CHAPTER # 7

CHEMICAL EQUILIBRUM

Q1. Differentiate between reversible and irreversible reaction.

Ans:

Reversible Reaction	**Irreversible Reaction**
1) The reaction which can proceed in both the direction i.e. forward and backward and are called reversible reaction.	1) The reaction that virtually go to completion i.e., reaction are completely consumed and converted into the products. Such reaction are called irreversible reactions.
2) The reactants are not completely consumed.	2) The limiting reactant is consumed completely.
3) In reversible reaction the reaction the reaction never goes to completion.	3) The reaction virtually goes to completion in irreversible reactions.
4) These reaction reach at a stage called chemical equilibrium. At this stage the concentration of reaction continues to proceed in both the direction without any change in concentrations of reactants and products under existing condition.	4) The concept of chemical equilibrium is not applicable on irreversible reaction.
5) It is represented by $\rightleftharpoons$ double arrow.	5) It is represented by $\rightarrow$ single arrow.

6) **Examples:**	7) **Examples:**
i. $2NO_2 \rightleftharpoons N_2O_4(g)$	i. $2H_2(g)+O_2(g) \rightarrow 2H_2O(g)$
ii. $PCl_5 \rightleftharpoons PCl_3(g)Cl_2(g)$	ii. $C+O_2 \rightarrow CO_2O$
iii. $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$	iii. $H_2(g)+Cl_2(g) \rightarrow 2HCl(g)$

Q2. What do you know about reversible reaction?

Ans: Reversible reaction:

The reactions which can proceed in both the 'directions i.e. forward and backward directions are called reversible reactions. Explanation: A reversible reaction is one in which the products once formed can react to form reactants. Such reactions do not go to completion even if stoichiometric amounts of the reactants are taken. These reactions take place both in the forward and backward directions under the existing conditions.

Examples:

Some examples of reversible reactions are given below:

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
$$2NO(g)+Cl_2(g) \rightleftharpoons 2NOCl(g)$$
$$PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$$

The double arrow tells that the reaction is reversible.

Consider the reaction between steam and carbon monoxide under appropriate conditions.

On mixing macroscopic changes are observed (e g. changes in concentration).

Q3. Define and explain dynamic equilibrium give its examples also draw the graph to explain your answer.

Ans: Dynamic Equilibrium/Chemical Equilibrium:

"The state of a reversible reaction at which compositions of the reacti0n mixture does not change is called the state of chemical equilibrium."

Explanation:

Suppose that the reaction is started with same number of moles of both reactants. When steam and carbon monoxide are mixed, a maximum number of collisions per second between them will occur. Therefore, the forward reaction has its maximum speed at the beginning. This leads to a decrease in the concentration of the reactants.

Example 1:

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

As H_2O and CO are gradually used up, the forward reaction gradually slows down. As the molecules of H_2 and CO_2, accumulate reverse reaction also starts. With the increase in concentrations of H_2 and CO_2, more and more collisions per second between these molecules occur.

Therefore reverse reaction proceeds with increasing speed. This means that forward reaction starts with maximum speed and gradually slows down, whereas the reverse reaction starts at zero speed and gradually increases its speed.

Example 2:

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

Eventually a time comes when both reactions proceed at the same speed. The reaction at this stage is said to be in chemical equilibrium. The concentrations of reactants and products become constant.

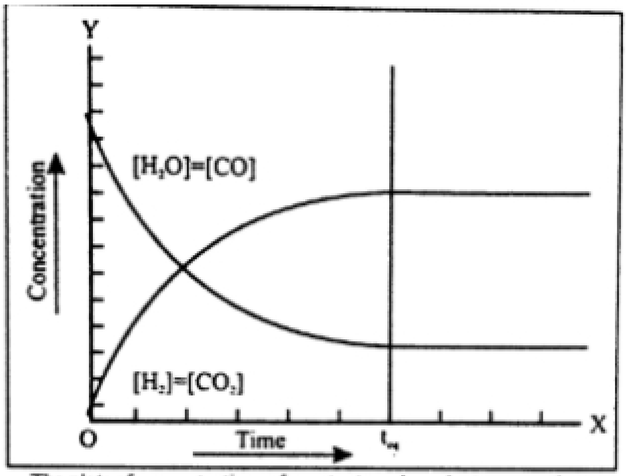
$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Unless the system is somehow disturbed no further changes in concentration will occur.

Graphical representation:

The plots of the concentrations of reactants and products versus time are shown in Fig.

(The plots of concentration of reactants and products versus time.)



The plots of concentrations of reactants and products versus time.

Microscopic analysis:

Since the concentration of reactants and products become constant it may appear that the reaction has stopped. But this is not true.

On the microscopic level there is excited activity. Individual molecules of reactants continue to combine. Individual molecules of products also continue to combine. But the rate of one process is exactly balanced by the rate of the other. Therefore, this is a **dynamic equilibrium.**

Dynamic System:

The system is dynamic because individual molecules react continuously, but the rate of the forward and reverse reactions are equal. It is at equilibrium because no net change occurs.

Q4. State law of mass action also derive equilibrium constant equation with the help of this law.

Ans: The Equilibrium Constant:

Two chemists CM Guldberg and P. Wage in 1864 proposed the law of mass action.

It states that "the rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances".

It can also be defined as "the rate of chemical reaction is proportional to the product of molar concentration of each reacting substance raised to a power equal to its stoichiometric coefficient in the balanced chemical equation."

Active mass:

The term active mass means, the concentration of the reactants and products in moles dm" for a dilute solution.

Derivation:

Consider the following general reversible reaction.

$$aA(g)+bB(g) \rightleftharpoons cC(g)+dD(g)$$

Where A, B, C and D represent chemical species and a, b, c and d are their coefficients in the balanced equation.

According to the law of mass action.

Rate of forward reaction, $R_f \alpha [A]^a[B]^b = k_r[A]^a[B]^b$ ....(1)

Where k, is the rate constant for the forward reaction.

Rate of reverse reaction, $R_r \alpha [C]^c[D]^d = k_r[C]^c[D]^d$ ....(ii)

Where k, is the rate constant for the reverse reaction.

At equilibrium state

Rate of forward reaction= Rate of reverse reaction

Thus $$k_c[A]^a[B]^b = k_r[C]^c[D]^d$$

On rearranging
$$\frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$
$$k_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where $K_c = \frac{k_f}{k_r}$ and is known as equilibrium constant, and the above equation is known as equilibrium constant expression. The square brackets indicate the concentration of the chemical species at equilibrium.

Method to write equilibrium constant expression:

Thus, the equilibrium constant expression for any reaction can be written from its balanced equation. Concentration of products are taken in the numerator and concentration of reactants in the denominator.

