Chemical Equilibrium

Introduction :

Equilibrium is a state in which there are no observable changes as time goes by. When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time and there are no visible changes in the system. However, there is much activity at the molecular level because reactant molecules continue to from product molecules while product molecules react to yield reactant molecules. This dynamic situation is the subject of this chapter. Here we will discuss different types of equilibrium reactions, the meaning of the equilibrium constant and its relationship to the rate constant and factors that can disrupt a system at equilibrium.

Types of chemical reactions

IRREVERSIBLE REACTION

The reaction which proceed in one direction only

(a) Precipitation reactions e.g.

$NaCl\ (aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl\downarrow$

(b) Neutralization reactions e.g.

$HCl\ (aq) + NaOH(aq) \rightarrow NaCl(s) + H_2O$

(c) Reactions in open vessels with one of the gaseous product

REVERSIBLE REACTION

Reactions which proceed in both the direction. These are possible only in closed vessel e.g.

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

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

Types of chemical reactions

	Irreversible reaction		Reversible reaction
1	The reaction which proceeds in one direction (forward direction) only.	1	The reaction which proceed in both the direction under the same set of experimental conditions.
2	Reactants are almost completely converted into products. Products do not react to form reactants again.	2	Reactants form products and products also react to form reactants in backward direction. These are possible in closed vessels .
3	Do not attain equilibrium state.	3	Attain the equilibrium state and never go to completion.
4	Such reactions are represented by single arrow {$\rightarrow$}	4	Represented by double arrow ($\rightleftharpoons$) or ($\rightleftarrows$)
5	Examples –	5	Examples :–
(a)	Precipitation reactions e.g. $NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl\downarrow$	(a)	Homogeneous reactions- only one phase is present (i) Gaseous phase–
(b)	Neutralization reactions e.g $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$		$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ [Birkland eyde process (HNO_3)]
(c)	$2KClO_3\ (s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$		$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (Haber's process)
(d)	Reactions in open vessel :– Even a reversible reaction will become irreversible if it is carried out in open vessel. Ex. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ Open vessel		(ii) Liquid phase $CH_3\ COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ Heterogeneous reactions– More than one phases are present $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
		(b)	$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ Closed vessel

State of Chemical equilibrium :

State of equilibrium means the balance of driving forces i.e. the factors taking the reaction in forward direction and the backword direction are balancing each other.

The equilibrium state represents a compromise between two opposing tendencies.

- Molecules try to minimise energy.
- Molecules try to maximise entropy.

In a reversible reaction like–

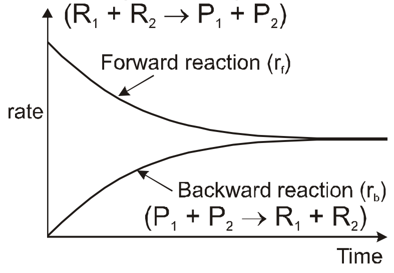
$$\underbrace{R_1 + R_2}_{\text{Reactants}} \rightleftharpoons \underbrace{P_1 + P_2}_{\text{Products}}$$

Initially only reactants are present. R_1 and R_2 combine to form P_1 and P_2. As soon as P_1 and P_2 are formed, they start the backward reaction. As concentrations of R_1 and R_2 decrease rate of forward reaction decreases and rate of backward reaction increases. Ultimately a stage is reached when both the rates become equal. Such a state is known as " Chemical Equilibrium" or "state of Equilibrium".

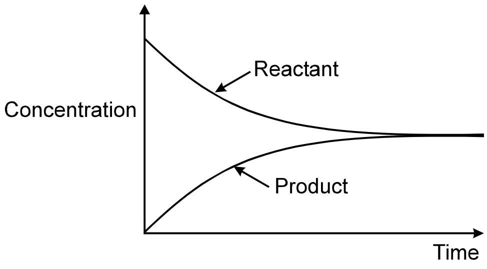
At equilibrium :

(i) Rate of forward reaction (r_f) = rate of backward reaction (r_b)

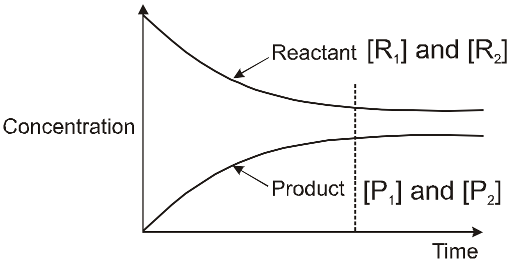
(ii) Concentration (mole/litre) of reactant and product remains constant with respect to time.



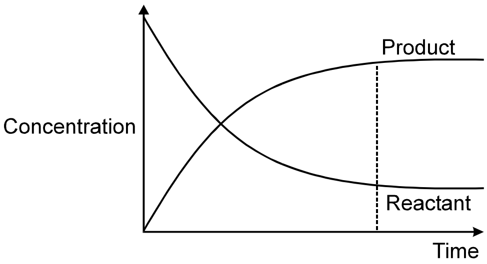
Equilibrium $r_f = r_b$



Equilibrium



Equilibrium



Equilibrium

Types of equilibria on the basis of process

Physical Equilibrium

Equilibrium in physical process is called physical equilibrium.

