

# Chemical Equilibrium (\*) and Equilibrium Constant. Lecture - ②



1. What is called Reversible Reaction?

Ans: A reaction which can go in the forward and backward direction simultaneously is called a reversible reaction. Such a reaction is represented by writing a pair of arrows between the reactants and products.



The arrow pointing right indicates the forward reaction while that pointing left shows the backward reaction.

2. What do you mean by chemical equilibrium and dynamic chemical equilibrium.

Chemical equilibrium: The state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.

Dynamic chemical equilibrium: A dynamic chemical equilibrium is one in which there is no net change of concentrations of the reactants

and the products, although the reaction is proceed in both directions.

- Q. State the law of mass action and derive the equation of the equilibrium constant?

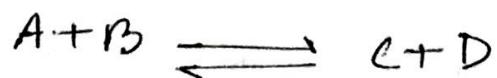
Law of Mass action: The rate of a chemical reaction at a given temperature is proportional to the active mass of each of the reactants present in the system.

Hence active mass means the molar concentration of the reactants. For gaseous reactions active mass means the partial pressure of the reactants.

Mathematical derivation of law of mass action:

or Derivation the equation of the equilibrium constant

Let us consider a  $\xrightleftharpoons{\text{reversible}}$  reaction



and let  $[A]$ ,  $[B]$ ,  $[C]$  and  $[D]$  represent the molar concentrations of A, B, C and D at the equilibrium point. According to the law of mass action

$$\text{Rate of forward reaction} \propto [A][B] = K_1[A][B]$$

$$\text{Rate of reverse reaction} \propto [C][D] = K_2[C][D]$$



where  $K_1$  and  $K_2$  are rate constants for the forward and reverse reactions.

At equilibrium,

rate of forward reaction = rate of reverse reaction

Therefore,

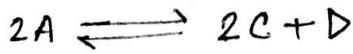
$$K_1 [A][B] = K_2 [C][D]$$

$$\text{or, } \frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

$$\text{or, } K_c = \frac{[C][D]}{[A][B]}$$

Here  $K_c$  is called the equilibrium constant.  $K_c$  is the ratio of rate of forward reaction and reverse reaction. At specific temperature, the value of  $K_c$  is constant. The subscript 'c' indicates that the value is in terms of concentrations of reactants and products.

Again consider the reaction



Applying the law of mass action on the above reaction, the equilibrium constant expression stands for,

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

Again consider the general reaction for equilibrium constant expression



Where  $a, b, c$  and  $d$  are numerical quotients of the substance A, B, C and D respectively.

The equilibrium constant stands for the above general reaction

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{--- (1)}$$

The partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature. Therefore, we can write the equilibrium constant expression in terms of partial pressure instead of molar concentrations and in this case equilibrium constant is expressed by  $K_p$ .

For the above general reaction.

$$K_p = \frac{[P_c]^c [P_d]^d}{[P_a]^a [P_b]^b} \quad \text{--- (2)}$$

where,  $P_A, P_B, P_C$  and  $P_D$  are the partial pressure of the substance A, B, C and D respectively.

If active mass is expressed by mole fraction, in this case, equilibrium constant is expressed by  $K_x$

*\* Hangpur*

For the above general reaction

$$K_x = \frac{[x_c]^c [x_d]^d}{[x_a]^a [x_b]^b} \quad \dots \quad (3)$$

where  $x_A, x_B, x_C$  and  $x_D$  are the mole fraction of the substance A, B, C and D respectively.

Equation ①, ② and ③ are the mathematical derivation of law of mass action.

or equation ①, ② and ③ are the equation of the equilibrium constant.

Q. 4. Deduce the relation between  $K_c$  and  $K_p$  ?

Let us consider the gaseous reversible general reaction



At equilibrium point, if the active mass of the reactants and products are expressed by molar concentrations, then according to the law of mass action, the equilibrium constant  $K_c$  stands for

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots \quad (1)$$

Hence,  $[A], [B], [C]$  and  $[D]$  are the molar concentration of A, B, C and D respectively at equilibrium point.

At equilibrium point, if the active mass of the reactants and products are expressed by partial pressure, then according to the law of mass action the equilibrium constant,  $K_p$  stands for the above general reaction

$$K_p = \frac{[P_c]^c [P_d]^d}{[P_A]^a [P_B]^b} \quad \text{--- (2)}$$

Hence  $P_A$ ,  $P_B$ ,  $P_c$  and  $P_d$  are the partial pressure of A, B, C and D respectively at equilibrium point.