Q5. Differentiate between rate law and equilibrium constant equation.

Ans:

Rate law	Equilibrium constant equation
1) The rate law describes how the rate of a reaction changes with concentration.	1)The equilibrium expression describes the concentration of reactants and products when the net rate of reaction is zero.
2) It cannot be written from the balanced chemical equation	2)It can be written from a balanced chemical equation.
3) It can be determined only with the help of experiment.	3)It can be determined theoretically with the help of balanced chemical equation.
4) Rate law is given by the equation. $Rate = k[A]^x$	4)Equilibrium constant equation for the given reaction is given below $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$ $\frac{k_i}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Note: In both these expressions, concentration terms are raised to powers.

Examples of Equilibrium Constant Expression:

Example 7.1:

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

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

Example 7.2:

$CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$

$$K_c = \frac{[CO_2]}{[CO][O_2]^{\frac{1}{2}}}$$

SELF-CHECK EXERCISE 7.1

1. **The following equations represent various industrial reaction at equilibrium. Write K_c expression for each of these reactions. Do not forget to balance the equations:**

   i. $SO_3(g) + O_2(g) \rightleftharpoons SO_3(g)$

   ii. $NH_3(g) + O_2(g) \rightleftharpoons NO(g) + H_2O(g)$

   iii. $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + H_2O(g)$

Solution: **1)** $SO_3(g) + O_2(g) \rightleftharpoons SO_3(g)$

Balancing the equation is

$$2NH_3(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

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

2) $NH_3(g) + O_2(g) \rightleftharpoons NO(g) + H_2O(g)$

Balancing the equation is

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

$$K_c = \frac{[NO][H_2O]^3}{[NH_3]^2[O_2]^{\frac{5}{2}}}$$

3) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + H_2O(g)$

Balancing the equation is

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + H_2O(g)$$

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

2) Give the balanced equations that correspond to following equilibrium expression.

i. $K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$

ii. $K_c = \frac{[N_2][H_2O]^2}{[CO][H_2]^2}$

Solution:

i. $CO + H_2 \rightleftharpoons CH_3O$

ii. $2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$

Q6. How can we determine units for equilibrium constant give at least two examples?

Ans: Units of Equilibrium Constant:

Equilibrium constant may or may not have units. Equilibrium constant has no units if the numbers of moles of the reactants are equal to the number of of the products.

For instance, K_c for the following reaction has no units.

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

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

$$K_c = \frac{(moldm^{-3})(moledm^{-3})}{(moldm^{-3})(moledm^{-3})} = noUnits$$

On the other hand, if the number of moles of products and reactants are not equal, K_c has units.

Example:

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = moledm^{-3}$$

In this way can determine the units for K_c. However units of equilibrium constant are not usually written.

SELF-CHECK EXERCISE 7.2

Determine the units for K_c for the following reaction:

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

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

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

The value of K_c at a given temperature can be calculated if we know the equilibrium concentration of the reaction components.

Solution:

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

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

$$K_c = \frac{moledm^{-3}(moledm^{-3})}{moledm^{-3}} = moledm^{-3}$$

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

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

$$K_c = \frac{(moledm^{-3})^2}{(moledm^{-3})^2(moledm^{-3})} = \frac{1}{(moledm^{-3})} = mole^{-1}dm^3$$

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

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

$$K_c = \frac{(moledm^{-3})^2}{(moledm^{-3})(moledm^{-3})} = NoUnits$$

Example 7.3:

The following equilibrium concentrations were observed for the reaction at 500^oC.

$$K_c = \frac{[AB]^2}{[A][B]^3}$$

$$K_c = \frac{(0.203 mole dm^{-3})^2}{(0.399 mole dm^{-3})(1.197 mole dm^{-3})} = 6\times10^{-2} dm^6 mole^{-2}$$

Q7. State Henry's law and how can we determine equilibrium constant expressions involving partial pressure, number of moles and mole fraction.

Ans: Equilibrium Expressions Involving partial pressure, Number of Moles and Mole Fraction:

Consider the general gaseous reversible reaction

$$aA(g) + bB(g) \rightleftharpoons aA(g) + bB(g)$$

For gases the expression often expressed in terms of partial pressure of each gas

According H**enry's Law**

"At constant temperature, the partial pressure of gas is directly proportional to its molar concentration."

Equilibrium constant K, (For partial pressure):

Equilibrium constant Kp in term of partial pressures is given by

$$K_p = \frac{P_c^c \times P_D^d}{P_A^a \times P_B^b}$$

Where P_A, P_B, P_C and P_D are partial pressures of gas A, B, C and D respectively Kp is related with K_c by the following equation.

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

Where Δn is the difference between the total number of moles of the products and the reactants.

Equilibrium constant K_n (For number of moles):

When equilibrium concentrations of reactants and products are expressed in terms of their moles, the equilibrium constant is represented by K_n and is given by the following equation,

$$K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}$$

Where n_A, n_B, n_C and n_D are the moles of A, B, C and D respectively at the equilibrium state. K_P is also related with K_n

$$K_P = K_n\left(\frac{P}{N}\right)^{\Delta n}$$

Where P is the pressure of reaction mixture at equilibrium and N is the total number of moles of reactants and products as shown by the balanced equation.

Equilibrium constant K_X (For mole fraction):

When the equilibrium concentration of the reactants and products are expressed by their mole fractions, the equilibrium constant is represented by K_X and is given by the following equations.

$$K_X = \frac{X_C^c \times X_D^d}{X_A^a \times X_B^b}$$

Where $X_A, X_B, X_C and X_D$ are mole fractions of A, B, C and D respectively. K_P is related with K_X by the following expression.

$$K_P = K_X(P)^{\Delta n}$$

Where P is the pressure of the equilibrium mixture.

Example 7.4:

Following reaction was studied at 25°C. Calculate its K_P and K_C .

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

The partial pressures at equilibrium were found to be

$$P_{NOCl} = 1.2atm$$
$$P_{NO} = 5.0 \times 10^{-2} atm$$
$$PCl_2 = 3.0 \times 10^{-1} atm$$
$$K_p = \frac{(P_{NOCl})^2}{(P_{NO})(P_{Cl2})}$$
$$K_P = \frac{(1.2)^2}{(5.0 \times 10^2)(3.0 \times 10^{-1})}$$

$$K_P = K_C(RT)^{\Delta n}$$
$$\Delta n = 2 - (2 + 1) = -1$$
$$R = 0.0820 dm^3 atm K^{-1} mole^{-1}$$
$$T = 25^o C + 273 = 298K$$

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

$$1.9 \times 10^3 = K_c(0.08205 \times 298)^{-1}$$
$$1.9 \times 10^3 = \frac{K_c}{(0.08205 \times 298)}$$
$$K_c = 4.65 \times 10^4$$

SELF-CHECK EXERCISE 7.3

The contact process prepares purest sulphuric acid commercially, following reaction takes place in the contact chamber in the presence of V_2O_5.