For example phase changes like $H_2O(l) \rightleftharpoons H_2O(g)$;
Solvation like
$NaCl(s) \underset{excess}{\overset{H_2O}{\rightleftharpoons}} NaCl(aq)$

Chemical Equilibrium

Equilibrium in chemical process is called chemical equilibrium.

For example
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

Types of equilibria on basis of physical state

Homogeneous equilibrium
When all reactants and products are in same phase
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

Heterogeneous equilibrium
When more than one phase are present
$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
$2Na_2O_2(s) + 2H_2O(\ell) \rightleftharpoons 4NaOH + O_2(g)$

Characteristics of chemical equilibrium :

- The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved from both direction.
- Equilibrium is dynamic in nature.
  It means that reaction has not stopped. It appears that no change is occuring but But both the opposing reactions are proceeding at the same rate. So there is no net change.Thus equilibrium is not static in nature.
- A catalyst can alter the rate of approach of equilibrium but does not change the state of equilibrium. By using catalyst, the equilibrium can be achieved in different (more/less) time, but the relative concentrations of reactants and products are same irrespective of the presence or absence of a catalyst.
- Equilibrium can be observed by constancy of some observable properties like colour, pressure, concentration, density, temperature, refractive index etc.which may be suitable in a given reaction.
- At equilibrium, free energy change $\Delta G = 0$
- Equilibrium state can be affected by altering factors like pressure, volume, concentration and temperature etc.(Le chateliers Principle).
- System moves toward an equilibrium state spontaneously even if it is disturbed. It will return to original state.

Law of mass action : [By Guldberg and Waage]

Rate at which a substance reacts $\propto$ [Active Mass of the substance]

Active Mass = Molar concentration i.e. Moles/Litres = $\dfrac{\text{Wt of substance (gram)}}{\text{Molar wt.} \times \text{Vol.(Litre)}}$

It is represented in square brackets i.e. [ ] e.g. [A], $[N_2]$ etc.

The rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients.

Ex. $aA + bB \longrightarrow$ products
Rate of reaction $\alpha\ [A]^a [B]^b$
Rate = $k [A]^a [B]^b$,
where k is the rate constant of the reaction.

Solved Examples

1. Four vessel each of volume V = 10 Lilres contains

(1) 16 g CH_4 (2) 18 g H_2O (3) 35.5 g Cl_2 (4) 44 g CO_2

Which container will contain same molar concentration and same active mass as that in (1)?

Sol. (1) $\Rightarrow [CH_4] = \dfrac{16}{16 \times 10} = 0.1$ M (2) $[H_2O] = \dfrac{18}{18 \times 10} = 0.1$ M

(3) $\Rightarrow [Cl_2] = \dfrac{35.5}{71 \times 10} = 0.05$ M (4) $[CO_2] = \dfrac{44}{44 \times 10} = 0.1$ M

Hence, (2) and (4) has same molar concentration as that in (1)

Equilibrium constant (K) :

For a general reaction

$aA + bB \rightleftharpoons cC + dD$,

Forward reaction rate $r_f = k_f [A]^a [B]^b$,

Backward reaction rate $r_b = k_b [C]^c [D]^d$,

At equilibrium $r_f = r_b$

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

The concentrations of reactants & products at equilibrium are related by

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

❍ **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.

e.g. $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2(g) \Rightarrow K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Rightarrow K_C = \frac{[NH_3]^2}{[N_2]\ [H_2]^3}$

e.g. $\frac{1}{2}\ H_2(g) + \frac{1}{2}\ I_2(g) \rightleftharpoons HI(g) \Rightarrow K_c = \frac{[HI]'}{[H_2]^{1/2}[I_2]^{1/2}}$

Solved Examples

2. What should be the relationship between K_2 and K_1, if the equilibrium constant of the reaction given below are K_1 and K_2 respectively ?

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $SO_2(g) + \frac{1}{2}\ O_2(g) \rightleftharpoons SO_3(g)$

(1) $K_2 = K_1$ (2) $K_2 = \sqrt{K_1}$ (3) $K_2 = K_1$ (4) $2K_2 = K_1$

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

$K_1 = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ $K_2 = \frac{[SO_3]}{[SO_2][O_2]}$

Therefore, $K_2 = \sqrt{K_1}$

3. In a reaction $A\ (g) + B\ (g) \rightleftharpoons C\ (g) + D(g)$, A, B, are mixed in a vessel at temperature T. The initial concentration of A was twice the initial concentration of B. After the equilibrium is reached, concentration of C was thrice the concentration of B Calculate K_C.