For  $n$  moles of a gas in a gaseous mixture of volume  $V$  and Temperature  $T$ , the partial pressure is,

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

$$\text{or } P = CRT \quad \left[ \text{As } c = \frac{n}{V} = \text{molar concentration} \right. \\ \left. = \frac{\text{number of moles}}{\text{volume}} \right]$$

So, the partial pressure for the above general reaction

$$\text{The partial pressure of } A = P_A = [A]RT$$

$$\text{The partial pressure of } B = P_B = [B]RT$$

$$\text{The partial pressure of } C = P_c = [C]RT$$

$$\text{The partial pressure of } D = P_d = [D]RT$$

putting the value of partial pressure of A, B, C and D in the equation (2) we get



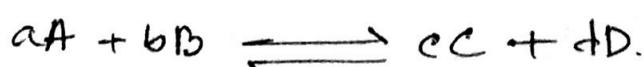
$$\begin{aligned}K_p &= \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} \\&= \frac{[C]^c [D]^d \times (RT)^{c+d}}{[A]^a [B]^b \times (RT)^{a+b}} \\&= \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{(c+d)-(a+b)} \\&= K_c (RT)^{\Delta n} \quad [\text{using the equation } ①] \\&\therefore K_p = K_c (RT)^{\Delta n} \quad \text{--- } ③\end{aligned}$$

Hence  $\Delta n$  = difference between the number of moles of the product gases and the number of moles of the reactant gases.

Equation ③ is the relation between  $K_p$  and  $K_c$ .

Q 5. Deduce the relation between  $K_p$  and  $K_X$ .

Let us consider the gaseous reversible general reaction



At equilibrium point, if the active masses of the reactants and products are expressed by partial pressure, then according to the law of

mass action, the equilibrium constant,  $K_p$  stands for

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad \text{--- } ①$$

Hence,  $P_A$ ,  $P_B$ ,  $P_C$  and  $P_D$  are the partial pressure of A, B, C and D respectively at equilibrium point.

Again, At equilibrium point, if the active mass of the substances are expressed by mole fraction, then according to the law of mass action, the equilibrium constant  $K_x$ , stands for

$$K_x = \frac{[x_C]^c [x_D]^d}{[x_A]^a [x_B]^b} \quad \text{--- } ②$$

Hence,  $x_A$ ,  $x_B$ ,  $x_C$  and  $x_D$  are the mole fraction of A, B, C and D respectively at equilibrium point.

Again, the partial pressure of a component is equal to the product of total pressure of the gaseous mixture and the mole fraction of the component gas.

$$\therefore p = x p$$

So, the partial pressure of A =  $p_A = x_A p$

the partial pressure of B =  $p_B = x_B p$

the partial pressure of C =  $p_C = x_C p$



the partial pressure of D =  $P_D = x_D P$

putting the value of partial pressure of A, B, C and D in the equation ① we get,

$$\begin{aligned}
 K_p &= \frac{[x_C]^c (P)^c [x_D]^d (P)^d}{[x_A]^a (P)^a [x_B]^b (P)^b} \\
 &= \frac{[x_C]^c [x_D]^d}{[x_A]^a [x_B]^b} \times \frac{P^{c+d}}{P^{a+b}} \\
 &= K_x P^{(c+d)-(a-b)} \quad [\text{using the equation } ②] \\
 \therefore K_p &= K_x P^{\Delta n} \quad ③
 \end{aligned}$$

Here  $\Delta n$  = difference between the number of moles of the product gases and the number of moles of the reactant gases.

Equation ③ is the relation between  $K_p$  and  $K_x$ .

Q. 6. Relation between  $K_p$  and  $K_x$ :

we know, from the relation between  $K_p$  and  $K_c$

$$K_p = K_c (RT)^{\Delta n} \quad ①$$

Again, from the relation between  $K_p$  and  $K_x$

$$K_p = K_x P^{\Delta n} \quad ②$$

From equation ① and ② we get

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

$$\text{or, } K_x = K_c \frac{(RT)^{\Delta n}}{P^{\Delta n}}$$

$$\text{or, } K_x = K_c \left(\frac{RT}{P}\right)^{\Delta n}$$

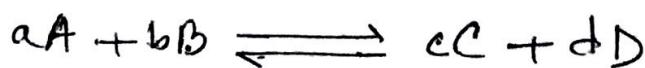
$$\text{or, } K_x = K_c V^{\Delta n} \quad [\text{As } PV = RT]$$

$$\text{or, } K_x = K_c V^{\Delta n} \quad \text{--- } ③$$

Equation ③ is the relation between  $K_c$  and  $K_x$

Q 7. Deduce the relation between  $K_c$ ,  $K_p$  and  $K_x$

Let us consider the gaseous reversible general reaction



At equilibrium point if the active mass of the reactants and products is expressed by molar concentrations, then according to the law of mass action, the equilibrium constant  $K_c$  stands for