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

(Ans: 0.1576)

Calculate K_p if the following concentrations are found at equilibrium.

$[SO_2] = 0.59M$, $[O_2] = 0.05M$ **&** $[SO_3] = 0.259M$

Solution:

For K_c

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$
$$K_c = \frac{(0.259)^2}{(0.59)^2(0.05)} = 3.85$$

For K_P

As we know that

$$K_p = K_c(RT)^{\Delta n} \ldots\ldots\ldots\ldots(1)$$
$$R = 0.0821 atmdm^3K^{-1}mole^{-1}$$
$$\Delta n = 2 - (2+1) = -1$$
$$T = 25^oC + 273 = 298K$$
$$K_c = 3.85$$

Putting values in equation(1)

$$K_p = 3.85 \times (0.0821 \times 298)^{-1}$$

$$K_p = \frac{3.85}{(0.0821 \times 298)^{-1}} 0.1574$$

Q8: Define and explain the following terms.

i. **Homogeneous Equilibria:**

ii. **Heterogeneous Equilibria**

Ans. Types of Equilibrium:

With respect to the physical states of reactants and products, there are two types of Chemical Equilibrium.

1)Homogeneous Equilibria:

An equilibrium system in which all of the reactants and products are in the same phase

Example:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$
$$CH_3COOH(l) + C_2H_2OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

2)Heterogeneous Equilibrium:

Equilibria which involve more than one phases are called Heterogeneous equilibria.

Example:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$C(g) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$
$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s)4H_2(g)$$

Note:

If pure solids or pure liquids are involved in an equilibrium system, their concentrations are not included in the equilibrium constant expression.

This because the change in concentrations of any pure solid or liquid has no effect on the equilibrium system.

(i)

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

$$K_c = [H_2]^2[O_2]$$

$$and \quad K_P = p_{H_2}^2 \times P_{o_2}$$

(ii)

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

$$K_c = \frac{[H_2]^2}{[H_2O]^4}$$

$$and \quad K_p = \frac{P_{H_2}^4}{P_{H_2O}^4}$$

SELF-CHECK EXERCISE 7.4

Write K, and K, expressions for each of the following reactions.

(i) $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

(ii) $P_4(s) + O_2(g) \rightleftharpoons P_4O_{10}(s)$

(iii) $CH_4(g) + 4Cl_2(g) \rightleftharpoons CCl_2(l) + 4HCl(g)$

Solution:

(i) $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

$$K_c = \frac{[CO_2]}{[CO]}$$

$$K_P = \frac{P_{CO_2}}{P_{CO}}$$

(ii) $P_4(s) + O_2(g) \rightleftharpoons P_4O_{10}(s)$

$$K_C = [O_2]^{-5}$$
$$K_P = P_{O_2}^{-5}$$

(iii) $CH_4(g) + 4Cl_2(g) \rightleftharpoons CCl_2(l) + 4HCl(g)$

$$K_C = \frac{[HCl]^4}{[CH_4][Cl_2]^2}$$
$$K_P = \frac{P_{HCl}^4}{P_{CH_4} \times P_{HCl}^4}$$

Example 7.5:

At 100°C, 0.1mole of N_2O_4 is heated in a one dm^3 flask. At equilibrium concentration of NO_2 was found to be 0.12 moles. Calculate K_c. for the reaction.

Solution:

$[NO_2]$ **= 0.12 mole**

Since one mole of N_2O_4 gives 2 moles of NO_2

$$2x = 0.12$$
$$x = \frac{0.12}{2}$$
$$x = 0.06$$
$$[N_2O_4] = 0.1 - 0.06$$
$$= 0.04 \text{ mole}$$

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

	$N_2O_4(g)$	$2NO_2$
Initial Conc (in moles)	0.1	zero
Eq. conc (in moles)	0.1-2x=0.12	
Eq Conc. $(mole/dm^3)$	$\frac{0.04}{1}$	$\frac{0.12}{1}$
	0.04	0.12

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(0.12)^2}{(0.04)}$$

$$K_c = 0.36$$

Example7.6:

Consider the following reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) K_c = 0.1 \text{ at } 2000^oC$$

If original concentrations of N_2 and O_2 were 0.1M each. Calculate the concentrations of NO at equilibrium.

Solution:

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

Initial Conc.	0.1M	0.1M	0
Eq.conc (mole/dm^3)	(0.1-x)	(0.1-x)	2x

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

$$0.1 = \frac{(2x)^2}{(0.1-x)(0.1-x)}$$

Taking square root of both the sides

$$0.32 = \frac{2x}{0.1-x}$$

$$x = 0.014M$$

$$[N_2] = [O_2] = 0.1 - x$$

$$= 0.1 - 0.014$$

$$= 0.086M \text{ each}$$

$$[NO]=2x$$

$$=2 \times 0.014$$

$$=0.028$$

SELF-CHECK EXERCISE 7.5

For the reaction

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

K. = 0.60 at 500°C. If a mixture of 0.30M of each H_2 and CO_2 is heated at 500°C, calculate the concentration of CO at equilibrium.

Solution

Initial Concentration	$H_2(g)$ +	$CO_2(g) \rightleftharpoons$	$H_2O(g)$ +	$CO(g)$
(in moles)	0.3	0.3	zero	zero
Equation Concentration. (in moles)	0.3-x	0.3-x	x	x

Kc is given as

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]}$$

$$0.06 = \frac{x^2}{(0.3-x)(0.3-x)} = \frac{x^2}{(0.3-x)^2}$$

Taking square root of both the sides

$$\sqrt{0.60} = \sqrt{\frac{x^2}{(0.3-x)^2}}$$

$$0.775 = \frac{x}{(0.3 - x)}$$
$$x = 0.775(0.3 - x)$$
$$x = 0.233 - 0.775x$$
$$x + 0.775x = 0.233$$
$$x = \frac{0.233}{1.775}$$
$$x = 0.131$$
Thus
$$[CO] = x = 0.131 \text{ moles}$$

Example 7.7:

When 60g of acetic acid and 46g of ethyl alcohol are heated to give and equilibrium mixture, 12g water and 58.7g of ethyl acetate are formed. Find K, for the reaction.

