Q)

At each point in a reaction, we can write a ratio of concentration terms having the same form as the equilibrium constant expression. This ratio is called the reaction quotient (Q). It helps in predicting the direction of a reaction.

The expression $Q = \frac{[B]^b}{[A]^a}$ at any time during reaction is called reaction quotient. The concentrations [A] and [B] are not necessarily at equilibrium.



The reaction quotient is a variable quantity with time.

If $Q > K_c$ reaction will proceed in backward direction until equilibrium is reached.

If $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.

If $Q = K_c$ Reaction is at equilibrium.

2. A reaction mixture containing H_2 , N_2 and NH_3 has partial pressure 2 atm, 1 atm and 3 atm respectively at 725 K. If the value of K_p for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is $4.28 \times 10^{-5} \text{ atm}^{-2}$ at 725 K, in which direction the net reaction will go :
- (A) Forward (B) Backward
(C) No net reaction (D) Direction of reaction cannot be predicted

Ans. (B)

Sol. $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $K_p = 4.28 \times 10^{-5} \text{ atm}^{-2}$

$$\text{Reaction Quotient, } Q_p = \frac{P_{NH_3}^2}{P_{N_2}(P_{H_2})^3} = \frac{3^2}{1 \times (2)^3} = \frac{9}{8}$$

$Q_p > K_p$ Reaction will go Backward.

3. At 460°C , $K_c = 81$ for the reaction, $SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$

A mixture of these gases has the following concentrations of the reactants and products :

$$\begin{aligned} [SO_2] &= 0.04M & [NO_2] &= 0.04M \\ [NO] &= 0.30M & [SO_3] &= 0.3M \end{aligned}$$

Is the system at equilibrium? If not, in which direction must the reaction proceed to reach equilibrium. What will be the molar concentrations of the four gases at equilibrium?

Ans. $[\text{SO}_2] = 0.034\text{M}$; $[\text{NO}_2] = 0.034\text{M}$; $[\text{NO}] = 0.306\text{M}$; $[\text{SO}_3] = 0.306\text{M}$

Sol. $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \text{SO}_3(\text{g})$ $Q_c = \frac{(0.3)^2}{(0.04)^2} = 56.25$

0.04 0.04 0.3 0.3

Here, $Q_c < K_c$ hence reaction will proceed in forward direction to reach at state of equilibrium

0.04 - x 0.04 - x 0.3 + x 0.3 + x $K_c = \frac{(0.3+x)^2}{(0.04-x)^2} = 81$

x = 0.006

3.5.2 To determine concentrations and partial pressures at equilibrium: Consider the following reaction:

	A	+	2B	→	C
t = 0	a		b		0
t _{eq}	a - x		b - 2x		x

$$K_c = \frac{\frac{x}{v}}{\left(\frac{a-x}{v}\right)\left(\frac{b-2x}{v}\right)^2} = \frac{x}{(a-x)(b-x)} \left(\frac{1}{v}\right)^{\Delta n_g}$$

$$K_p = \frac{\frac{x}{a+b-2x} P_T}{\frac{a-x}{a+b-2x} P_T \left(\frac{b-2x}{a+b-2x} P_T\right)^2}$$

$$K_p = \frac{x}{(a-x)(b-2x)^2} \left(\frac{P_T}{\Sigma n}\right)^{\Delta n_g}$$

4. One mole of $\text{PCl}_5(\text{g})$ is taken in a container of volume 10 L. If $K_c = 10^{-5}\text{M}$ then find equilibrium concentrations of $\text{PCl}_5(\text{g})$, $\text{PCl}_3(\text{g})$ and $\text{Cl}_2(\text{g})$.

Ans. $[\text{PCl}_5] = 0.1\text{M}$, $[\text{PCl}_3] = 0.001\text{M}$ and $[\text{Cl}_2] = 0.001\text{M}$

Sol. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ $K_c = 10^{-5}$

n _i	1	0	0
n _{eq}	1 - x	x	x

≈ 1 (Since K_c is very small, so x is negligible as compare to 1)

$$C_{eq} \frac{1}{10} \frac{x}{10} \frac{x}{10}$$

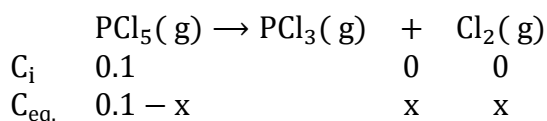
$$10^{-5} = \frac{\frac{x^2}{100}}{\frac{1}{10}}$$

$$x^2 = 10^{-4}x = 10^{-2} = 0.01$$

$$[\text{PCl}_3] = 0.001\text{M} \quad [\text{Cl}_2] = 0.001\text{M}$$

Note: If $\frac{K_c}{M} \leq 10^{-3}$, then x can be neglected with respect to initial conc.

Alternative solution with exact calculations:



$$10^{-5} = \frac{x^2}{0.1-x}$$

$$x^2 + 10^{-5}x - 10^{-6} = 0$$

$$x = \frac{-10^{-5} \pm \sqrt{10^{-10} + 4 \times 10^{-6}}}{2}$$

$$= \frac{-10^{-5} \pm \sqrt{(200 \times 10^{-5})^2}}{2}$$

$$= \frac{-10^{-5} + 200 \times 10^{-5}}{2} = \frac{199 \times 10^{-5}}{2}$$

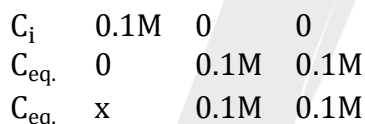
$$= 0.995 \times 10^{-3} = 10^{-3}$$

(II) If K_{eq} is very large:

6. Initial concentration of $\text{PCl}_5(\text{g})$ is 0.1M. If $K_C = 10^5$ then find equilibrium concentrations of $\text{PCl}_5(\text{g})$, $\text{PCl}_3(\text{g})$ and $\text{Cl}_2(\text{g})$.

Ans. $[\text{PCl}_5] = 10^{-7}\text{M}$, $[\text{PCl}_3] = 0.1\text{M}$ and $[\text{Cl}_2] = 0.1\text{M}$

Sol. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \quad K_C = 10^5$



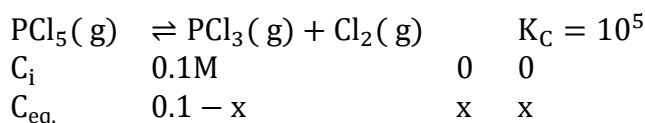
(Since K_C is very large, so extent of progress of reaction is near to 100%)

$$K_C = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \quad 10^5 = \frac{0.1 \times 0.1}{x}$$

$$x = 10^{-7}$$

$$[\text{PCl}_5] = 10^{-7}\text{M} \quad [\text{PCl}_3] = 0.1\text{M} \quad [\text{Cl}_2] = 0.1\text{M}$$

Alternative solution with exact calculations:



$$10^5 = \frac{x^2}{0.1-x}$$

$$x = \frac{-10^{-5} \pm \sqrt{10^{-10} + 4 \times 10^4}}{2}$$

$$= \frac{-10^{-5} \pm 10^5 (1 + 4 \times 10^{-6})^{\frac{1}{2}}}{2}$$

$$= \frac{-10^{-5} + 10^5 \left(1 + \frac{4 \times 10^{-6}}{2}\right)}{2}$$

$$x = 0.1$$

7. Initial concentrations of A(g) and B(g) are 0.1M and 0.11M respectively. If $K_C = 10^{10}$ then find equilibrium concentrations of A(g) and B(g).