Sol. Let concentration of B initially is 'a' mole/litre

	A +	B ⇌	C +	D	⇒ Δn = 0
at t = 0	2a	a	0	0	
at $t = t_{eq}$	2a – x	a – x	x	x	

Given that

$x = 3\ (a - x) \Rightarrow x = \frac{3}{4}a$ $K_C = \frac{[C]\ [D]}{[A]\ [B]}$

$$K_c = \frac{x.x}{(2a - x)(a - x)} \Rightarrow K_c = \frac{\left(\frac{3a}{4}\right)^2}{\left(2a - \frac{3a}{4}\right)\ \left(a - \frac{3a}{4}\right)} \Rightarrow K_c = \frac{9}{5} = 1.8$$

- K_P → **Equilibrium constant in terms of partial pressure.** It is defined for the equilibrium reaction which contains at least one gaseous component.

  e.g. $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

  $$K_P = \frac{[P_C]^c\,[P_D]^d}{[P_A]^a\,[P_B]^b}$$

  where various pressures are the partial pressures of various gases substancs.

Solved Examples

4. What should be the value of K_C for the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$. If the amount are SO_3 = 48g, SO_2 = 12.8 and O_2 = 9.6 at equilibrium and the volume of the container is one litre ?

(1) 64 (2) 0.30 (3) 42 (4) 8.5

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

$K_C = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ Concentration in gram mole/litre, therefore

$[SO_3] = \dfrac{48}{80 \times 1}$ (Where 80 is molecular weight of SO_3)

$[SO_2] = \dfrac{128}{64 \times 1}$ (Where 64 is molecular weight of SO_2)

$[O_2] = \dfrac{9.6}{32 \times 1}$ (Where 32 is molecular weight of O_2)

$$\text{Thus, } K_C = \frac{\left(\frac{48}{80}\right)^2}{\left(\frac{12.8}{64}\right)^2\left(\frac{9.6}{32}\right)} = 0.30$$

5. If 0.5 mole H_2 is reacted with 0.5 mole I_2 in a ten-litre container at 444°C and at same temperature value of equilibrium constant K_C is 49, the ratio of [H] and $[I_2]$ will be :

(1) 7 (2) $\dfrac{1}{7}$ (3) $\sqrt{\dfrac{1}{7}}$ (4) 49

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

$K_C = \dfrac{[HI]^2}{[H_2][I_2]}$ if $[H_2] = [I_2]$

$K_C = \dfrac{[HI]^2}{[I_2]^2}$ $[HI]^2 = K_C \times [I_2]^2$

or $\dfrac{[HI]^2}{[I_2]^2} = K_C$ or $\dfrac{[HI]}{[I_2]} = \sqrt{K_C} = \sqrt{49} = 7$

6. 1.1 mole of A mixed with 2.2 mole of B and the mixture is kept in a 1 litre at the equilibrium $A + 2B \rightleftharpoons 2C + D$ is reached. At equilibrium 0.2 mole of C is formed then the value of K_C will be :

Ans.

	A	+	2B	$\rightleftharpoons$	2C	+	D
Initial mole	1.1		2.2		0		0
At Eq.	1.1 – x		2.2 – 2x		2x		x
	1.1 – 0.1		2.2 – 0.2		0.2		0.1

	1	2	0.2	0.1
Active mass	$\frac{1}{1}$	$\frac{2}{1}$	0.2	0.1

$$K_C = \frac{[C]^2[D]}{[A][B]^2} = \frac{\frac{2}{10}\times\frac{2}{10}\times\frac{1}{10}}{1\times 2\times 2} = \frac{1}{1000} = 0.001$$

7. In the reaction, $N_2 + O_2 \rightleftharpoons 2NO$, the moles/litre of N_2, O_2 and NO respectively 0.25, 0.05 and 1.0 at equilibrium, the initial concentration of N_2 and O_2 will respectively be :

(1) 0.75 mol/litre, 0.55 mole/litre
(2) 0.50 mole/litre, 0.75 mole/litre
(3) 0.25 mole/litre, 0.50 mole/ litre
(4) 0.25 mole/litre, 1.0 mole/litre

Ans.

N_2	+	O_2	$\rightleftharpoons$	$2NO$	
a		b		0	2x = 1.0 mole/litre
(a – x)		(b–x)		2x	x = 1.0/2 mole/litre = 0.50 mole/litre

If a – x = 0.25, b – x = 0.05

$[N_2]$ = a = a – x + x = 0.25 + 0.50 = 0.75 mole/litre

8. In the reaction, $PCl_5 \rightleftharpoons Cl_2$, the amount of each PCl_5, PCl_3 and Cl_2 is 2 mole at equilibrium and total pressure is 3 atmosphere. The value of K_P will be

(1) 1.0 atm (2) 3.0 atm (3) 2.9 atm (4) 6.0 atm

Ans.

PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
2		2		2

Total mole of equilibrium = 2 + 2 + 2 = 6 mole

and total pressure (P) = 3 atm

$$K_P = \frac{p_{PCl_3}p_{Cl_2}}{p_{PCl_5}}$$

$$(p_{PCl_5}) = \frac{2}{6}\times 3 = 1$$

$$(p_{PCl_5}) = \frac{2}{6}\times 3 = 1$$

$$(p_{PCl_5}) = \frac{2}{6}\times 3 = 1$$

$$\therefore K_P = \frac{1\times 1}{1}\ 1\text{ atm}$$

9. How many moles per litre of PCl_5 has to be taken to obtain 0.1 mole Cl_2, if the value of equilibrium contant K_C is 0.04 ?