Solution:

$$\text{Initial moles of } \mathrm{CH_3}COOH = \frac{60g}{60g\,/\,mole} = 1 \text{ mole}$$
$$\text{Initial moles of } \mathrm{C_2}H_5OH = \frac{46g}{46g\,/\,mole} = mole$$
At equilibrium
$$\text{Mole of } \mathrm{CH_3}COOC_2H_5 = \frac{58.7g}{88g\,/\,moles} = 0.666moles$$
$$Moles \text{ of } \mathrm{H_2}O = \frac{12g}{18g\,/\,moles} = 0.666moles$$

$$CH_3COOH(1) + C_2H_5OH(1) \rightleftharpoons CH_3COOC_2H_5(1) + H_20(1)$$

Init. conc	1	1	0	0
(in moles)				
Eq. conc.	1-0.666	1-0.666	0.666	0.666
(moles)	0.333	0.333		

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_2COOH][C_2H_5OH]}$$

$$K_c = \frac{(0.666)(0.666)}{(0.333)(0.333)}$$

$$K_c = 4$$

SELF-CHECK EXERCISE 7.6

When dissolved in water, glucose and fructose exists in equilibrium as follows:

Fructose $\rightleftharpoons$ Glucose

An analyst prepared a 0.25M fructose solution at room temperature. At equilibrium he found that its concentration decreased by 0.038M. Calculate K. for the reaction.

Solution:	Fructose $\rightleftharpoons$	Glucose
Initial Concentration (in moles)	0.25	zero
Equation Concentration (in moles)	0.25-x	x

Given that the concentration of fructose is decreases by 0.038M. Thus,

X = 0.038

| Fructose] = 0.25 - x

= 0.25 - 0, 038 M

= 0.212 M

| Glucose] =x = 0.038M

$$K_c = \frac{[Glu\cos e]}{[Fructose]} = \frac{[0.038]}{[0.212]} = 0.179$$

When 3.88 moles of NO and 0.88 moles of CO, were heated in a flask at a certain temperature. At equilibrium 0.11 moles of each of the product were present. Calculate K, for the reaction.

$$CO_2(g) + NO(g) \rightleftharpoons CO(g) + NO_2(g)$$

Solution:

$$CO_2(g) + NO(g) \rightleftharpoons CO(g) + NO_2(g)$$

Initial Concentration. 0.88 3.88 0 0

(in moles)

Equation Concentration. 0.88-x 3.88-x x x

(in moles)

Given that 0.11 moles of each of the product are present at equilibrium,

Thus,

$$\begin{aligned}
&x = 0.11 \\
&[CO_2] = x = 0.11 moles \\
&[NO] = x = 0.11 moles \\
&[CO_2] = 0.88 - x = 0.88 - 0.11 = 0.77 moles \\
&[NO] = 3.88 - x = 3.88 - 0.11 = 3.77 moles
\end{aligned}$$

$$\begin{aligned}
K_c &= \frac{[CO][NO_2]}{[CO_2][No]} \\
0.60 &= \frac{(0.11)(0.11)}{(0.77)(3.77)} = 0.0042
\end{aligned}$$

Q9. Write the applications of the equilibrium constant K_c.

ANS. Applications of the Equilibrium Constant:

Equilibrium constant for a reaction can be used to predict many important features of the reactions.

For instance, it can be used to predict

(i) Direction of the chemical reaction.

(ii) Extent of the chemical reaction.

(iii) Effect of changes in condition of the chemical reaction on the equilibrium position and equilibrium constant.

Q10. How equilibrium constant K, help us to determine.

i. **The Direction of a Reaction.**

ii. **The Extent of Chemical Reaction.**

Ans. The Direction of a Reaction:

The direction of reaction when reactants and products of a given chemical reaction are mixed, it is important to know whether the mixture is at equilibrium and if not, in which direction it will move to achieve equilibrium state. For this purpose, we use the reaction quotient (Q).

Reaction quotient (Q):

The ratio of concentrations of products to reactant at any particular time is called reaction quotient. It is obtained by applying the law of mass action, using initial concentrations or concentrations at any particular time instead of equilibrium concentration.

$$Q = \frac{(\text{Products})}{[reac\tan t]}$$

The value Q leads to one of the following possibilities.

a. Q<Kc

This indicates that more product is needed to acquire equilibrium. Therefore, system must shift to the right until equilibrium in reached.

b. Q> Kc

This indicates that less product or more reactant is needed to acquire equilibrium. Therefore, system must shift to the left until equilibrium in reached.

c. Q = Kc

This shows that reaction is at equilibrium. No shift will occur.

ii . The Extent of Chemical Reaction:

The extent of a chemical reaction can be predicated by considering the magnitude of equilibrium constant. Again, there are there possibilities.

a. Kç is very large:

Many reactions have very large equilibrium.

Example:

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

If concentration of each of the reactant at equilibrium is 1 mole then concentration of HBr would be

$$\frac{[Hbr]^2}{1\times1} = 5.4\times10^{18}$$
$$[HBr] = \sqrt{5.4\times10^{18}}$$
$$= 2.32\times10^{9} M$$

Conclusion:

It means that the concentration of HBr is very large as compared to that of reactants. At equilibrium the mixture will have mainly products. Thus large value of Kç indicates that the reaction goes virtually to completion.

b. Kc is very small:

Reactions having very small Kc do not proceed appreciably in the forward direction.

Example:

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

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 1.0 \times 10^{-30}$$

If one mole of each of the reactant is present at equilibrium, then the concentration of NO would be

[NOJ = 1 x 1030 1x1 INO] = Vix 10 (NO) = 1 x 1015 moles

Conclusion

Thus concentration of NO will be very small. Equilibrium mixture will have mainly reactants Therefore, small value of Kc indicates that the reaction has very little tendency to move in the forward direction.

C. Kc is neither very small nor very large:

When Kc in neither very small nor very large, the equilibrium mixture contains appreciable amounts of both products and reactants.

Example:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 0.36 at 25^oC$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.36$$

If 1 mole of N_2O_4 is present at equilibrium, 0.6 mole of NO_2 will be present in the equilibrium mixture.

Conclusion:

Hence the equilibrium mixture will contain appreciable amount of reactants and products. In such cases neither forward nor the reverse reaction go to completion.

Example7.8:

For the synthesis of ammonia at 500°C, Kc = 6.0 x 10^{-1}

$$N_2(g) = 3H_2(g) \rightleftharpoons 2NH_2(g)$$

Predict the direction in which the system will shift to attain equilibrium when the concentrations of species were found to be

$$[H_2] = 1.0 \times 10^{-2} M$$
$$[N_2] = 1.0 \times 10^{-3} M$$
$$[NH_3] = 1.0 \times 10^{-3} M$$

Solution:

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
$$Q = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-3})(1.0 \times 10^{2})}$$
$$Q = 1.0 \times 10^3$$
$$But$$
$$K_c = 6.0 \times 10^{-2}$$

Therefore Q > Kc. The system will shift to the left to achieve equilibrium.