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{--- } ①$$

Similarly, if the active mass of the substances is expressed by partial pressure, then according to the law of mass action, the equilibrium constant  $K_p$  stands for

$$K_p = \frac{[P_c]^c [P_d]^d}{[P_a]^a [P_b]^b} \quad \text{--- (2)}$$

Similarly, if the active mass of the substances is expressed by mole fraction, then according to the law of mass action, the equilibrium constant,  $K_x$  stands for

$$K_x = \frac{[x_c]^c [x_d]^d}{[x_a]^a [x_b]^b} \quad \text{--- (3)}$$

For  $n$  moles of a gas in a gaseous mixture of volume  $V$  and temperature  $T$ , the partial pressure of the gaseous component is

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

or  $P = CRT$  [As  $C = \frac{n}{V}$  = molar concentration]

So, the partial pressure for the above general reaction.

The partial pressure of  $A = P_A = [A]RT$

The partial pressure of  $B = P_B = [B]RT$

The partial pressure of C =  $P_C = [C]RT$

The partial pressure of D =  $P_D = [D]RT$

Putting the value of partial pressure of A, B, C and D in the equation ② we get,

$$K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

$$= \frac{[C]^c [D]^d \times (RT)^{c+d}}{[A]^a [B]^b \times (RT)^{a+b}}$$

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

$$\therefore K_p = K_c (RT)^{\Delta n} \quad \text{[using the equation ①]}$$

Hence  $\Delta n$  = difference between the number of moles of the product gases and the number of moles of the reactant gases.

Again we know, <sup>the</sup> partial pressure  $\phi$  is the product of total pressure and the mole fraction of the component.

$$\therefore \phi = xP$$

So, the partial pressure of A =  $p_A = X_A P$

the partial pressure of B =  $p_B = X_B P$

the partial pressure of C =  $p_C = X_C P$

the partial pressure of D =  $p_D = X_D P$

putting the value of partial pressure of A, B, C and D in the equation ② we get

$$K_P = \frac{[X_C]^c P^c [X_D]^d P^d}{[X_A]^a P^a [X_B]^b P^b}$$

$$= \frac{[X_C]^c [X_D]^d}{[X_A]^a [X_B]^b} \cdot \frac{P^{c+d}}{P^{a+b}}$$

$$= K_X P^{(c+d)-(a+b)} \quad [\text{using equation ③}]$$

$$\therefore K_P = K_X P^{\Delta n} \quad \text{--- } ⑤$$

Hence  $\Delta n$  = difference between the number of moles of the product gases and the number of moles of the reactant gases.

From equation ④ and ⑤ we get,

$$K_C \cdot (RT)^{\Delta n} = K_X P^{\Delta n}$$

$$\text{or } K_p = K_c \left( \frac{RT}{P} \right)^{\Delta n}$$

$$\text{or } K_p = K_c V^{\Delta n} \quad \text{--- (6)}$$

if  $\Delta n = 0$ ,

i.e. ~~if~~ if the number of moles of the products and the number of moles of the reactants be equal, then from equation (1), (5) and (6) we get

$$K_p = K_c$$

$$K_p = K_x$$

$$\text{and } K_x = K_c$$

$$\therefore K_p = K_c = K_x$$

It is the relation among  $K_p$ ,  $K_c$  and  $K_x$

Q. 8. Write expressions for the equilibrium constant  $K_c$  and  $K_p$  for the following reactions:

Q.C. — Applying the law of mass action find out the equilibrium constant for the following reaction.