(1) 1.15 (2) 0.25 (3) 0.35 (4) 0.05

Ans.

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$	Here a = ?
Initial mole	a		0		0	V = 1 litre
Mole at equilibrium	a – x		x		x	$K_C = 0.04$

$$K_C = \frac{x^2}{(a-x)V} = \frac{0.1\times 0.1}{V(a-x)}$$

$$a - x = \frac{0.1\times 0.1}{1\times 0.04} = \frac{1}{4} = 0.25$$

a = a – x + x = 0.25 + 0.10 = 0.35

❍ **Relation between K_p & K_c**

$$PV = nRT \qquad \text{or,} \qquad P = \frac{n}{V} RT$$

$$P = CRT \text{ where } C = \frac{n}{V} = \text{(moles per litre)}$$

$$P_C = [C]\,RT\ ;\ P_D = [D]\,RT\ ;\ P_A = [A]\,RT\ ; P_B = [B]\,RT$$

$$\Rightarrow \qquad K_P = \frac{[C]^c(RT)^c[D]^d(RT)^d}{[A]^a(RT)^a[B]^b(RT)^b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}\,(RT)^{(c+d)-(a+b)}$$

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

Where $\Delta n = (c + d) - (a + b)$, calculation of Δn involves only gaseous components.

$\Rightarrow$ Δn = sum of the number of moles of gaseous products – sum of the number of moles of gaseous reactants. <u>Δn can be positive, negative, zero or even fraction.</u>

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

$\Delta n = 1$ (because there is only one gas component in the products and no gas component in the reaction)

$\Rightarrow$ $K_p = K_c.(RT)$

Unit of Equilibrium contants :

- Unit of K_p is $(\text{atm})^{\Delta n}$
- Unit of K_c is $(\text{mole/Lit})^{\Delta n} = (\text{conc.})^{\Delta n}$

Note : ❍ In fact, equilibrium constant does not carry any unit because it is based upon the activities of reactants and products and activities are unitless quantities. Under ordinary circumstances, where activities are not known, above types of equilibrium constant and their units are employed.

❍ **For pure solids and pure liquids, although they have their own active masses but they remain constant during a chemical change (reaction). Therefore, these are taken to be unity for the sake of convenience.**

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

$K_C = [CO_2]$, $K_P = P_{CO_2}$

Solved Examples

10. Calculate k_p and K_c if initially a moles of PCl_5 is taken

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

Sol.

$$\begin{array}{llccc} & & PCl_5\,(g) & \rightleftharpoons PCl_3(g) & + \ Cl_2(g) \\ \text{At} & t = 0 & a & 0 & 0 \\ \text{At} & t = t_{eq} & (a - x) & x & x \end{array}$$

$$[PCl_5] = \frac{a - x}{V}, \qquad [PCl_3] = \frac{x}{V}, \qquad [Cl_2] = \frac{x}{V}$$

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

Total no. of moles = a – x + x + x = a + x

$$[P_{PCl_5}] = \frac{(a-x)P}{a+x}, \qquad [P_{PCl_3}] = \frac{x\ .\ P}{a+x}, \qquad [P_{Cl_2}] = \frac{x.P}{a+x}$$

$$K_P = \frac{\left(\frac{xP}{a+x}\right).\left(\frac{xP}{a+x}\right)}{\left(\frac{a-x\quad P}{a+x}\right)} = \frac{x^2P}{a^2-x^2}$$

Applications of Equilibrium constant :

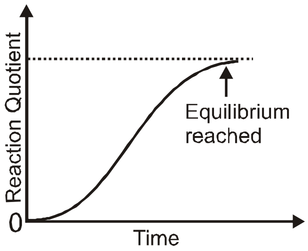
- **Predicting the direction of the reaction**

  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 denoted by symbol Q.

It helps in predicting the direction of a reaction.

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



- *The reaction quotient is a variable quantity with time.*
- *It helps in predicting the direction of a reaction.*

- if $Q > K_c$ reaction will proceed in backward direction until equilibrium in reached.
- if $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.
- if $Q = K_c$ Reaction is at equilibrium.

eg. $2A(g) + B(g) \rightleftharpoons C(g) + D(g)$

Q_C = Reaction quotient in terms of concentration

$$Q_C = \frac{[C][D]}{[A]^2[B]}$$

$K_C = \frac{[C]_{eq}[D]_{eq}}{[A]^2_{eq}[B]_{eq}}$ [Here all the conc. are at equilibrium]

Solved Examples

11. At 227°C, 60% of 2 gram moles of PCl_5 gets dissociated in a two litre container. The value of K_p will be

(1) 450 R (2) 400 R (3) 50 R (4) 100 R

Ans.

PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2	
					Initial mole
$\frac{2-12}{2}$		$\frac{12}{2}$		$\frac{12}{2}$	Mole at equilibrium

$$K_C = \frac{x^2}{V(a-x)} = \frac{12\times12}{2(2-12)}$$

$$K_C = \frac{12\times12}{2\times0.80} = 0.9$$

$K_p = K_C \times (RT)^1 = 0.9 \times (R \times 500) = 450$ R

12. For the reaction $NOBr\,(g) \rightleftharpoons NO(g) + \frac{1}{2} Br_2\,(g)$

$K_P = 0.15$ atm at 90°C. If NOBr, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2 atm respectively, will Br_2 be consumed or formed ?

Sol. $$Q_P = \frac{\left[P_{Br_2}\right]^{1/2}[P_{NO}]}{[P_{NOBr}]} = \frac{[0.2]^{1/2}\ \ [0.4]}{[0.50]} = 0.36$$

$K_P = 0.15$

$\therefore$ $Q_P > K_P$

Hence, reaction will shift in backward direction

$\therefore$ Br_2 will be consumed

13. The reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is statrted in a five litre container by taking one mole of PCl_5. If 0.3 mole of PCl_5 is there at equilibrium, the total mole and concentration of PCl_5 and K_C will respectively be

(1) 0.70, 0.14, $\frac{49}{150}$ (2) 0.30, 0.12, $\frac{23}{100}$

(3) 0.10, 0.07, $\frac{23}{100}$ (4) 0.05, 20, $\frac{49}{150}$

Ans.

PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2	
1		0		0	Initial mole
					Conc. at equilibrium

Total mole of PCl_3 = 0.7

Concentration = 0.14

$$K_C = \frac{x^2}{(1-x)V} = \frac{0.7\times0.7}{0.3\times5} = \frac{49}{150}$$

14. When sulphur in the form of S_8 is heated at 900 K, the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the value of equilibrium constant for this reaction.

Sol. $S_8(g) \rightleftharpoons 4S_2(g)$

Initial pressure 1 atm 0

Eq. Pressure (1–x) atm 4x atm

But x = 0.29 atm

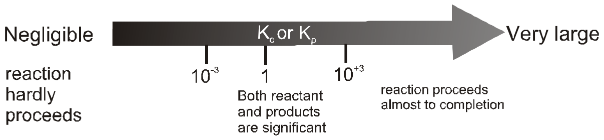
$\therefore \quad P_{S_8} = 1 - x = 1 - 0.29 = 0.71$ atm

$P_{S_2} = 4x = 4 \times 029 = 1.16$ atm

$$K_p = \frac{(pS_2)^4}{pS_8} = \frac{(1.16)^4}{0.71} = 2.55 \text{ atm}^3$$

- **Predicting the extent of the reaction**

$$K = \frac{[\text{Product}]}{[\text{Reactant}]}$$



Case-I : If K is large ($k > 10^3$) then product concentration is very very larger than the reactant ([Product] >>[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] << [Reactant]

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

In this case, the reaction is reactant favourable.

Solved Examples

15. The K_P values for three reactions are 10^{-5} , 20 and 300 then what will be the correct order of the percentage composition of the products.

Sol. Since K_p order is $10^{-5} < 20 < 300$ so the percentage composition of products will be greatest for $K_p = 300$.

- **Calculating equilibrium concentrations**

  The concentration of various reactants and products can be calculated using the equilibrium constant and the initial concentrations.

Solved Examples

16. 1 mole of N_2 and 3 moles of H_2 are placed in 1L vessel. Find the concentration of NH_3 at equilibrium, if equilibrium pressure is 1 atm and the equilibrium constant at 400K is $\frac{4}{27}$

Sol. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $(\Delta n < 0)$

1mol 3 mol 0

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

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

$$K_C = \frac{[NH_3]^2}{[N_2]\ [H_2]^3} = \frac{(2x)^2}{(3-3x)^3(1-x)} = \frac{4}{27}$$

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

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

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

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

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

$[NH_3] = 0.38 \times 2 = 0.76$

Characteristics of equilibrium constant & factors affecting it :

- Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached
- The equilibrium constant does not give any idea about time taken to attain equilibrium.
- **K depends on the stoichiometry of the reaction.**
  - ○ If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1 . K_2$

		Equation constant
	$A(g) \rightleftharpoons B(g)$	K_1
	$B(g) \rightleftharpoons C(g)$	K_2
On adding	$A(g) \rightleftharpoons C(g)$	$K = K_1 . K_2$

  - ○ If the reaction having eq. constant K_1 is reversed then resulting equation has eq. constant $\frac{1}{K_1}$

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$

On reversing, $C(g) + D(g) \rightleftharpoons A(g) + B(g)$ $K = \frac{1}{K_1}$

  - ○ If a chemical reaction having equilibrium constant K_1 is multiplied by a factor n then the resulting equation has equilibrium constant $K = (K_1)^n$, n can be fraction

eg. $D_2(g) \rightleftharpoons 2A(g)$ K_1

Multiplying by $\left(\frac{1}{2}\right)$, $\frac{1}{2} D_2(g) \rightleftharpoons A(g)$ $K = (K_1)^{1/2} = \sqrt{K_1}$

Solved Examples

17. The value of K_c for the reaction, $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ at a certain temperature is 400. calculate the value of equilibrium constant for.