Ans. $[PCl_5] = 10^{-7}M$, $[PCl_3] = 0.1M$ and $[Cl_2] = 0.1M$

Sol. $A(g) + B(g) \rightleftharpoons C(s)$ $K_C = 10^{10}$

$$C_i \quad 0.1M \quad 0.11M$$

$$C_{eq} \quad 0 \quad 0.01 \quad 0.1$$

$$x \quad 0.01 + x \quad 0.1 - x$$

$$10^{10} = \frac{1}{x \times 0.01} \quad x = 10^{-8}M$$

3.6 CALCULATION OF K_P & K_C :

3.6.1 Homogeneous equilibrium in gaseous phase:

(I) If $\Delta n_g = 0$

Suppose the initial concentration of N_2 and O_2 is a M and b M respectively. xM of both N_2 and O_2 are dissociated at equilibrium.

	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 $K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$

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

* $K_P = K_C(RT)^{\Delta n_g}$ but $\Delta n_g = 0$, so, $K_P = K_C$

(II) If $\Delta n_g > 0$

Suppose one mole of PCl_5 is taken in a closed container of V litres. 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})	$\frac{1-x}{V}$		$\frac{x}{V}$		$\frac{x}{V}$

Calculation of K_c -

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

Substituting the values in the above equation.

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

$$K_c = \frac{x^2}{(1-x)v}$$

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,

$$K_c = \frac{x^2}{v}$$

$$x^2 = K_c \cdot v$$

$$x^2 \propto v$$

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

On increasing volume, the x is also increased.

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,					
$(1 - x) + x + x = (1 + x)$ moles					

According to law of mass action

$$K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{n_{\text{PCl}_3} \times n_{\text{Cl}_2}}{n_{\text{PCl}_5}} \left[\frac{P_T}{n_T} \right]^{\Delta n_g}$$

Substituting the values in the above equation of K_p -

$$K_p = \frac{x \times x}{1 - x} \left[\frac{P_T}{1 + x} \right]^{\Delta n_g}$$

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

The equation of K_p is not independent of pressure.

If, $x \ll 1$ then $1 - x^2 \approx 1$

$$K_p = x^2 P$$

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

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

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

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 .

(III) If $\Delta n_g < 0$

Suppose one mole of N_2 and three moles of H_2 are taken in a closed container of V litre. Further at equilibrium x mol of PCl_5 dissociated.

	N_2	3H_2	$\rightleftharpoons 2\text{NH}_3$
Initial moles	1	3	0
moles at equilibrium	$(1 - x)$	$(3 - 3x)$	$2x$
Active mass (mol l^{-1})	$\left(\frac{1-x}{v}\right)$	$\left(\frac{3-3x}{v}\right)$	$\left(\frac{2x}{v}\right)$

Calculation of K_C :

$$K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Substituting the values in the above equation-

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

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

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

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

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

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

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

$$x^2 \propto \frac{1}{v^2} \quad x \propto \frac{1}{v}$$

Calculation of K_P :

	N_2	+	3H_2	$\rightleftharpoons 2\text{NH}_3$
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

$$K_P = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2}) \times (P_{\text{H}_2})^3} = \frac{n_{\text{NH}_3}^2}{n_{\text{N}_2} \times n_{\text{H}_2}^3} \left[\frac{P_T}{n_T} \right]^{\Delta n_g}$$

$$K_P = \frac{4x^2}{(1-x)(3-3x)^3} \left[\frac{P_T}{4-2x} \right]^{-2}$$

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

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

The equation of K_P is not independent of pressure

Suppose, $x \ll 1$ then,

$$(1-x)^4 = 1$$

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

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

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

$$x \propto P$$

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

8. For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$,

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 = $2 + 2 + 2 = 6$

$$P_{\text{PCl}_5} = \frac{2}{6} \times 3, P_{\text{PCl}_3} = \frac{2}{6} \times 3, P_{\text{Cl}_2} = \frac{2}{6} \times 3$$

$$K_P = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{1 \times 1}{1} = 1 \text{ atmosphere}$$

9. For the reaction $\text{N}_2 \rightleftharpoons 2\text{NH}_3$, 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. $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

Initially 1 3 0

At equilibrium $1 - 0.5$ $3 - 1.5$ 2×0.5

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

$$P_{\text{NH}_3} = \frac{1}{3} P$$

10. 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?

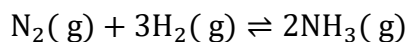
- (A) 1.25 (B) 1.50 (C) 0.75 (D) 2.0

Ans. (A)

Sol. $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$

$$\begin{array}{ccc} 3 & 2 & 0 \\ 3 - x & 2 - x & 2x \\ 2x = 1; x = 0.5 \\ [N_2] = \frac{3-0.5}{2} = 1.25 \end{array}$$

11. At a certain temperature (T), the equilibrium constant (K_C) is 1 for the reaction

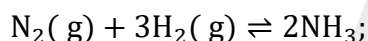


If 2 moles of N_2 , 4 moles of H_2 , 6 moles of NH_3 & 3 moles of inert gas are introduced into a two litre rigid vessel at constant temperature T. It has been found that equilibrium concentration of H_2 , & NH_3 are equal then what is the equilibrium concentration of N_2 (in M) ?

Ans. 1.2M

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

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



at equilibrium : $2 + x \quad 4 + 3x \quad 6 - 2x$

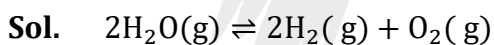
\therefore At equilibrium $[H_2(g)] = [NH_3(g)]$

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

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

12. n mole each of $H_2O(g)$, $H_2(g)$ and $O_2(g)$ are mixed at a suitable high temperature to attain the equilibrium $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$. If y mole of $H_2O(g)$ are the dissociated and the total pressure maintained is P, calculate the K_P .

Ans. $\frac{P(n+y/2)(n+y)^2}{(3n+y/2)(n-y)^2}$



t=0 n n n

$$\text{teq. } (n-y) \quad (n+y) \quad (n+y/2) \quad n_T = (3n+y/2)$$

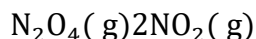
$$\text{so, } K_P = \frac{(P_{H_2(g)})_{eq.}^2 \cdot (P_{O_2(g)})_{eq.}}{(P_{H_2O(g)})_{eq.}^2} = \frac{(n+y)^2(n+y/2)P}{(n-y)^2(3n+y/2)}$$

13. The partial pressures of N_2O_4 and NO_2 at $40^\circ C$ for the following equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ are 0.1 atm and 0.3 atm respectively. Find K_P for the reaction.

Ans. 0.9 atm

Sol. $P_{N_2O_4} = 0.1 \text{ atm}; P_{NO_2} = 0.3 \text{ atm}.$

reaction is



$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{(0.3)^2}{0.1} = \mathbf{0.9 \text{ atm.}}$$

- 14.** 1 mole of N_2 and 3 moles of H_2 are placed in 1 L vessel. Find the concentration of NH_3 at equilibrium, if the equilibrium constant (K_C) at 400 K is $\frac{4}{27}$.