①



At Initial  $a$   $b$

0

At equilibrium  $(a-\alpha)$   $(b-\alpha)$   $2\alpha$

Let us consider,  $a$  mole hydrogen and  $b$  mole iodine are kept in a sealed vessel of volume,  $V$  litre and are heated until the reaction reached at equilibrium. At equilibrium  $2\alpha$  moles of  $HI$  are produced. Thus at equilibrium the amount of hydrogen and the amount of iodine will be  $(a-\alpha)$  and  $b-\alpha$  moles respectively. In this condition

the molar concentration of  $H_2 = \frac{a-\alpha}{V}$  mol/litre

the molar concentration of  $I_2 = \frac{b-\alpha}{V}$  mol/litre

the molar concentration of  $HI = \frac{2\alpha}{V}$  mol/litre

Applying the law of mass action and substituting these values in the law of mass action equation, we get,

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \\ = \frac{(2\alpha/v)^2}{(\frac{a-\alpha}{v})(\frac{b-\alpha}{v})}$$

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

This is the equilibrium constant reaction.

Again,

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

For this reaction  $\Delta n = 0$

Thus,  $K_p = K_c$ .



At initial:  $2\alpha \quad 0 \quad 0$

At equilibrium:  $2\alpha - 2\alpha \quad \alpha \quad \alpha$

Let us consider,  $2\alpha$  mole of hydrogen iodide are heated in a sealed vessel of volume  $v$  litre.

At equilibrium  $2\alpha$  mole of hydrogen iodide are dissociated and are produced  $\alpha$  mole of hydrogen and  $\alpha$  mole of iodine. Thus at equilibrium  $2\alpha - 2\alpha$  mole of hydrogen iodide will remain undissociated.

In these condition.

The molar concentration of  $\text{HI} = \frac{2a - 2\alpha}{V}$  mole litre $^{-1}$

The molar concentration of  $\text{H}_2 = \frac{\alpha}{V}$  mole litre $^{-1}$

The molar concentration of  $\text{I}_2 = \frac{\alpha}{V}$  mole litre $^{-1}$

Applying the law of mass action equation, we get equilibrium constant,

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

$$= \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\left(\frac{2a - 2\alpha}{V}\right)^2}$$

$$= \frac{\alpha^2/V^2}{4(a-\alpha)^2/V^2}$$

$$\therefore K_c = \frac{\alpha^2}{4(a-\alpha)^2}$$

This is the equilibrium constant equation.

As in this reaction  $\Delta n = 0$

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

$$\therefore K_p = K_c$$



At initial:  $a$

$0$

At equilibrium.  $a-\alpha$

$2\alpha$

Let  $a$  mole of nitrogen tetroxide are heated in a sealed vessel of volume,  $V \text{ litre}$ . At equilibrium  $\alpha$  mole of  $\text{N}_2\text{O}_4$  is dissociated and  $2\alpha$  mole of  $\text{NO}_2$  is produced. So, the undissociated  $\text{N}_2\text{O}_4$  is  $a-\alpha$  mole. Therefore at equilibrium

$$\text{the molar concentration of } \text{N}_2\text{O}_4 = \frac{a-\alpha}{V} \text{ mol litre}^{-1}$$

$$\text{the molar concentration of } \text{NO}_2 = \frac{2\alpha}{V} \text{ mol litre}^{-1}$$

Applying the law of mass action equation, we get the equilibrium constant equation.

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$= \frac{\left(\frac{2\alpha}{V}\right)^2}{\left(\frac{a-\alpha}{V}\right)^2}$$

$$= \frac{4\alpha^2/V^2}{(a-\alpha)^2/V^2}$$

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

This is the equilibrium constant equation expressed by molar concentration.



NOW we shall calculate the equilibrium constant equation expressed by partial pressure.

Let, at equilibrium, the total pressure of the gaseous mixture is  $P$  and the number of total mole =  $a-\alpha + 2\alpha = a+\alpha$ . Therefore at equilibrium

$$\text{the partial pressure of } \text{N}_2\text{O}_4 = P_{\text{N}_2\text{O}_4} = \frac{a-\alpha}{a+\alpha} \times P$$

$$\text{the partial pressure of } \text{NO}_2 = P_{\text{NO}_2} = \frac{2\alpha}{a+\alpha} \times P$$

Applying the law of mass action equation, we get,  
the equilibrium constant.

$$K_p = \frac{\left[ P_{\text{NO}_2} \right]^2}{\left[ P_{\text{N}_2\text{O}_4} \right]} \\ = \frac{\left( \frac{2\alpha}{a+\alpha} \cdot P \right)^2}{\left( \frac{a-\alpha}{a+\alpha} \cdot P \right)}$$

$$= \frac{4\alpha^2 / (a+\alpha)^2}{(a-\alpha) / (a+\alpha)} \cdot P$$

$$\therefore K_p = \frac{\cancel{4\alpha^2} / \cancel{(a+\alpha)^2}}{\cancel{(a-\alpha)}^2} \cdot \frac{a+1}{a-\alpha} \cdot P \\ = \frac{4\alpha^2}{(a+\alpha)(a-\alpha)} \cdot P$$

This is the equilibrium constant expressed by partial pressure.