(i) $2NO_2(g) \rightleftharpoons N_2(g) + 2\ O_2(g)$; (ii) $1/2\ N_2(g) + O_2(g) \rightleftharpoons NO_2(g)$

Sol. Equilibrium constant (K_c) for the reaction N_2 (g)+ $2O_2$(g) $2NO_2$(g) is

$$K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 400$$

(i) For the reaction $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$, $K'_C = \frac{[N_2][O_2]^2}{[NO_2]^2} = \frac{1}{K_c}$

$$K'_c = \frac{1}{400} = 0.0025 \text{ mole litre}^{-1}$$

(ii) For the reaction $1/2\ N_2(g) + O_2(g) \rightleftharpoons NO_2(g)$

$$K''_c = \frac{[NO_2]}{[N_2]^{1/2}[O_2]} = \sqrt{K_c} \qquad \Rightarrow \qquad K''_c = \sqrt{400} = 20 \text{ litre}^{-1/2} \text{ mole}^{-1/2}$$

- **Equilibrium constant is dependent only on the temperature.**

  It means k_p and k_c will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.

  ❍ However if temperature is changed,

$$\log \frac{k_2}{k_1} = \frac{\Delta H}{2.303 \quad R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \text{ ; } \Delta H = \text{Enthalpy of reaction}$$

  If $T_2 > T_1$ then $K_2 > K_1$ provided ΔH = +ve (endothermic reaction)

  $K_2 < K_1$ if ΔH = –ve (exothermic reaction)

  In the above equation, the unit of R and $\Delta H/T$ should be same.

- **Relation between equilibrium constant & standard free energy change.**

  $\Delta G^o = -2.303\ RT \log K$

  Where $\Delta G°$ = standard free energy change

  T = Absolute temperature,

  R = universal gas constant.

Solved Examples

18. From the following data :

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

$K_{2000K} = 4.4$

(ii) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$

$K_{2000K} = 5.31 \times 10^{-10}$

(iii) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

$K_{1000K} = 2.24 \times 10^{22}$

State whether the reaction (iii) is exothermic or endothermic?

Sol. Equation (iii) = – [2 × (i) + (ii)]

$$\therefore K_{2000\ (iii)} = \frac{1}{K_1^2\ \ K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$\because T\uparrow\ K\downarrow \qquad \Rightarrow$ reaction is exothermic.

Homogeneous liquid system : Formation of ethyl acetate :

The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.

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

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Solved Examples

19. In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at T°C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterfied. Calculate the equilibrium constant of this reaction.

Sol. $CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$

	$CH_3COOH(\ell)$	$C_2H_5OH(\ell)$	$CH_3COOC_2H_5(\ell)$	$H_2O(\ell)$
Initial	1	1	0	1
At equilibrium	1 – x	1 – x	x	1 + x
	1 – 0.543	1 – 0.543	0.543	1 + 0.543

(54.3% of 1 mole = $\frac{1 \times 54.3}{100}$ = 0.543 mole)

Hence given x = 0.543 mole

Applying law of mass action :

$$K_C = \frac{[ester][water]}{[acid][alcohol]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$$

❍ **EQUATION INVOLVING IONS :**

Equilibrium involving ions always take place in aquous medium . In case of expression of K_C concentration of ion is taken.

Ex. $Ag^+(aq.) + Cl^-(aq.) \rightleftharpoons AgCl(s)$ $K_c = \frac{1}{[Ag^+][Cl^-]}$

Heterogenous Equilibrium :

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

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

  $K_P = P_{CO_2}$, $K_C = [CO_2\,(g)]$

  $$[CaCO_3(s)] = \frac{moles}{volume} = \frac{W_{CaCO_3}}{\frac{M_{CaCO_3}}{V}} = \frac{density\ \ CaCO_3}{M_{CaCO_3}} = constant$$

  $$K = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]} \Rightarrow \frac{K.[CaCO_3(s)]}{[CaO(s)]} = [CO_2(g)]$$

  $K_C = [CO_2(g)]$

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

  $K_P = P_{H_2O\,(g)}$, $K_C = [H_2O\,(g)]$

  [For pure solid and pure liquid active mass is taken as unity i.e. = 1]

Solved Examples

20. In a reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts. Calculate K_P.

Sol.

	$C(s) + CO_2(g) \rightleftharpoons$	$2CO(g)$
$t = 0$	a	0
$t = t_{eq}$	$a - \frac{a}{2}$	$2\frac{a}{2}$

$P_{eq} = 12$ atm

$X_{CO_2} = \frac{1}{3}$, $X_{CO} = \frac{2}{3}$

$P_{CO_2} = \frac{1}{3} \times 12 = 4$

$P_{CO} = \frac{2}{3} \times 12 = 8$

$\therefore \quad K_P = \frac{8 \times 8}{4} = 16$

Degree of Dissociation (α) :

It is the fraction of one mole dissociated into the products.

(Defined for one mole of substance)

So, α = no. of moles dissociated / initial no. of moles taken

= fraction of moles dissociated out of 1 mole.