SELF-CHECK EXERCISE 7.7

Phosgene is potent chemical warfare agent and has been used in World War II. It decomposes by the following reaction.

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g) K_c = 8.3\times10^{-10} at 350^oC$$

Predict the direction in which system will shift to attain equilibrium, when the concentrations of species were found to be

$$[COCl_2] = 0.5M$$
$$[CO] = 2.5\times10^{-10} M$$
$$[Cl_2] = 2.5\times10^{-10} M$$

Solution:

$$Q = \frac{[CO][Cl_2]}{[COCl_2]}$$
$$Q = \frac{(2.5\times10^{-2})(2.5\times10^{-2})}{(0.5)} = 1.25\times10^{-3}$$
$$but$$
$$K_c = 8.3\times10^{-4}$$

Since Q > K.

Hence the system will shift towards left.

SELF-CHECK EXERCISE 7.8

White phosphorus P, is produced by the reaction of phosphorite rock, Ca, (PO.), with coke. When exposed to air it bursts into smoke and fumes and releases a large amount of heat. Predict whether K. for this reaction is large or small.

$$P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$$

Solution:

This reaction is exothermic and when exposed to air it bursts into smoke and fumes and releases a large amount of heat All these things show that the reaction virtually goes to completion Thus the value of K. will be very large and the reaction will go in forward direction.

Q11. Define Le Chatellier's principle and how can it help us to predict the various factors which can affect the chemical equilibrium?

Ans. Le Chatellier's principle

It states that it a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction which tends to reduce that change".

Factors Affecting Equilibrium:

We can predict the effect of various factors such as concentration pressure and temperature on a system at equilibrium by using Le Chatellier's s principle.

i. The Effect of a Change in Concentration:

When the concentration of one or more of the reactants or products present in equilibrium mixture is disturbed, the system will not remain at equilibrium state According to Le Chatelaine's principle, the equilibrium shifts to accommodate the substance added or removed and restore equilibrium again.

Explanation:

Consider the following gas phase equilibrium:

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

i. When CO_2 is added to this equilibrium system, it is no longer in equilibrium. Higher concentration of CO_2 increases the rate of forward reaction relative to the reverse reaction.

ii. Thus more CO_2 and H_2 combine and more CO and H_2 form.

iii. As time passes the concentrations of CO_2 and H_2 decrease, lowering the rate of forward reaction.

iv. At the same time increased concentrations of the products accelerate the reverse reaction ultimately the two rates become equal again and equilibrium is re-established,

v. At the new equilibrium concentrations of CO and H_20 is higher than were present before the CO_2 was added.

vi. Thus, equilibrium is said to have shifted to the products side.

Effect of increase in concentration:

In all chemical systems, an increase in concentration of any reactant shifts the equilibrium towards the formation of the products. If concentration of a product is increased, the equilibrium shifts towards the reactants. A shift towards the reactant lowers the concentration of the added product.

Effect of decrease in concentration:

The opposite happens when we decrease the concentration of a reactant or product If the reactant concentration is decreased the equilibrium system shifts towards the reactants Removal of product shifts equilibrium towards the products

ii. **The Effect of Pressure Change:**

Equilibria that contain gases are influenced by pressure changes When pressure on a gaseous system at equilibrium Is increased the system tends to reduce the volume to undo or minimize the effect of increased pressure. This is done by decreasing the total number of gaseous molecules in the system. This is because at constant temperature and pressure, the volume of gas is directly proportional to the total number of molecules of the gas present.

Consider the following equilibrium system.

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

Increase in pressure:

When pressure increases the reaction system will reduce its volume by reducing the number of molecules present.

This means that the reaction will shift to the right, because in this direction three molecules (two of SO2 and one of O2) react to produce two molecules (of SO_3), thus reducing the total number of gaseous molecules present.

This means the equilibrium position will shift towards the side involving the smaller number of gaseous molecules in the balanced equation.

When the pressure is reduced:

When the pressure is reduced the system will shift so as to increase its volume.

When number of molecules are same:

When the total number of molecules is same on either side then.

Example:

$$\underbrace{H_2(g)+I_2(g)}_{\text{2 moles}} \rightleftharpoons \underbrace{2HI(g)}_{\text{2 moles}}$$

Whenever the pressure is changed on such a system, neither forward nor the reverse reaction is favored because the number of molecules is the same on each side Such equilibria are not affected by pressure or volume changes.

iii. The Effect of Change in Temperature:

Chemical reactions that liberate heat are called exothermic.

Chemical reactions that absorb heat are called endothermic.

Explanation:

Heat is placed on the right side of the equation in case of exothermic reactions.

In endothermic reaction it is placed on the left side of the equation. We can use Le Chatellier's Principle to predict the direction of change.

Endothermic process:

Treat heat as a reactant in the endothermic process. Predict the direction of shift in the same way as an actual reactant or product is added or removed. As an increase in temperature adding heat favors the endothermic reaction.

Example:

Now consider the following reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H^o = +57.2KJ$$

Because the reaction is endothermic, we can write left side of N2O.(g) equation.

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

Conclusion:

As the temperature increased, heat enters the system and the reaction will shift from left to right. As a result of this change, concentration of NO_2 will increase and that of N_2O_4 will decrease. This will increase the value of K.

$$K_c = \frac{[NO_2]^2}{[N_2O_2]} \qquad \begin{array}{l} \leftarrow increses \\ \leftarrow decreases \end{array}$$

That is why Kc for this reaction is 7.7 x at 0°C and 0,4 at 100°C

Exothermic process:

Treat heat as a product in the exothermic process. Predict the direction of shift in the shift in the same way as an actual reactant or product id added or removed.

Example:

As decrease in temperature (removing heat) favors the exothermic reaction.

Consider the following reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^o = 198KJ$$

Because the reaction is exothermic, we can write

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

Heat can be treated as if it were a substance involved in the reaction.

Conclusion:

According to the Le Chatellier's Principle an increase in temperature will shift counteract the temperature increase. As a result of this change concentration of SO, will decrease and concentrations of SO_2 and O_2 will increase. As a result, the value of equilibrium constant will decrease.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad \begin{array}{l} \leftarrow \text{increses} \\ \leftarrow \text{decreases} \end{array}$$

That is why Kc= 2.8 x 10^2 at 100OK whereas at 298K the value of Kc=$1x10^{26}$. The equilibrium production of SO_3 is favored at lower temperature. This is because Kc in much larger at 298K than at 1000K.

iv. The Effect of Addition of Catalyst:

A catalyst added to a reaction mixture speeds up both the forward and the reverse reaction to the same degree. Thus catalyst has no effect on the equilibrium concentrations of reaction mixture. However, the catalyst is important in enhancing the rate at which equilibrium is established.