### Calculation of $K_x$ :

The total number of moles =  $a + \alpha + 2\alpha = a + \alpha$

$$\text{the mole fraction of } N_2O_4 = x_{N_2O_4} = \frac{a-\alpha}{a+\alpha}$$

$$\text{the mole fraction of } NO_2 = x_{NO_2} = \frac{2\alpha}{a+\alpha}$$

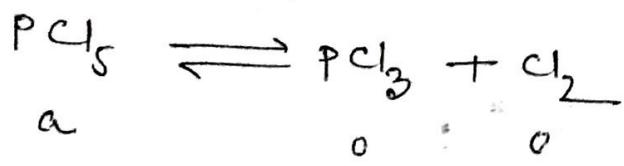
Applying the law of mass action equation we get equilibrium constant

$$\begin{aligned} K_x &= \frac{\left[ x_{NO_2} \right]^2}{x_{N_2O_4}} \\ &= \frac{\left( \frac{2\alpha}{a+\alpha} \right)^2}{\frac{a-\alpha}{a+\alpha}} \\ &= \frac{4\alpha^2 / (a+\alpha)^2}{(a-\alpha) / (a+\alpha)} \\ &= \frac{4\alpha^2}{a^2 - \alpha^2} \end{aligned}$$

This is the equation of equilibrium constant in terms of mole fraction.



(4)



At initial: a

0 0

At equilibrium: a- $\alpha$

$\alpha$   $\alpha$

Let, a mole of phosphorus pentachloride are heated in a sealed vessel of volume,  $V$  litres. At equilibrium  $\alpha$  mole of  $PCl_5$  are dissociated and are produced  $\alpha$  mole of  $PCl_3$  and  $\alpha$  mole of  $Cl_2$ . So, the undissociated  $PCl_5$  is  $a-\alpha$  mole. Therefore at equilibrium

$$\text{the molar concentration of } PCl_5 = [PCl_5] = \frac{a-\alpha}{V} \text{ mole L}^{-1}$$

$$\text{the molar concentration of } PCl_3 = [PCl_3] = \frac{\alpha}{V} \text{ mole L}^{-1}$$

$$\text{the molar concentration of } Cl_2 = [Cl_2] = \frac{\alpha}{V} \text{ mole L}^{-1}$$

Applying the law of mass action equation. -

- in terms of molar concentration we get

the equilibrium constant.

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

$$= \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{a-\alpha}{V}}$$

$$= \frac{\alpha^2/V^2}{\alpha-a/V}$$

$$= \frac{\alpha^2}{V(\alpha-a)}$$

NOW we calculate the equilibrium constant in terms of partial pressure.

At equilibrium

the total number of mole =  $a-\alpha+\alpha+\alpha = a+\alpha$

the total pressure of the gaseous mixture =  $P$ .

So, the partial pressure of  $\text{PCl}_5 = P_{\text{PCl}_5} = \frac{a-\alpha}{a+\alpha} \cdot P$

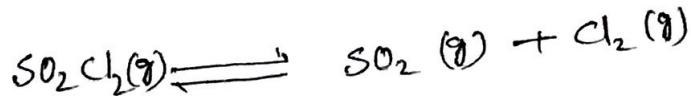
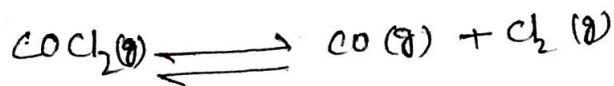
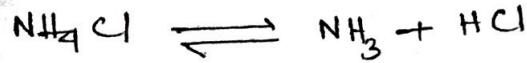
the partial pressure of  $\text{PCl}_3 = P_{\text{PCl}_3} = \frac{\alpha}{a+\alpha} \cdot P$

the partial pressure of  $\text{Cl}_2 = P_{\text{Cl}_2} = \frac{\alpha}{a+\alpha} \cdot P$