Note : % dissociation = α x 100

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

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

	$A_n(g) \rightleftharpoons$	$n\,A(g)$	
$t = 0$	a	0	
$t = t_{eq}$	$a - x$	$n.x$	$\alpha = \frac{x}{a} \Rightarrow x = a\alpha.$
	$a - a\alpha = a(1-\alpha)$	$n\,a\,\alpha$	

Total no. of moles $= a - a\alpha + n\,a\,\alpha$

$= [1 + (n - 1)\alpha]\,a$

<u>Significance of n</u>

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

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

Solved Examples

21. Calculate the degree of dissociation and K_p for the following reaction.

$$\begin{array}{llll} & PCl_5(g) \rightleftharpoons & PCl_3(g) + & Cl_2(g) \\ t = 0 & a & 0 & 0 \\ t = t & a - x & x & x \end{array}$$

Since for a mole, x moles are dissociated

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

$x = a\alpha$

$$\begin{array}{lllll} & & PCl_5(g) \rightleftharpoons & PCl_3(g) + & Cl_2(g) \\ \text{At} & t = t_{eq} & a - a\alpha & a\alpha & a\alpha \end{array}$$

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

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

$$K_P = \frac{\left\{\left(\frac{\alpha P}{1+\alpha}\right)\right\}^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P} \qquad K_P = \frac{\alpha^2.P}{1-\alpha^2} \quad \text{(Remember)}$$

Observed molecular weight and Observed Vapour Density of the mixture

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

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

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

where M_{th} = theoritical 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.

❍ D = vapour density without dissociation = $\frac{M_{A_n}}{2}$

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

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

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

where M_T = Theoritical molecular wt. M_0 = observed molecular wt. or molecular wt. of the mixture at equilibrium.

Note : It is not applicable for n = 1 [eg. Dissociation of HI & NO].

Solved Examples

22. One mole PCl_5 is heated in a closed container of one litre capacity. At equilibrium 20% PCl_5 is not dissociated. What should be the value of K_C ?

(1) $(3-2)^{-1}$ (2) 3.2 (3) 2.4 (4) 42

Ans. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (20% is not dissociated, i.e., 80% is dissociated)

PCl_5	PCl_3	Cl_2
1	0	0
(1– 0.8)	0.8	0.8

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.8\times0.8}{0.2} = 3.2$$

23. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 33°C calculate the no. of moles of NO_2 if 100g of N_2O_4 were taken initially.

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

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

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

	$N_2O_4 \rightleftharpoons$	$2NO_2$
t = 0	a	0
t = t	$a - a\alpha$	$2a\alpha$

$$\text{no. of moles of } NO_2 = 2a\alpha = \frac{2\times100\times0.2}{92} = 0.435$$

External factors affecting equilibrium :

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.

- **Effect of 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.

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

[reactant] ↑ Forward shift
[Product] ↑ 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

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

- **Effect of volume :**
  - ❍ 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
    $\Delta n_g > 0$ reaction will shift in the forward direction
    $\Delta n_g < 0$ reaction will shift in the backward direction
    $\Delta n_g = 0$ reaction will not shift. eg. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (No effect)

Explanation :

(i) $\Delta n_g > 0$, eg. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_C = \frac{\frac{(n_{Cl_2})}{V} \times \frac{(n_{PCl_3})}{V}}{\frac{(n_{PCl_5})}{V}} \quad \Rightarrow \quad Q_C \propto \frac{1}{V} \text{ for } \Delta n_g > 0 \qquad [() = \text{moles}]$$

On increasing V, Q_C, decreases.

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

Thus, if, Volume ↑ Q_C ↓ (Forward shift)

Volume ↓ Q_C ↑ (Backward shift)

(ii) $\Delta n_g < 0$, eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_C = \frac{\left\{\frac{(n_{NH_3})}{V}\right\}^2}{\left\{\frac{(n_{N_2})}{V}\right\}\left\{\frac{(n_{H_2})}{V}\right\}^3} \quad \Rightarrow \quad Q_C \propto V^2 \qquad \text{for } \Delta n_g < 0$$

V ↑ Q_C ↑ (Backward shift) ; V ↓ Q_C ↓ (Forward shift)

- **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.

  ∵ $P \propto$ no. of moles

  (i) For $\Delta n_g = 0 \rightarrow$ No. effects

  (ii) For $\Delta n_g > 0$, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

  $$Q_p = \frac{(X_{PCl_3}P).(X_{Cl_2}P)}{(X_{PCl_5}.P)} \quad \Rightarrow \quad Q_P \propto P \qquad [X = \text{mole fraction}]$$

  P ↓ ; ↓ Q_P ; (Forward shift) [P = Total pressure at equilibrium]

  P↑ ; ↑ Q_P ; (Backward shift)

  (iii) For $\Delta n < 0$, eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

  $$Q_P = \frac{[(X_{NH_3})\ P)]^2}{[(X_{N_2}).\ P][(X_{H_2})\ P]^3} \quad \Rightarrow \quad Q_P \propto \frac{1}{P^2}$$

  P↑ ; Q_P↓ ; (Forward shift) ; P↓ ; Q_P↑ ; (Backward shift)

- **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.