Ans. $[\text{NH}_3] = 0.76\text{M}$

Sol. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ($\Delta n < 0$)

1 mol 3 mol 0

$(1-x) \quad (3-3x) \quad 2x$

$P_{\text{eq}} = 1 \text{ atm}, T = 400 \text{ K}$

$$K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2x)^2}{(1-x)(3-3x)^3} = \frac{4}{27}$$

$$\frac{x^2}{(1-x)^4} = 1; x = (1-x)^2; x^2 - 3x + 1 = 0$$

$$x = \frac{3 \pm \sqrt{9-4}}{2}; x = \frac{3 \pm \sqrt{5}}{2}$$

$$x = \frac{3+2.24}{2} \text{ or } x = \frac{3-2.24}{2}$$

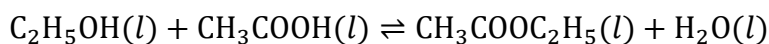
$$x = \frac{5.24}{2} = 2.62 \text{ or } x = \frac{0.76}{2}$$

$x = 0.38$ (since x cannot be greater than 1)

$$[\text{NH}_3] = 0.38 \times 2 = 0.76$$

3.6.2 Homogeneous equilibrium in solution phase:

Equilibrium for the formation of ethyl acetate is represented as



Initial moles	1	1	0	0
Moles at equilibrium	$1-x$	$1-x$	x	x
Active mass (mol l^{-1})	$\frac{1-x}{V}$	$\frac{1-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_C = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]}$$

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

- 15.** 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.

Ans. 0.903 mole

Sol. $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{H} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$

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

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

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

$$x = 0.903$$

Amount of ester at equilibrium = 0.903 mole

3.6.2 Heterogeneous equilibrium:

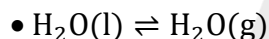
Heterogeneous equilibrium results from a reversible reaction involving reactants and product that are in different phases.

For pure solid and pure liquid, active mass is taken to be unity i.e. 1 as they remain constant throughout the reaction:



$$K_P = (P_{\text{CO}_2})_{\text{eq}}, K_C = [\text{CO}_2(\text{g})]_{\text{eq}}$$

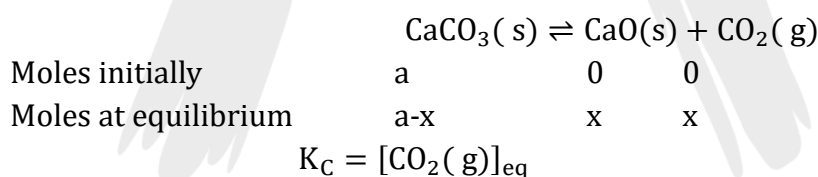
$$[\text{CaCO}_3(\text{s})] = \frac{\text{moles}}{\text{volume}} = \frac{W_{\text{CaCO}_3}}{M_{\text{CaCO}_3} V} = \frac{\text{density CaCO}_3}{M_{\text{CaCO}_3}} = \text{constant}$$



$$\bullet K_P = (P_{\text{H}_2\text{O}(\text{g})})_{\text{eq}}, K_C = [\text{H}_2\text{O}(\text{g})]_{\text{eq}}$$

E.g. Decomposition of solid CaCO_3 into solid CaO and gaseous CO_2

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



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

$$\therefore K_C = [\text{CO}_2] = \frac{x}{V} \dots\dots(1)$$

Assuming CO_2 gas is to behaving ideally at the temperature & pressure of the reaction. the

molar concentration of CO_2 can be written using ideal equation as $\frac{P_{\text{CO}_2}}{RT}$

$$\therefore K_C = \frac{P_{\text{CO}_2}}{RT}$$

$$K_C(RT) = P_{\text{CO}_2}$$

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

$$\therefore K_P = P_{\text{CO}_2} = \frac{xRT}{V} \dots\dots(2)$$

16. In the reaction $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO(g)}$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts then K_p will be :

(A) 12 atm (B) 16 atm (C) 20 atm (D) 24 atm

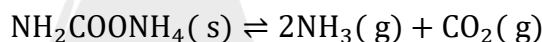
Ans. (B)

Sol. $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO(g)}$

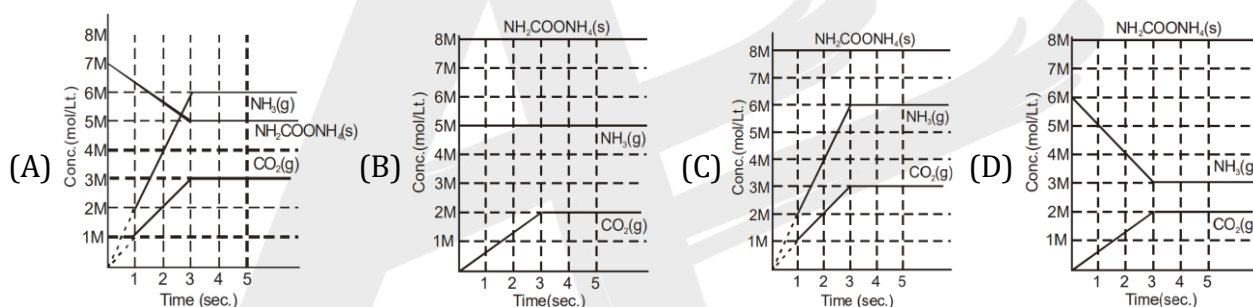
$$P - P/2 \quad P = \frac{3P}{2} = 12$$

$$\text{So } K_p = \frac{P^2}{(P/2)} = 2P = 2 \times 8 = 16 \text{ atm}$$

17. Solid ammonium carbamate dissociate to give ammonia and carbon dioxide as follows



which of the following graph correctly represents the equilibrium.



Ans. (C)

Sol. Gas product concentration increases while that of solid reactant is constant.

18. For $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$ reaction started only with $\text{NH}_4\text{HS(s)}$, the observed pressure for reaction mixture in equilibrium is 1.2 atm at 106°C . What is the value of K_p for the reaction?

(A) 1.44 atm^2 (B) 0.36 atm^2 (C) 0.16 atm^2 (D) 3.6 atm^2

Sol. $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$

$$P \quad P$$

$$2P = 1.2$$

$$P = 0.6$$

$$K_p = P^2 = (0.6)^2 = 0.36 \text{ atm}^2$$

19. Consider the decomposition of solid NH_4HS in a flask containing $\text{NH}_3(\text{g})$ at a pressure of 2 atm. What will be the partial pressure of $\text{NH}_3(\text{g})$ and $\text{H}_2\text{S(g)}$ after the equilibrium has been attained? K_p for the reaction is 3 atm.