Applying the law of mass action equation in terms of partial pressure, we get.

$$\begin{aligned} K_p &= \frac{[P_{\text{PCl}_3}][P_{\text{Cl}_2}]}{[P_{\text{PCl}_5}]} \\ &= \frac{\frac{\alpha}{a+\alpha} \cdot P \cdot \frac{\alpha}{a+\alpha} \cdot P}{\frac{a-\alpha}{a+\alpha} \cdot P} \\ &= \frac{\alpha^2 / (a+\alpha)^2}{(a-\alpha)(a+\alpha)} \cdot P \\ &= \frac{\alpha^2}{a^2 - \alpha^2} \cdot P \end{aligned}$$

This is the equation of equilibrium constant expressed by partial pressure.



at initial :  $a \quad 0 \quad 0$

at equilibrium:  $a-\alpha \quad \alpha \quad \alpha$

NOW same as ④



At initial:  $a \quad 3b \quad 0$

At equilibrium:  $a-\alpha \quad 3b-3\alpha \quad 2\alpha$

Let  $a$  mole of  $\text{N}_2$  and  $3b$  moles of  $\text{H}_2$  are kept in a sealed vessel of volume  $V$  litre, and are heated at specific temperature and pressure.

At equilibrium  $2\alpha$  mole of  $\text{NH}_3$  and  $a-\alpha$  mole of  $\text{N}_2$  and  $(3b-3\alpha)$  mole of  $\text{H}_2$  are obtained.

Therefore, at equilibrium,

$$\text{the molar concentration of } \text{N}_2 = [\text{N}_2] = \frac{a-\alpha}{V} \text{ mole L}^{-1}$$

$$\text{the molar concentration of } \text{H}_2 = [\text{H}_2] = \frac{3b-3\alpha}{V} \text{ mole L}^{-1}$$

$$\text{the molar concentration of } \text{NH}_3 = [\text{NH}_3] = \frac{2\alpha}{V} \text{ mole L}^{-1}$$

Applying the law of mass action in terms of molar concentration, we get the equilibrium constant

$$\begin{aligned}
 K_c &= \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]} \\
 &= \frac{\left(\frac{2\alpha}{v}\right)^2}{\left(\frac{3b-3\alpha}{v}\right)^3 \cdot \left(\frac{a-\alpha}{v}\right)} \\
 &= \frac{4\alpha^2/v^2}{(3b-3\alpha)^3 (a-\alpha)/v^4} \\
 K_c &= \frac{4\alpha^2 v^2}{(a-\alpha)(3b-3\alpha)^2}
 \end{aligned}$$

This is the equation of equilibrium constant in terms of molar concentration:

calculation of  $K_p$ :

The total number of moles at equilibrium =

$$a-\alpha + 3b-3\alpha + 2\alpha = a+3b-2\alpha$$

The total pressure of the gaseous mixture =  $P$

Partial pressure of  $\text{N}_2 = P_{\text{N}_2} = \frac{a-\alpha}{a+3b-2\alpha} \cdot P$

Partial pressure of  $\text{H}_2 = P_{\text{H}_2} = \frac{3b-3\alpha}{a+3b-2\alpha} \cdot P$

Partial pressure of  $\text{NH}_3 = P_{\text{NH}_3} = \frac{2\alpha}{a+3b-2\alpha} \cdot P$

in terms of partial pressure

Applying the law of mass action, the equilibrium constant  $K_p$  can be determined.

$$\begin{aligned}
 K_p &= \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} \\
 &= \frac{\frac{4\alpha^2}{(a+3b-2\alpha)^2} \cdot P}{\frac{a-\alpha}{a+3b-2\alpha} \cdot P \cdot \frac{(3b-3\alpha)^3}{(a+3b-2\alpha)^3} \cdot P^3} \\
 &= \frac{P^{4\alpha^2}}{(a+3b-2\alpha)^2} \times \frac{(a+3b-2\alpha)^9}{(a-\alpha) \cdot 27(b-1)^3 \cdot P^3} \\
 K_p &= \frac{4\alpha^2(a+3b-2\alpha)^2}{27(a-\alpha)(b-1)^3 \cdot P^2}
 \end{aligned}$$

This is the equation of equilibrium constant in terms of partial pressure.

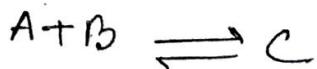
Q.9: Write Le Chatelier's principle and explain it.