Example7.9:

Kc for, the following reaction is 1.0 x 10^{-3} at 230°C

$$2ICl(g) \rightleftharpoons Cl_2(g) + I_2(g)$$

1.6 moles of ICl, 0.05 mole of I_2 and 0.05 mole of Cl_2 is present in the equilibrium mixture in 2dm³ container at 230°C. Determine the equilibrium concentrations of I_2 Cl_2 and ICl when the equilibrium is restored after the addition of another mole of ICl.

Solution:

On adding one mole of ICl into the equilibrium mixture will shift equilibrium in the forward direction. Thus the concentration of ICl will decrease and concentration of 1_2 and Cl_2 will increase by x whereas decrease by 2x.

$$2ICl(g) \rightleftharpoons Cl_2(g) + I_2(g)$$

Initial conc. (in moles)	1.6+1=2.6	0.05	0.05
Conc. At new Equilibrium (in moles)	2.6-2x	0.05+x	0.05+x
Eq. conc in Moles dm^{-3}	$\frac{2.6-2x}{2}$	$\frac{0.05+x}{2}$	$\frac{0.05+x}{2}$

$$K_c = \frac{[Cl_2][I_2]}{[ICl]_2}$$

$$1.0\times10^{-3} = \frac{\left(\frac{0.05+x}{2}\right)\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)^2}$$

Taking square root of both the sides

$$\sqrt{1.0\times10^{-3}}=\frac{\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)}$$

$$3.1\times10^{-3}=\frac{0.05-x}{2.6-2x}$$

$$x=0.029\text{ moles dm}^{-3}$$

$$[ICl]=2.6-2x$$

$$=2.6-2x\ 0.029$$

$$=2.571\text{ moles dm}^{-3}$$

$$[I_2]=[Cl_2]=0.05+x$$

$$=0.05+0.029$$

$$=0.079\text{ moles dm}^{-3}$$

Self-Check Exercise7.9

K_c for , the following reaction is 1.0×10^{-3} **at** 230^oC

$$2ICl \rightleftharpoons Cl_2(g)+I_2(g)$$

1.6 moles of ICl, 0.05 mole of I_2, and 0.05 mote of Cl_2, is present in the equilibrium mixture in 2dm^{3}' container at 230°C. Determine the equilibrium concentrations of I_2 Cl_2 and ICl when the equilibrium is restored after the removal of one mole of ICl.

(Ans:0.00478M, 0.00478, 0.6904M)

Solution;

When we add ICl into the equilibrium mixture will shift equilibrium in the forward direction Therefore the concentration of 1Cl will decrease while the concentration of I_2 and Cl_2 will increase

Initial Concentration (in moles)

$$21Cl(g) \rightleftharpoons Cl_2(g)+I_2(g)$$

$$16+1=26 \qquad 0.05 \qquad 0.05$$

Concentration at new equilibrium (in moles) $2.6-2x$

$0.05+x \quad 0.05+x$

Equation concentration (in mole dm^{-3}) $\frac{2.6-2x}{2}$

$\frac{0.05+x}{2} \quad \frac{0.05+x}{2}$

$$K_c=\frac{|Cl_2||I_2|}{|ICl|}$$

$$1.0\times10^{-3}=\frac{\left(\frac{0.05+x}{2}\right)\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)^2}$$

$$1.0\times10^{-3}=\frac{\left(\frac{0.05+x}{2}\right)^2}{\left(\frac{2.6-2x}{2}\right)^2}$$

Taking square root of both sides

$$\sqrt{1.0\times10^{-3}}=\sqrt{\frac{\left(\frac{0.05+x}{2}\right)^2}{\left(\frac{2.6-2x}{2}\right)^2}}$$

$$\sqrt{1.0\times10^{-3}} = \frac{\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)}$$

$$0.0316 = \frac{0.05+x}{2.6-2x}$$

$$0.0316(2.6-2x) = 0.05+x$$

$$0.0822 - 0.0632x = 0.05+x$$

$$x + 0.0632x = 0.0822 - 0.0632x$$

$$1.0632x = 0.0322$$

$$x = \frac{0.0322}{1.0632} = 0.030 mole-dm^{-3}$$

$$[ICl] = 2.6 - 2x$$

$$= 2.6 - 2x\times0.030 = 2.54\text{mole-dm}^{-3}$$

$$[I_2][Cl_2] = 0.05 + x$$

$$= 0.05 + 0.030 = 0.080 mole - dm^{-3}$$

Do you know?

Cigarette smoke is a major source of CO Smokers inhale it directly through burning cigarette ever non- smoker also inhale CO when they are exposed to cigarette smoke of others co combines with hemoglobin to form car boxy-hemoglobin Because car boxy hemoglobin is unable to transport oxygen, the heart must pump more blood to get the needed oxygen Also heavy smokers do not give their hemoglobin much opportunity to recover Thus chronic exposure to CO from smoking is believed to cause heart disease and heart attacks. Other substances in cigarette smoke can cause lung cancer and respiratory problems. Infect, smoking is a habit with many higher risks.

Self-Check Exercise 7.10

The formation of methanol is an important industrial reaction in the processing of new fuels

$$Co(g) + 2H_2(g) \rightleftharpoons CH_3,OH(g)$$

A student decreases system in an attempt to increase the yield of methanol. Is this approach reasonable? Explain.

Solution:

There is present one molecule of CO and two molecules of H; on reactant side (total thee molecules). while one molecule of $CH3OH$ is present on product side. Thus, total number of molecules of products is less than that of reactants. Hence, if pressure is decreased, the system will increase its volume and it will shift in backward direction. Therefore, the approach of the student is not correct. In order to increase the yield of methanol, the equilibrium must shift in forward direction. This is done by increasing the pressure.

Self-Check Exercise 7.11

Consider the following equilibrium

$$21(g) \rightleftharpoons I_2(g)$$

What would be the effect on the position of equilibrium when temperature is decreased?

Solution: and in as the reaction is exothermic it is favored at low temperature exothermic reactions heat is written on the product side as a product.

$2I(g) \rightleftharpoons I_2(g)$ + heat

According to the Le-Cafetiere Principle decrease in temperature will shift the reaction in forward direction.

Predict the effect of increasing the temperature on the amount of product in the following reaction.

$Co(g) + 2H_2(g)$ $CH_3OH(g)$ (exothermic)

Solution: As the reaction is exothermic it is favored at low temperature and in exothermic reactions heat is written on the product side as a product.