(A) $p_{\text{NH}_3} = 4 \text{ atm}$, $p_{\text{H}_2\text{S}} = 2 \text{ atm}$

(B) $p_{\text{NH}_3} = 1.732 \text{ atm}$, $p_{\text{H}_2\text{S}} = 1.732 \text{ atm}$

(C) $p_{\text{NH}_3} = 3 \text{ atm}$, $p_{\text{H}_2\text{S}} = 1 \text{ atm}$

(D) $p_{\text{NH}_3} = 1 \text{ atm}$, $p_{\text{H}_2\text{S}} = 1 \text{ atm}$

Ans. (C)**Sol.** $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$

Since flask already contain $\text{NH}_3(\text{g})$, the equilibrium pressure of NH_3 and H_2S will not be equal.

$$p_{\text{NH}_3} = 2 + p_{\text{H}_2\text{S}}$$

$$K_P = p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} = 3$$

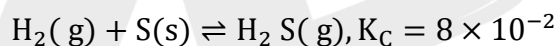
$$(p_{\text{H}_2\text{S}} + 2)p_{\text{H}_2\text{S}} = 3$$

$$p_{\text{H}_2\text{S}}^2 + 2p_{\text{H}_2\text{S}} - 3 = 0$$

$$p_{\text{H}_2\text{S}} = \frac{-2 \pm \sqrt{4 + 12}}{2} = \frac{-2 \pm 4}{2}$$

$$p_{\text{H}_2\text{S}} = 1 \text{ atm}$$

$$p_{\text{NH}_3} = 2 + 1 = 3 \text{ atm}$$

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

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 $R = 0.08 \text{ atm. L/mol. K}$]

(A) 0.32 atm

(B) 0.43 atm

(C) 0.62 atm

(D) 4.0 atm

Ans. (A)

$$\text{Sol. } K_C = \frac{[\text{H}_2\text{S(g)}]}{[\text{H}_2(\text{g})]} \Rightarrow 8 \times 10^{-2} = \frac{x}{0.3-x}$$

$$0.024 - 0.08x = x$$

$$0.024 = 1.08x \quad p_{\text{H}_2\text{S}} = \frac{0.022 \times 0.08 \times 360}{2} \Rightarrow \approx 0.32 \text{ atm}$$

$$x = 0.022$$

3.7 EQUILIBRIUM CONSTANT IN TERMS OF DEGREE OF DISSOCIATION :**3.7.1 Degree of dissociation (α) :**

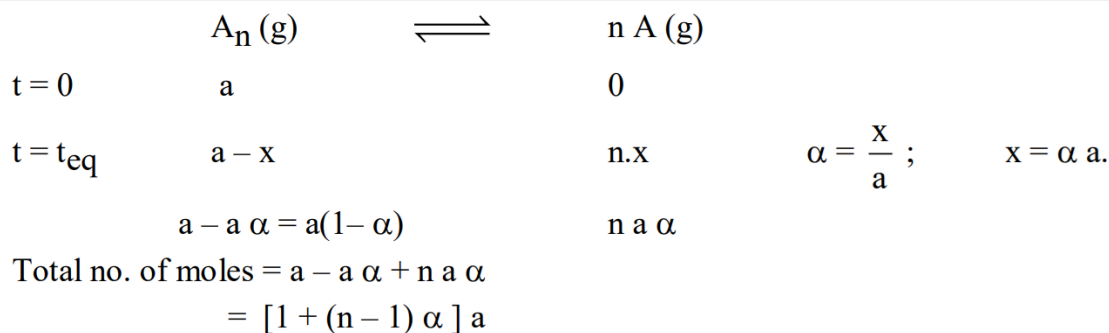
Degree of dissociation is the fraction of a mole of the reactant that underwent dissociation. It is represented by ' α '

$$\alpha = \frac{\text{number of moles of reactant dissociated}}{\text{number of moles of reactant present initially}}$$

Note: % dissociation = $a \times 100$

Suppose 5 moles of PCl_5 is taken and if 2 moles of PCl_5 dissociated then $a = \frac{2}{5} = 0.4$

Let a gas A_n dissociates to give n moles of A as follows-

**Significance of n**

$$n = \frac{\text{sum of stoichiometric coefficient of product}}{\text{sum of coefficient of reactants}}$$

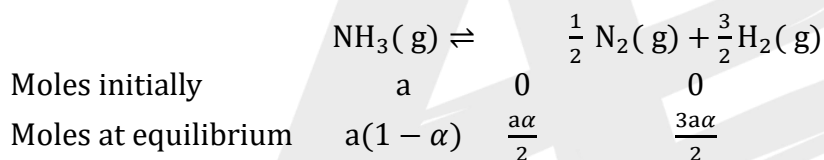
(i) for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ ($n = 2$)

(ii) for $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ ($n = \frac{3}{2} + \frac{1}{2} = 2$)

(iii) for $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ ($n = 1$)

For example,

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

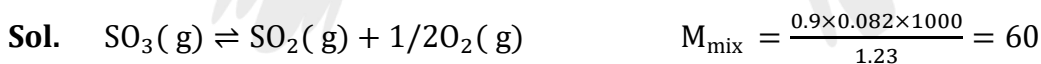


Here, α represented the degree of dissociation.

- 21.** At $727^\circ C$ and 1.23 atm of total equilibrium pressure, SO_3 is partially dissociated into SO_2 and O_2 according to $SO_3(g) \rightleftharpoons SO_2(g) + 1/2 O_2(g)$. The density of equilibrium mixture is 0.9 g/litre. The degree of dissociation is:

(A) 1/3 (B) 2/3 (C) 1/4 (D) 1/5.

Ans. (B)

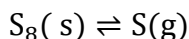


$1 - \alpha$	α	$\frac{\alpha}{2}$	$M_{mix} = \frac{\alpha \cdot M_{SO_2} + \frac{\alpha}{2} \cdot M_{O_2} + (1 - \alpha) M_{SO_3}}{1 + \frac{\alpha}{2}}$
--------------	----------	--------------------	---

$$1 + \frac{\alpha}{2} = \frac{80}{60} \quad \frac{\alpha}{2} =$$

$$\alpha = \frac{2}{3}$$

- 22.** 2.56 gm of sulphur $S_8(s)$ is taken which is in equilibrium with its vapour according to reaction,



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

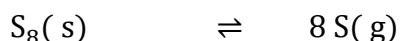
(B) 0.55

(C) 0.4

(D) 0.44

Ans. (B)

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



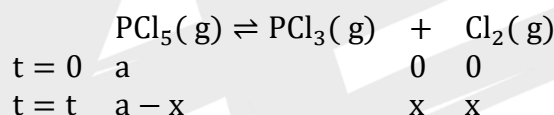
$$0.01(1 - \alpha) \quad 8 \times 0.01 \times \alpha$$

$$PV = nRT$$

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

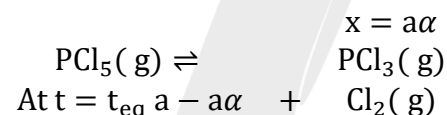
$$\alpha = 0.55$$

23. Calculate the degree of dissociation and K_p for the following reaction if a moles of PCl_5 are taken initially.



Since for x moles of PCl_5 are dissociated

Sol. For 1 mole, $\frac{x}{a} = \alpha$ are dissociated



$$\text{Total no. of moles at equilibrium} = a + a\alpha = a(1 + \alpha)$$

$$P_{PCl_5} = \frac{a(1-\alpha)P}{a(1+\alpha)}, \quad P_{PCl_3} = \frac{a\alpha \cdot P}{a(1+\alpha)}, \quad P_{Cl_2} = \frac{a\alpha}{a(1+\alpha)} \cdot P$$

$$K_p = \frac{\left\{ \frac{a\alpha P}{a(1+\alpha)} \right\}^2}{\left(\frac{a(1-\alpha)P}{a(1+\alpha)} \right)} \quad K_p = \frac{\alpha^2 \cdot P}{1-\alpha^2}$$

24. For the dissociation reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the degree of dissociation (α) in terms of K_p and total equilibrium pressure P is:

(A) $\alpha = \sqrt{\frac{4p+K_p}{K_p}}$

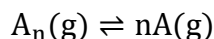
(B) $\alpha = \sqrt{\frac{K_p}{4p+K_p}}$