Le Chatelier's principle: If a change in concentration, pressure or temperature is caused to a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimise the change.

Explanation:

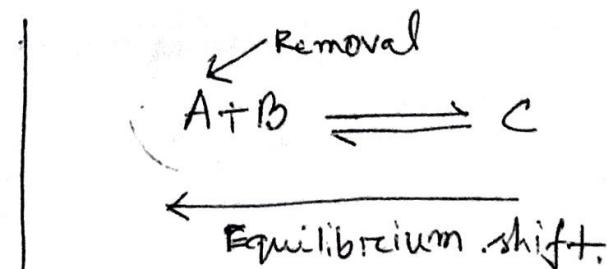
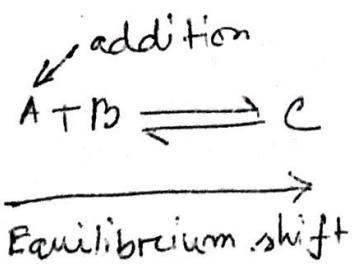
Effect of change of concentration:

A change in the concentration of a reactant or product can be effected by the addition or removal of that species. Let us consider a general reaction



When a reactant, say, A is added at equilibrium its concentration is increased. The forward reaction alone occurs momentarily. According to Le Chatelier's principle, a new equilibrium will be established so as to reduce the concentration of A. Thus the addition of A causes the equilibrium to shift to right. This increases the concentration of the product C.

Following the same line of argument, a decrease in the concentration of A by its removal from the equilibrium mixture, will be undone by shift to the equilibrium position to the left. This reduces the concentration of the product C.





## Effect of a change in pressure:

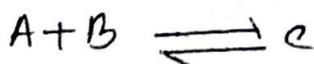
The pressure of a gaseous reaction at equilibrium is determined by the total number of molecules it contains. If the forward reaction proceeds by the reduction of molecules, it will be accompanied by a decrease of pressure of the system and vice versa.

Let us consider a reaction



The combination of A and B produces a decrease of number of molecules while the decomposition of C into A and B results in the increase of molecules. Therefore, by the increase of pressure on the equilibrium it will shift to right and give more C. A decrease in pressure will cause the opposite effect. The equilibrium will shift to the left when C will decompose to form more of A and B.

Molecules decrease



Equilibrium shift on increase of P

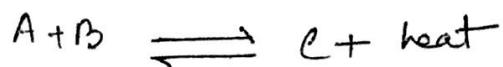
Molecules increase



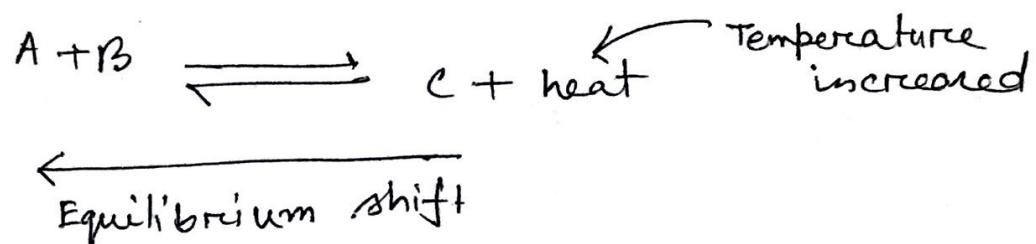
Equilibrium shift on decrease of P.

## Effect of change of Temperature:

Let us consider an exothermic reaction



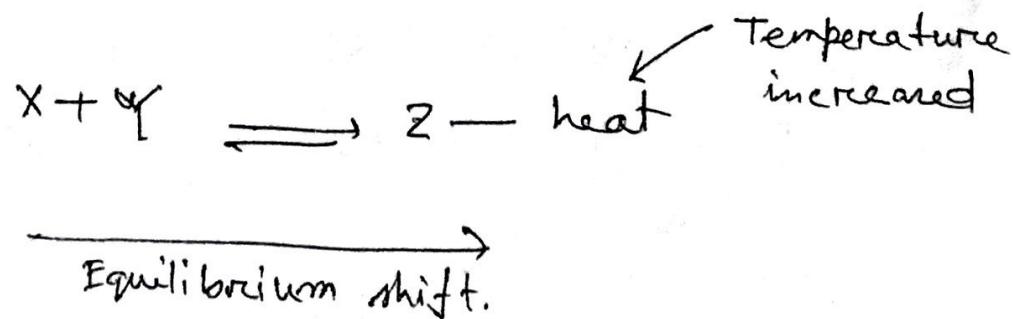
When the temperature of the system is increased, heat is supplied to it from outside. According to Le Chatelier's principle, the equilibrium will shift to the left which involves the absorption of heat. This would result in the increase of the concentration of the reactants A and B.