$Co(g) + 2H_2(g)$ $CH_3OH(g)$ + heat

According to the Le-Chatellier's Principle an increase in temperature will shift this reaction in backward direction in order to absorb the added heat and to compensate the added heat.

Q12. Define and explain the solubility product.

Ans: Solubility Product: It is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balanced equation.

Explanation:

When an excess of slightly soluble ionic compound is mixed with water. Some of it dissolves and remaining compound settle at the bottom Dynamic equilibrium is established between undissolved solid compound and its ions in the saturated solution.

Example: For example, when CaF_2, is mixed with water. Following equilibrium is established.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F(aq)$$

Mathematically:

K_c for this equilibrium can be written

$$K_C = \frac{[Ca^{+2}][F]^2}{[CaF_2]}$$

Since CaF_2, is slightly soluble salt its concentration almost remains constant Therefore,

$$K_c[CaF_2] = [Ca^{+2}][F]^2$$
$$K_{sp} = [Ca^{+2}][F]^2$$

Where Ksp is a constant known as the solubility product constant.

General, Ksp expression:

In general, K_{sp} expression of any slightly soluble ionic compound A_mB_n 278 be written as

$$A_mB_n\,(s) \rightleftharpoons mA^{+n}(aq) + nB^{-m}(aq)$$

$$K_{sp} = [A^{+n}]^m[B^{-m}]^n$$

Conclusion:

This means that the solubility product constant is equal to the product of the equilibrium concentration of ions each raised to a power equal to the number of such ions in the formula unit of the compound.

Q13. Define and explain precipitation reactions.

Ans: Precipitation Reactions:

An aqueous reaction that takes place when two or more solution are mixed together, yielding a solid insoluble substance is called precipitation reaction.

Explanation:

Consider the reverse process i.e the formation of a solid from solution. For the prediction whether a precipitate will form when two solutions are mixed. We will use the term ion product (Q'). It is obtained by substituting initial concentrations instead of equilibrium concentrations in the expression for K_{sp}.

Example:

For example, ion product expression for solid CaF_2, is given by

Q' = [Initial conc. of Ca^{+2} (Initial conc. of F $)^2$

If we add a solution containing Ca^{+2} ions to a solution containing F' ions, precipitate may or may not form. To predict whether a precipitation will occur, we compare Q' and K_{SP}. There are two possibilities.

Conditions for precipitation:

a). If $Q' > K_{sp}$, precipitation occurs and will continue until the concentration a) satisfy K_{sp}.

b). If Q'< K_{sp}, precipitation does not occur.

Example 7.10:

50cm^3 of 0.001M NaOH Is mixed with 150cm^3 of 0.01M $MgCl_2$ precipitate? K_{sp} for $Mg(OH)_2$ = 2x10^{-11}

Solution:

First, we will determine the concentrations of the ions present after mixing Total volume of solution

$$= 50cm^3 + 150cm^3$$
$$= 200cm^3$$
$$= 0.2.dm^3$$
$$NaOH \rightleftharpoons Na^+(aq) + OH(aq)$$
$$0.001M \quad 0.001\text{M} \quad 0.001\text{M}$$
$$[OH] = \frac{0.05dm^3 \times 0.001M}{0.2dm^3}$$
$$= 2.5 \times 10^{-4} M$$
$$MgCl_2 \rightleftharpoons Mg^{+2}(aq) + 2Cl(aq)$$
$$0.01\text{M} \quad 0.01\text{M} \quad 2 \times 0.01\text{M}$$
$$150\text{cm}^3 MgCl_2\_solution = 0.15dm^3$$
$$\left[Mg^{-2}\right] = \frac{0.05dm^3 \times 0.001M}{0.2dm^3}$$
$$= 7.5 \times 10^{-3} M$$
$$Now$$
$$Q' - \left[Mg^{+2}\right][OH]^2$$
$$= \left(7.5 \times 10^{-3}\right)\left(2.5 \times 10^{-4}\right)^2$$
$$= 47 \times 10^{-11}$$

As $Q' > K_{SP}$ therefore precipitation will occur.

Example 7.11:

The solubility of Ag Br is $7.1\times10^{-7}M$ **at** $25^{O}C$ **.Calculate its** K_{SP} **.**

Solution:

$7.1\times10^{-7}M$ Of dissolved Ag Br produces equal moles of Ag and Br ions.

$$AgBr(s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq)$$
$$7.1\times10^{-7}M \_ 7.1\times10^{-7}M \_ 7.1\times10^{-7}M$$
$$K_{SP} = \left[Ag^{+}\right]\left[Br^{-}\right]$$
$$K_{SP} = \left(7.1\times10^{-7}\right)\left(7.1\times10^{7}\right)$$
$$K_{SP} = 5.0\times10^{-15}$$

Self-check exercise 7.12

i. **Write K_{SP} expressions for**

- **Iron (II)Hydroxide**
- **Calcium Şulphate**

Solution:

Iron(II)Hydroxide

$$\mathrm{Fe(OH)_2(s)} \rightleftharpoons \mathrm{Fe^{+2}(ag) + 20H^{-}(aq)}$$
$$\mathrm{K}_{SP} = |\mathrm{Fe{+}2}|\,|\mathrm{OH^{-}}|^{2}$$

Calcium Sulphate

$$\mathrm{CaSO_4(s)} \rightleftharpoons \mathrm{Ca^{+2}(aq)} + SO_4^{-2}\mathrm{(aq)}$$
$$\mathrm{K}_{SP} = \left[\mathrm{Ca^{+2}}\right]\left[SO_4^{-2}\right]$$

ii. **Lead (II)Sulphate is used as white pigment. What is the solubility of $PbSo_4$? K_{SP}= 1.96x10 at 25°C**

(Ans: 1.4x10^{-4}M)

$$PbSO_4(s) \rightleftharpoons Pb^{+2}(aq) + SO_4^{-2}(aq)$$

Initial Concentration. (in moles)	a	0	0
Concentration at a -X equilibrium. (in moles)	a-x	x	x

$$K_{SP} = |Pb^{+2}||SO_4^{-2}|$$
$$K_{SP} = |X \times X| = 1.96 \text{ x } 10^{-8}$$
$$x^2 = 1.96 \text{ x } 10^{-8}$$

Taking square root on both sides

$$\sqrt{x} = \sqrt{1.96 \text{ x } 10^{-8}}$$
$$x = 1.40 \text{ x } 10^{-4} M$$

iii. **Phosphate in natural water often precipitates as insoluble $Ca_3(PO_4)_2$. In Indus river concentration of $Ca^{+2} and PO_4^{-3}$ ions is $1.0\times10^{-9}M$ each. Will calcium phosphate precipitate?** $K_{SP} = 1.2\times10^{-29}$ **at** 25^OC.