(C) $\alpha = \sqrt{\frac{K_p}{4p}}$

(D) None of these

Ans. (B)

3.7.2 Observed molecular weight and Observed Vapour Density of the mixture:



$$\text{Observed molecular weight of } A_n(g) = \frac{\text{molecular weight of } A_n(g)}{\text{total no. of moles equilibrium}}$$

$$= \frac{a \cdot M_{th}}{a(1+(n-1)\alpha)}$$

$$M_{obs} = \frac{M_{th}}{[1+(n-1)\alpha]}$$

where M_{th} = theoretical molecular weight (n = atomicity)

$$M_{mixture} = \frac{M_{A_n}}{[1+(n-1)\alpha]}, M_{A_n} = \text{Molar mass of gas } A_n$$

Vapour density (V.D.): Density of the gas divided by density of hydrogen under same temp & pressure is called vapour density.

$$m \quad D = \text{vapour density without dissociation} = \frac{M_{A_n}}{2}$$

$$d = \text{vapour density of eq. mixture} = \text{observed v.d.} = \frac{M_{mix}}{2}$$

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

$$\alpha = \frac{D-d}{(n-1) \times d} = \frac{M_T - M_0}{(n-1)M_0}$$

25. Vapour density of the equilibrium mixture of NO_2 and N_2O_4 is found to be 38.33. For the equilibrium $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

Calculate :

- (i) abnormal molecular weight.
- (ii) degree of dissociation.
- (iii) percentage of NO_2 in the mixture.
- (iv) K_p for the reaction if total pressure is 2 atm.

Ans. (i) 76.66 (ii) 0.2 (iii) 33.33% (iv) 1/3

Sol. $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

$$a(1-\alpha) \quad 2a\alpha$$

$$(i) M_{obs} = 38.33 \times 2 = 76.66$$

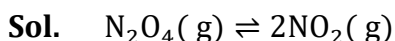
$$(ii) 76.66 = \frac{a(1-\alpha) \times 92 + 2a\alpha \times 46}{a(1+\alpha)}$$

$$\alpha = 0.2$$

$$(iii) \% \text{ of } NO_2 = \frac{2a\alpha}{a(1+\alpha)} \times 100 = 33.33\%$$

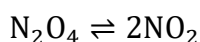
$$(iv) K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha} \times 2\right)^2}{\left(\frac{1-\alpha}{1+\alpha} \times 2\right)} = 0.33$$

26. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at $33^\circ C$ calculate the no. of moles of NO_2 if 100 g of N_2O_4 were taken initially.



$$M_{\text{mix}} = 2 \times 38.3 = 76.6$$

$$M_{\text{mix}} = \frac{M_{\text{th}}}{1+\alpha} = \frac{92}{1+\alpha} \quad \alpha = 0.2$$



$$t = 0 \text{ a } 0$$

$$t = t \text{ a } -a\alpha \quad 2a\alpha$$

$$\text{no. of moles of } NO_2 = 2a\alpha = 0.435$$

27. 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?

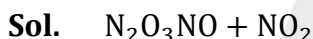
(A) 80%

(B) 60%

(C) 40%

(D) 20%

Ans. (C)



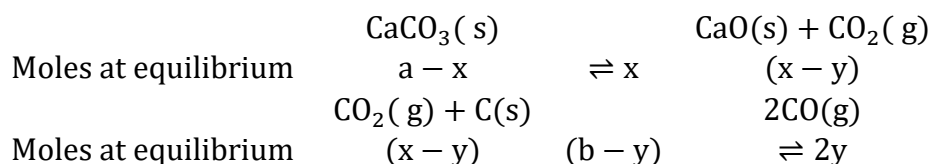
$$1 - \alpha \rightleftharpoons \alpha \quad \alpha \quad \alpha = \frac{D-d}{d(n-1)} = \frac{38-23.72}{23.75(2-1)} = 0.6$$

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

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

4. 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.



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, $K_{C_1} = [\text{CO}_2] = \frac{x-y}{V}$

Equilibrium constant for second equilibrium, $K_{C_2} = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(2y)^2 V}{V^2(x-y)} = \frac{4y^2}{V(x-y)}$

28. Two solid compounds A and B dissociate into gaseous products at 20°C as



At 20°C pressure over excess solid A is 50 mm and that over excess solid B is 68 mm find :

(a) The dissociation constant of A and B

(b) Relative no. of moles of A' and B' in the vapour phase over a mixture of solid A and B.

(c) Show that the total pressure of the gas over the solid mixture would be 84.4 mm

Ans. (a) $K_{p_1} = 625 \text{ mm}^2$, $K_{p_2} = 1156 \text{ mm}^2$ (b) $\frac{625}{1156}$

Sol. $\text{A}(\text{s}) \rightleftharpoons \text{A}'(\text{g}) + \text{H}_2\text{S}(\text{g})$ $P = 50 \text{ mm}$; $P_{\text{H}_2\text{S}} = P_{\text{A}'} = P/2 = 25 \text{ mm}$

$\text{B}(\text{s}) \rightleftharpoons \text{B}'(\text{g}) + \text{H}_2\text{S}(\text{g})$ $P = 68 \text{ mm}$; $P_{\text{H}_2\text{S}} = P_{\text{B}'} = P/2 = 34 \text{ mm}$

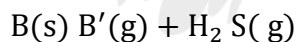
(i) $K_{p_1} = (25)^2 = 625 \text{ mm}^2$

$K_{p_2} = (34)^2 = 1156 \text{ mm}^2$

(ii) Ratio of moles is same as that of partial pressure so (eksy dk vuqikr vkaf'kd nkcksa ds vuqikrksa ds leku gS),



$$P_1 \quad P_1 + P_2$$



$$P_2 \quad P_2 + P_1$$

$$K_{p_1} = P_{\text{A}'} \times P_{\text{H}_2\text{S}} = P_1(P_1 + P_2)$$

$$K_{p_2} = P_{\text{B}'} \times P_{\text{H}_2\text{S}} = P_2(P_1 + P_2)$$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{P_1}{P_2} = \frac{625}{1156}$$

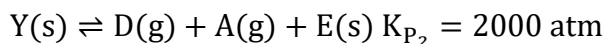
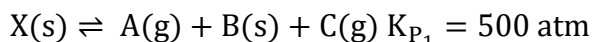
(iii) total pressure = $P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2)$

(i) + (ii) = $(P_1 + P_2)^2$

$$\sqrt{K_{p_1} + K_{p_2}} = P_1 + P_2$$

$$P_T = 2 \times (\sqrt{K_{p_1} + K_{p_2}}) = 84.4 \text{ mm}$$

29. For given simultaneous reaction :

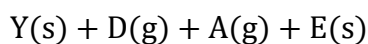


Find total pressure at equilibrium.