- **Effect of inert gas addition :**

  (i) At constant volume : Inert gas addition has no effect at constant volume

  (ii) At constant pressure : If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

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

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

  (iii) $\Delta n_g = 0$, no effect

- **Effect of temperature :**

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

$A(g) + B(g) \rightleftharpoons C(g) + D(g) + \text{Heat} \qquad \Delta H = -\text{ve}$

eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$

$T\uparrow \Rightarrow$ K' will decrease (from vant' hoff equation)

$$\log \frac{K_1}{K_2} = \frac{\Delta H^o}{2.303\ R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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

$$\Rightarrow \qquad \log K_1 > \log K_2$$

$$\Rightarrow \qquad K_1 > K_2$$

Reaction will shift in backward direction.

$T\downarrow \Rightarrow$ K will increases.

Reaction will shift in forward direction.

(ii) **Endothermic reaction :** energy consumed.

$A(g) + B(g) \rightleftharpoons C(g) + D(g) - \text{Heat} \qquad \therefore \Delta H = +\text{ve}$

$T\uparrow \Rightarrow K\uparrow \Rightarrow$ Forward ; $T\downarrow \Rightarrow K\downarrow \Rightarrow$ Backward

Solved Examples

24. The volume of a closed reaction vessel in which the equilibrium, $2SO_2(g) + O_2(g)$ $2SO_3(g)$ is halved, Now

(1) The rates of forward and backward reactions will remains the same.

(2) The equilibrium will not shift.

(3) the equilibrium will shift to the right.

(4) The rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

Sol. **(4)** In the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

In this reaction three moles (or volumes) of reactants are converted into two moles (or volumes) of products i.e. there is a decreases in volume and so if the volume of the reaction vessel is halved the equilibrium will be shifted to the right i.e. more product will be formed and the rate of forward reaction will incerases i.e. double that of reverse reaction.

25. Nitrogen and hydrogen react to form ammonia as per the reaction, $\frac{1}{2}N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3\ (g)$

When the mixture of the three gases is in equilibrium predict whether the amount of ammonia increases or decreases if

(i) The pressure on the system is increased,

(ii) The temperature of the system is raised,

(iii) The concentration of hydrogen is increased.

Sol. (i) When pressure is increased, equilibrium shifts to that direction in which pressure decreases i.e. in the direction in which the number i of moles of gases decreases. hence, the reaction shifts in the forward direction and thus the amount of NH_3 increases.

(ii) As the forward reaction is exthormic, increases of temperature will shifts the equilibrium in the back directiuon (endothermic direction) and thus the amout of Nh_2 decreases.

(iii) On increasing the concentration of H_2 the equilibrium will shifts in the forward direction and thus the amount of NH_3 increases.

26. An endothermic reaction, $A(g) + 2B(g) \rightleftharpoons 2C(g)$
is in equilibrium at a certain temperature. can we increase the amount of C by
(i) adding catalyst (ii) Increasing pressure (iii) Increasing temperature

Sol. No, because catalyst does not distrub the equilibrium state
(ii) Yes, because increase in pressure will shift the equilibrium in forward direction as the number of moles of products is less than that of reactants.
(iii) Yes, because increase in temperature would shift the reaction in the forward direction endothermic direction)

Application of le chatelier's principle : Practical equilibrium situations :

- **Formation of diamond :**

$$\underset{\substack{\text{Density Low}\\ \text{Volume High}}}{\underset{\downarrow}{C\text{ (graphite)}}} \rightleftharpoons \underset{\substack{\text{Density High}\\ \text{Volume Low}}}{\underset{\downarrow}{C\text{ (diamond)}}} - \text{Heat}; \qquad \Delta H = +\text{ve}$$

Formation of diamond is favourable at high pressure and high temperature

- **Melting of ice :**

$$\underset{\substack{\text{Density Low}\\ \text{Volume High}}}{\underset{\downarrow}{H_2O\text{ (s)}}} \rightleftharpoons \underset{\substack{\text{Density High}\\ \text{Volume Low}}}{\underset{\downarrow}{H_2O\ (\ell)}}\ ; \qquad \Delta H = +\text{ve}$$

Melting of ice is favourable at high temperature and high pressure.

- **Boiling of water :**

$$\underset{\substack{\text{Density High}\\ \text{Volume Low}}}{\underset{\downarrow}{H_2O(\ell)}} \rightleftharpoons \underset{\substack{\text{Density Low}\\ \text{Volume High}}}{\underset{\downarrow}{H_2O(g)}}$$

On incerasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward.
Hence, on incerasing pressure, the boiling point increases.

- **Formation of ammonia by Haber's process :**

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -22.4$ Kcal/mol.

(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.

- **Manufacturing of SO_3 by contact process**

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 45.2$ kcal

High pressure (1.5 to 1.7 atm), Low temperature (500°C), Higher qunatity of SO_2 and O_2 are favourable conditions for the formation of SO_3.

- **Manufacturing of NO by Birkeland–Eyde process**

$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) - 43.2$ kcal

  - 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.