Let us consider this endothermic reaction



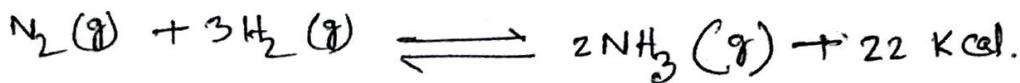
The increase of temperature will shift the equilibrium to the right as it involves the absorption of heat. This increases the concentration of the product Z.



10. Discuss the application of Le Chatelier's principle in industrial reactions.

### ① Synthesis of Ammonia (Haber process)

The manufacture of ammonia by Haber process is represented by the equation



A look at the equation provides the following informations.

① the reaction is exothermic

② the reaction proceeds with a decrease in the number of moles.

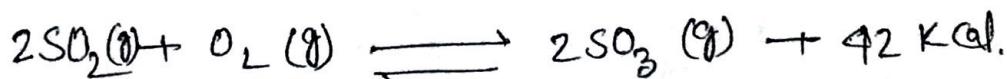
① Low temperature: By applying Le Chatelier's principle, low temperature will shift the equilibrium to the right. This gives greater yield of ammonia. In actual practice a temperature of about  $450^\circ\text{C}$  is used when the percentage of ammonia in the equilibrium mixture is 15.

② High pressure: High pressure on the reaction at equilibrium favours the shift of the equilibrium to the right. This is so because the forward reaction proceeds with a decrease in the number of moles. A pressure of about 200 atmospheres is applied in practice.

③ Catalyst: As already stated, low temperature is necessary for higher yield of ammonia. But at relatively low temperatures, the rate of reaction is slow and the equilibrium is attained in a long time. To increase the rate of reaction and thus quicken the attainment of equilibrium, a catalyst is used. Finely divided iron containing molybdenum is employed in actual practice. Molybdenum acts as a promoter that increases the life and efficiency of the catalyst.

### Manufacture of Sulphuric acid:

The chief reaction used in the process is



Following information is revealed by the above equation.

- (a) the reaction is exothermic
- (b) the reaction proceeds with a decrease in number of moles.

On the basis of Le Chatelier's principle, the conditions for the maximum yield can be worked out as below:

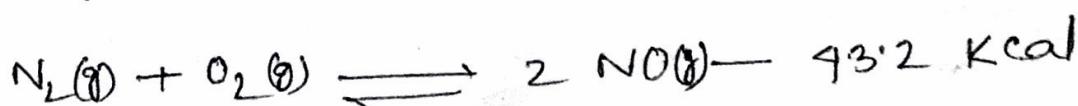
① Low temperature: Since the forward reaction is exothermic, the equilibrium will shift on the right at low temperature. An optimum temperature between  $400-450^{\circ}\text{C}$  is required for the maximum yield of sulphur trioxide.

② High pressure: Since the number of moles are decreased in the forward reaction, increase of pressure will shift the equilibrium to the right. Thus for maximum yield of  $\text{SO}_3$ , 2 to 3 atmosphere pressure is used.

③ Catalyst: At the low temperature used in the reaction, the rate of reaction is slow and the equilibrium is attained slowly. A catalyst is, therefore, used to speed up the establishment of the equilibrium. Vanadium pentoxide,  $\text{V}_2\text{O}_5$ , is commonly used. ~~is~~

### Manufacture of Nitric acid

Nitric acid is prepared on a large scale by making use of the reaction.



The equation tells us that

- (a) the reaction proceeds with no change in the number of moles
- (b) the reaction is endothermic and proceeds by absorption of heat.

The favourable conditions for the maximum yield of NO are

- ① High temperature: Since the forward reaction is endothermic, increase of temperature will favour it as per Le Chatelier's principle. Thus a high temperature of the order of 300°C is employed to get high yield of nitric acid.
- ② No effect of pressure: Since the forward reaction involves no change in the number of moles, a change in pressure has no effect on the equilibrium.
- ③ High concentration: The formation of nitric acid is favoured by using high concentrations of the reactants i.e.  $N_2$  and  $O_2$ .