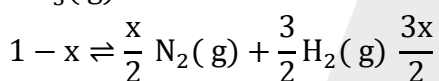
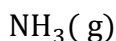
Ans. 100 atm

Sol. $X(s) \rightleftharpoons A(g) + B(s) + C(g)$

$$p_1 + p_2$$



$$p_2 \quad p_2 + p_1$$



$$\text{Given that moles of } H_2 = \frac{3x}{2} = 0.75 \quad K_{C_2}$$

$$K_{C_1} = \frac{1}{2} \frac{(1-x)}{2} = \frac{1}{8} \quad [\text{Since } V = 2 \text{ L}]$$

$$K_{C_2} = \frac{\left(\frac{3x}{4}\right)^{3/2} \left(\frac{x}{4}\right)^{1/2}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2} \left(\frac{1}{8}\right)^{1/2}}{\frac{1}{4}} = (3)^{3/2} \frac{1}{64} \times \frac{4}{1} = \frac{(3)^{3/2}}{16}$$

EXTERNAL FACTORS AFFECTING EQUILIBRIUM :

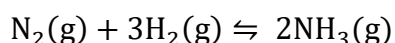
Chemical equilibrium represents a balance between forward and reverse reactions. In most cases changes in concentration, pressure, volume and temperature may disturb this balance and shifts the equilibrium position so that more or less of the desired product is formed. There is a general rule (named Le Chatelier 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:

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.

5.1 Effect of change in concentration :

If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration. e.g. In the following example.



[reactant] \uparrow Forward shift
 [Product] \uparrow Backward shift

- If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction.
 - If concentration of product is increased then reaction shifts in the backward direction.
- Le Chatelier principle can be explained using the following equilibrium reaction.

Note : The addition of any solid component does not affect the equilibrium.

5.2 Effect of change in volume of container :

If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.

If volume is increased then, for

$n_g > 0$ reaction will shift in the forward direction
 $n_g < 0$ reaction will shift in the backward direction
 $n_g = 0$ reaction will not shift. (No effect)

Explanation :

(i) $n_g > 0$, e.g. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$$Q_C = \frac{\frac{(n_{\text{Cl}_2})}{V} \times \frac{(n_{\text{PCl}_3})}{V}}{\frac{(n_{\text{PCl}_5})}{V}}; Q_C \propto \frac{1}{V} \text{ for } n_g > 0$$

On increasing V, Q_C , decreases.

Now, for $Q_C < K_C$ reaction will shift in forward direction.

Thus, if, Volume $\uparrow \Rightarrow Q_C \downarrow$ (Forward shift)

Volume $\downarrow \Rightarrow Q_C \uparrow$ (Backward shift)

(ii) $n_g < 0$, e.g. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$$Q_C = \frac{\left\{ \frac{(n_{\text{NH}_3})}{V} \right\}^2}{\left\{ \frac{(n_{\text{N}_2})}{V} \right\} \left\{ \frac{(n_{\text{H}_2})}{V} \right\}^3} \Rightarrow Q_C \propto V^2$$

for $n_g < 0$

$V \uparrow \Rightarrow Q_C \uparrow$ (Backward shift)

$V \downarrow \Rightarrow Q_C \downarrow$ (Forward shift)

5.3 Effect of pressure :

On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.

$P \propto \text{no. of moles}$

(i) For $n_g = 0$ No. effects

(ii) For $n_g > 0$, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$$Q_p = \frac{(x_{\text{PCl}_3}P) \cdot (x_{\text{Cl}_2}P)}{(x_{\text{PCl}_5} \cdot P)}; Q_p \propto P$$

$P \downarrow \Rightarrow Q_p \downarrow$; (Forward shift)

$P \uparrow \Rightarrow Q_p$; (Backward shift)

(iii) For $n < 0$, e.g. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$$Q_p = \frac{[(x_{\text{NH}_3})P]^2}{[(x_{\text{N}_2}) \cdot P][(x_{\text{H}_2})P]^3} \Rightarrow Q_p \propto \frac{1}{P^2}$$

$P \uparrow \Rightarrow Q_p \downarrow$; (Forward shift);

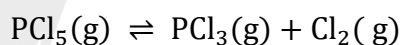
$P \downarrow \Rightarrow Q_p \uparrow$; (Backward shift)

5.4 Effect of catalyst :

Due to catalyst, the state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus altering the forward & reverse rate equally and hence, the equilibrium will be attained faster i.e. time taken to reach the equilibrium is less.

5.5 Effect of inert gas addition :

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



Moles at eq. a b c

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

$$\frac{P_T'}{(a+b+c+d)} = \frac{RT}{V}. \text{ As } R, T \text{ and } V \text{ are constant, so the expression } \frac{bc \times RT}{a \times V} \text{ would still be equal to } K_p.$$

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. Inert gas addition has no effect at constant volume

(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 increase. 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.

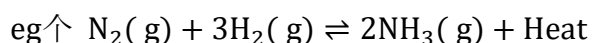
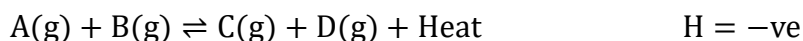
(i) $n_g > 0$, reaction will shift in the forward direction

(ii) $n_g < 0$, reaction will shift in the backward direction

(iii) $n_g = 0$, no effect

5.6 Effect of temperature :

(i) Exothermic reaction : The reaction in which heat is evolved



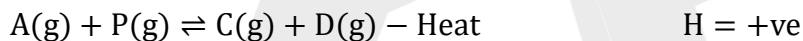
$T \Rightarrow K$ will decrease

$$\log \frac{K_1}{K_2} = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \text{ (from vant' hoff equation)}$$

$$\log \frac{K_1}{K_2} < 0 \Rightarrow \log K_1 - \log K_2 > 0 \Rightarrow$$

$\log K_1 > \log K_2 \Rightarrow K_1 > K_2$ Reaction will shift in backward direction.

(ii) Endothermic reaction : energy consumed.

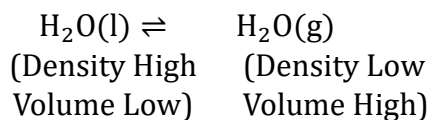


$T \uparrow K \uparrow \Rightarrow$ Forward shift

APPLICATION OF LE CBATELIER PRINCIPLE ON PHYSICAL EQUILIBRIUM :

6.1 Boiling of water :

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.

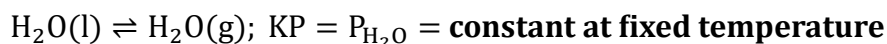


On increasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward shift.

Hence, on increasing pressure, the boiling point increases.

6.2 Vapour Pressure of Liquid :

It is the pressure exerted by the vapours over its liquid when it is in equilibrium with the liquid. Vapour pressure of water is also called aqueous tension.



Hence V.P. of liquid is independent of pressure, volume and concentration change. e.g. at 25°C, vapour pressure of water 24 mm of Hg

$$\text{Relative Humidity} = \frac{\text{Partial pressure of H}_2\text{O vapours}}{\text{Vapour pressure of H}_2\text{O at that temp.}}$$

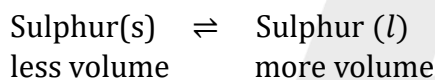
6.2 Melting of ice :

Solids whose volume decreases on melting, e.g., ice, diamond, carborundum, magnesium nitride and quartz, 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.**



(Density Low Volume High)	(Density High Volume Low)
------------------------------	------------------------------

6.3 Melting of Sulphur :



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.

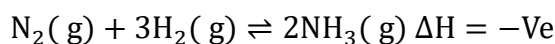
6.4 Formation of diamond :



(Density Low Volume High)	(Density High Volume Low)
------------------------------	------------------------------

High pressure and low temperature are favourable conditions for the formation of SO_3 .