(Ans: No)

Solution:

$$K_{SP} = 1.2\times10^{-29} at 25^O C$$

Concentration of Ca^{+2} **ions=**

Concentration of PO_4^{-3} ions=

$Ca_3(PO_4)_2$ **Ionizes in water as**

$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{+2}(aq) + PO_4^{-3}(aq)$

Its ion product is given as

$Q' = |Ca^{+2}|^3 |PO_4^{-3}|^2$

$= (1.0\times10^{-9})^3 (1.0\times10^{-9})^2$

$= 1.0\times10^{-45}$

Since $Q' < K^{SP}$ Hence the precipitation will not occur.

Q14. Define and explain the Common Ion Effect.

Ans: Common Ion Effect: "The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of highly soluble electrolyte containing a common ion is cuiiea common ion effect"

Explanation:

Consider a solution of weak acid, hydrofluoric acid K, = 7.2 x 10, its salt sodium fluoride produces the common ion

$$HF(aq) \xrightleftharpoons{H_2O} H^+(aq) + F(aq)$$
$$NaF(s) \xrightleftharpoons{H_2O} Na^+(aq) + F(aq)$$

- **i.** Since HF is a weak electrolyte it slightly dissociates
- **ii.** NaF being strong electrolyte breaks up completely into its ions
- **iii.** The common ion F is produced by Naf will upset its equilibrium
- **iv.** This will increase concentration of F ions.
- **v.** According, to the Le Chatellier's principle, the aquarium will shift to the left to use some of F ions.

vi. This will decrease the dissociation of HF. Thus dissociation of HF will decrease in the presence of dissolved NaF.

vii. This means as a result of equilibrium shift, the concentration of HF will increase

viii. Similarly when a highly soluble salt is added to the saturated solution of less soluble salt containing a common ion.

ix. The degree of dissociation of less soluble salt decreases. Therefore it causes to decrease its solubility.

Q15. Give the different applications of common ion effect.

Ans: Applications of common ion effect:

The term common ion effect is used to describe the behavior of a solution in which same ion is produced by two different compounds.

i. **Precipitation of Potassium per chlorate (KClO,):**

Potassium per chlorate $KClO_4$ is moderately soluble in water. When highly soluble KCl is added to the saturated solution of $KClO_4$ It causes to increase the concentration of K' ion.

$$KClO_4(s) \rightleftharpoons K^+(aq)^+ ClO_4(aq)$$
$$KCl(s) \rightleftharpoons K^+(aq)^+ Cl(aq)$$

According to the Le Chatelier's principle K' ions will react with ClO, ions to form $KClO_4$(s). This will suppress, the ionization of $KClO_4$. Thus it will precipitate out.

ii. **Precipitation of pure NaCl:**

When HCI gas is passed through the saturated solution of NaCl (Brine), it causes to increases the concentration of Cl ion.

$$NaCl(s) \rightleftharpoons Na^{+}\ (aq)\ +\ CI^{-}\ (aq)$$
$$HCI\ (aq) \rightleftharpoons H^{+}\ (aq)\ +\ CI^{-}\ (aq)$$

According to Le Chatelier's principle Cl^- ions will combine with Na ions to form precipitate of pure NaCl.

Self-check Exercise 7.13

i. **Ammonium Chloride, NH_4Cl is a water soluble salt. What will happen if this salt is added to a solution containing ammonium hydroxide.**

$$NH_4OH(aq) \rightleftharpoons NH_4^{+}(aq) + OH\ (aq)$$

Solution:

NH_4Cl ionizes in water as

$$NH_4OH(aq) \rightleftharpoons NH_4^{+}(aq)\ +\ OH^{-}\ (aq)$$

Since, NH_4 Cl is highly soluble in water, therefore, it increases the concentration of NH, ions in the solution. According to the Le Chatellier's principle, NH_4, ions will react with OH ions to form NH_4OH Thus, it will suppress the ionization of NH_4OH and concentration of OH ions is decreased in the solution

ii. **Carbonic acid is a weak acid. It ionizes in water as follows**

$$H_2CO_3(aq) \rightleftharpoons 2H^{+}(aq)\ +\ Co_3^{-2}(aq)$$

What will happen if a strong electrolyte such as Na_2CO_3 is added to a solution containing carbonic acid.

Solution:

Na_2CO_3 ionizes in water as

$$Na_2CO_3(aq) \rightleftharpoons 2Na^+(aq) + CO_3^{-2}(aq)$$

Since, Na_2CO_3, is more soluble in water than H_2CO_3,. therefore, it increases the concentration of CO_3^{-2} in the solution. According to the Le-Chatellier's principle, Co, ions will react with H^+ ions to form H_2CO_3, Thus, it will suppress the ionization of H_2CO_3, and concentration of H^+ ions is decreased in the solution.

SUMMARY

- Chemical Equilibrium is a dynamic state in which the reaction proceeds with equal rates in both the directions.
- At equilibrium state reactants are converted continuously into products and vice versa, as molecules collide with each other.
- The law of mass action is a general description of the equilibrium condition. It states that for the reaction of type

  $$aA(g)+bB(g) \rightleftharpoons cC(g)+dD(g)$$

  The equilibrium equation is given by

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

  where K. is equilibrium constant
- The equilibrium can be expressed in terms of the equilibrium partial pressure of gases as K_P.

- The reaction quotient Q has the same form as the equilibrium constant expression, but it applies to the reaction that may not be at equilibrium
  If $Q > K$, the reaction will proceed from right to left to achieve equilibrium
  If $Q < K$., the reaction will proceed from left to right to achieve equilibrium.
  If $Q = K$, the reaction is at equilibrium
- There is only value of K_C for each reaction at a given temperature. However, there are infinite numbers of equilibrium positions. An equilibrium position is defined as a particular set of equilibrium concentrations that satisfies the equilibrium expressions.
- The concentration of pure solids, pure liquids and solvents are constant and do not appear in equilibrium constant expression of a reaction.
- Le Chatellier's Principle allows us to predict the effect of changes in concentration, pressure and temperature on a system at equilibrium. It states that when a change is imposed on system equilibrium, the equilibrium position with shift in a direction that tends to undo the effect of imposed change
- Only a change in temperature changes the value of K_C for a particular reaction.
- The addition of catalyst has no effect CO the equilibrium concentrations of reactants and products However, it decreases time to achieve equilibrium state.
- The principle of equilibrium can also be applied when an excess of solid is added to form a saturated solution.