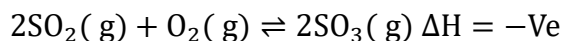
6.5 Formation of ammonia by Haber's process :



(i) The reaction will shift in the forward direction at low temperature, but at very low temperature the rate of reaction becomes very low; thus moderate temperature is used for this reaction.

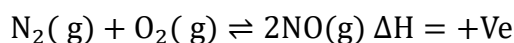
(ii) At high pressure, reaction will shift in forward direction to form more product.

6.6 Manufacturing of SO_3 by contact process



High pressure and low temperature are favourable conditions for the formation of SO_3 .

6.6 Manufacturing of NO :



- No effect on change of pressure
- High temperature (1200°C to 2000°C), High concentration of N_2 and O_2 are favourable condition for the formation of NO.

31. The equilibrium constant of the reaction at 25°C



is $1.084 \times 10^{-4} \text{ atm}^2$. Find out under what conditions of relative humidity, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ will start losing its water of crystallization according to above reaction. (Vapour pressure of water at 25°C is 24 mm of Hg).

Sol. $K_p = (P_{\text{H}_2\text{O}})^2$ so $= \sqrt{1.084 \times 10^{-4}} = 1.041 \times 10^{-2} \text{ atm}$ 8 mm of Hg

will absorb water from air and will form $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ & will keep absorbing until partial pressure of H_2O becomes 8 mm of Hg.

* If $< 8 \text{ mm of Hg}$ then $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ will lose water of crystallization and reaction will move in forward direction.

i.e. If relative humidity $< \frac{8}{24} < 33.33\%$

then $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ will lose water of crystallization.

32. In the Haber process for the industrial manufacturing of ammonia involving the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 200 atm pressure in the presence of a catalyst, a temperature of about 500°C is used. This is considered as optimum temperature for the process because

(A) yield is maximum at this temperature
 (B) catalyst is active only at this temperature
 (C) energy needed for the reaction is easily obtained at this temperature
 (D) rate of the catalytic reaction is fast enough while the yield is also appreciable for this exothermic reaction at this temperature.

Ans. (D)

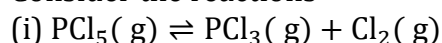
Sol. On increasing temperature though reaction equilibrium shifts in the backward direction but for rate of reaction to be higher, higher temperature is required and at 500°C is found to be optimum temperature.

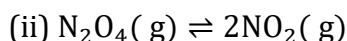
33. Addition of water to which of the following equilibria causes it to shift in the backward direction?

- (A) $\text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
 (B) $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 (C) $\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CN}^-(\text{aq})$
 (D) $[\text{Cr}(\text{dien})_2]^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + 3\text{Cl}^-(\text{aq}) \rightleftharpoons [\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3](\text{aq}) + 2\text{dien}(\text{aq})$

Ans. (D)

34. Consider the reactions





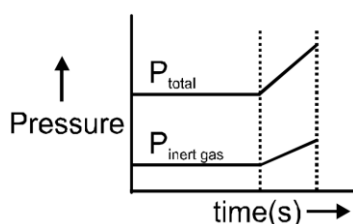
The addition of an inert gas at constant volume

- (A) will increase the dissociation of PCl_5 as well as N_2O_4
- (B) will reduce the dissociation of PCl_5 as well as N_2O_4
- (C) will increase the dissociation of PCl_5 and step up the formation of NO_2
- (D) will not disturb the equilibrium of the reactions

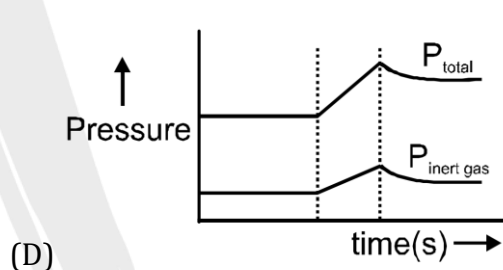
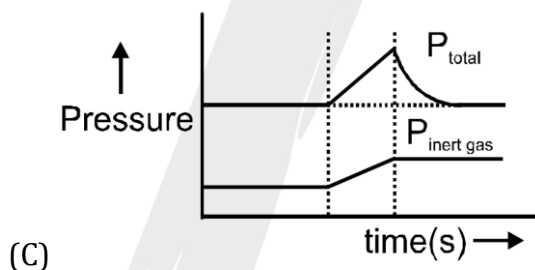
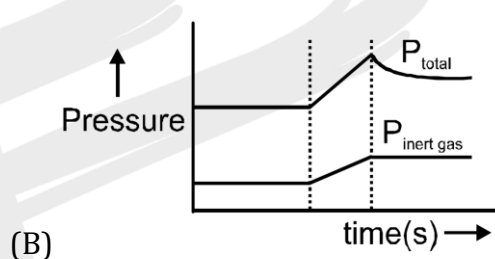
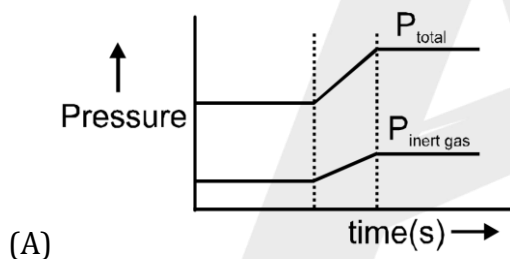
Ans. (D)

Sol. Since inert gas addition has no effect at const. volume.

35. For a system at equilibrium some changes are made which is reported by a graph (shown below). Changes has been made at constant temperature.



Choose the correct options :



Sol. P_{inert} remains same as number of moles of inert gas & volume remains same after changes been done.

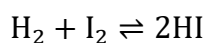
→ P_{total} increased more than increase in P_{inert} , so clearly there has been reduction in volume, by Le chatelier's principle pressure will decrease but will remain more than initial.

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	$K_P = K_C(RT)^0$	$K_P = K_C$	$\frac{x^2}{4(1-x)^2}$	$\frac{x^2}{4(1-x)}$	None	None	+ve (endothermic)	High temperature No pressure High concentration of reactant
3.	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	+1	$K_P = K_C(RT)^1$	$K_P > K_C$	$\frac{x^2}{(1-x)v}$	$\frac{x^2 p}{1-x^2}$	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_P, K_C	$\frac{4x^2}{(1-x)v}$	$\frac{4x^4 p}{1-x^2}$	Mol L ⁻¹	atm	+ve (endothermic)	High temperature Low pressure High concentration of reactant
5.	$2NH_3 \rightleftharpoons N_2 + 3H_2$	+2	$K_P = K_C(RT)^2$	$K_P > K_C$	$\frac{27x^4}{4(1-x)^2 v^2}$	$\frac{27x^4 p^2}{16(1-x)^2 (1-x)^2}$	Mol ² L ⁻²	atm ²	+ve (endothermic)	High temperature Low pressure High concentration of reactant

6.	$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$	-2	$\frac{K_p}{K_c(RT)^{-2}} =$	$K_p < K_c$	$\frac{4x^4 v^2}{27(1-x)^4}$	$\frac{16x^2(2-x)^2}{27(1-x)^4 p^2}$	$\text{L}^2 \text{mol}^2$	atm^{-2}	-ve (endothermic)	Low temperature Low pressure High concentration of reactant
7.	$\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$	-1	$\frac{K_p}{K_c(RT)^{-1}} =$	$K_p < K_c$	$\frac{xv}{(1-x)^2}$	$\frac{x(2-x)}{(1-x)^2 p}$	L mol^1	atm^{-1}	-ve (endothermic)	Low temperature Low pressure High concentration of reactant
8.	$2\text{SO}_3 + \text{O}_2 \rightleftharpoons 2\text{SO}_2$	-1	$\frac{K_p}{K_c(RT)^{-1}} =$	$K_p < K_c$	$\frac{x^2 v}{(1-x)^2}$	$\frac{x^2(3-x)}{(1-x)^3 p}$	L mol^1	atm^{-1}	-ve (endothermic)	Low temperature Low pressure High concentration of reactant

36. For the reaction

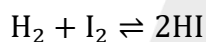


The value of equilibrium constant is 9.0 . The degree of dissociation of HI will be-

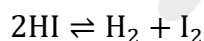
- (A) 2 (B) 2/5 (C) 5/2 (D) 1/2

Ans. (B)

Sol. Equilibrium constant of the reaction



So the equilibrium constant for the dissociation of HI i.e. $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ will be 1/9.



$$1 \quad 0 \quad 0$$

$$1-x \quad \frac{x}{2} \quad \frac{x}{2}$$

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

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

$$\text{or } 2 - 2x = 3x$$

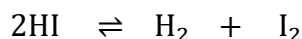
$$5x = 2$$

$$x = 2/5$$

37. HI was heated in a sealed tube at 440°C till the equilibrium was established. The dissociation 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



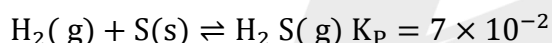
$$1 \quad 0 \quad 0$$

$$1 - \frac{22}{100} \quad \frac{22}{100 \times 2} \quad \frac{22}{100 \times 2}$$

$$0.78 \quad 0.11 \quad 0.11$$

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

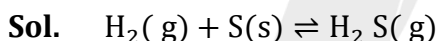
38. At 87°C , the following equilibrium is established



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)



Concentration at equilibrium $0.5 - x \quad x$

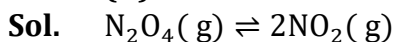
$$K_C = \frac{[\text{H}_2\text{S}]}{[\text{H}_2]} \Rightarrow 7 \times 10^{-2} = \frac{x}{0.5-x}$$

$$x = 0.0327$$

$$P_{\text{H}_2\text{S}} = \left(\frac{n_{\text{H}_2\text{S}}}{V} \right) RT \Rightarrow 0.0327 \times 0.0821 \times 360 \Rightarrow 0.966 \text{ atm.}$$

39. 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)



$$\text{at } P_1 (t = \text{Eq}) \quad 1 - 0.4 \quad 2(0.4)$$

$$= 0.6 = 0.8$$

$$\text{at } P_2(t = \text{Eq}) \quad 1 - 0.5 \times 2(0.5)$$

$$= 0.5 = 1$$

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

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

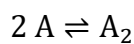
40. ΔG° for the dissociation of the dimer ($A_2 \rightleftharpoons 2 A$) in benzene solution at 27°C is 6.909 kJ/mol . If 8 moles of A is dissolved in 10 dm^3 of benzene at 27°C . What is the ratio of equilibrium concentration of monomer to dimer ($[A]/[A_2]$)? Given : $R = 2 \text{ Cal/mol} \cdot \text{K}$
 (A) 1: 200 (B) 1: 100 (C) 200: 1 (D) 800: 1

Ans. (A)

Sol. $\Delta G^\circ = -RT \ln K_{\text{eq}}$

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

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



$$0.8 - 2x$$

$\therefore K'_C$ is very high

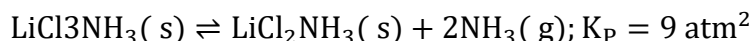
$$\text{so } 2x = 0.8 \Rightarrow x \approx 0.4$$

$$\therefore 0.8 - 2x \approx y$$

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

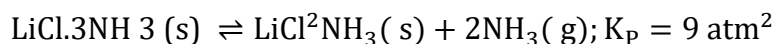
$$\frac{[A]}{[A_2]} = \frac{y}{x} = \frac{2 \times 10^{-3}}{0.4} = \frac{5}{1000} = \frac{1}{200}$$

41. For the equilibrium at 27°C .



at this temperature to drive backward reaction for completion.

For the equilibrium at 27°C .



A 24.63 litre flask contain $1 \text{ mol LiCl} \cdot \text{NH}_3$. How many moles of NH_3 should be added to flask

at this temperature to drive backward reaction for completion.

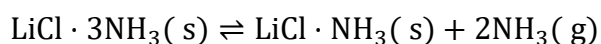
Sol. $K_P = 9 \text{ atm}^2$

$$p_{\text{NH}_3}^2 = 9 \text{ atm}^2$$

$$p_{\text{NH}_3} = 3 \text{ atm}$$

$$3 \times 24.63 = n_{\text{NH}_3} \times R \times 300$$

$$n_{\text{NH}_3} = 3 \text{ (at equilibrium)}$$

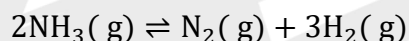


$$\begin{array}{ccc} 1 & n & \\ 0 & n - 2 & \end{array}$$

$$n - 2 = 3$$

$$n = \text{moles}$$

42. In a system, the equilibrium reaction:



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 $\text{NH}_3(\text{g})$ and $\text{Ne}(\text{g})$. Calculate K_P (in atm^2)

Sol. $X_{\text{N}_2} + X_{\text{H}_2} = 1 - 0.1 - 0.1 = 0.8$

$$X_{\text{N}_2} = \frac{1}{4} \times 0.8 \Rightarrow 0.2$$

$$X_{\text{H}_2} = \frac{3}{4} \times 0.8 \Rightarrow 0.6$$

$$P_{\text{NH}_3} = 0.1 \times 10 = 1 \text{ atm}$$

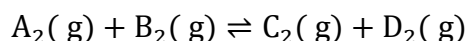
$$P_{\text{N}_2} = 0.2 \times 10 = 2 \text{ atm}$$

$$P_{\text{H}_2} = 0.6 \times 10 \Rightarrow 6 \text{ atm}$$

$$K_P = 2 \times 216$$

$$K_P = 432 (\text{atm})^2$$

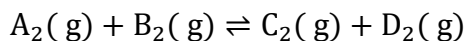
43. At a certain temperature the equilibrium constant K_C is 0.25 for the reaction



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. $Q = \frac{1 \times 1}{1 \times 1} \Rightarrow 1$

$\therefore Q > K_C$ so reaction will proceed in backward direction

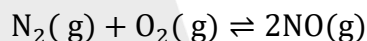


concentration at equilibrium $\frac{1.0+x}{10} \quad \frac{1.0+x}{10} \quad \frac{1.0-x}{10} \quad \frac{1.0-x}{10}$

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

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

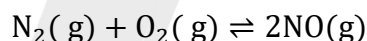
- 44.** At a certain temperature, equilibrium constant $K_C = 4 \times 10^{-2}$ for the reaction



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

reaction will proceed in backward direction



Initial moles 2 2 1.5

Moles at eq^m 2 + x 2 + x 1.5 - 2x

conⁿ at eq^m $\frac{2+x}{5} \quad \frac{2+x}{5} \quad \frac{1.5-2x}{5}$

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

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

$$1.5 - 2x = 0.4 + 0.2x \quad x = 0.5$$

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