CHAPTER # 7
CHEMICAL EQUILIBRUM

Q1. Differentiate between reversible and irreversible reaction.

Ans:

Reversible Reaction	Irreversible Reaction
i. The reactions which can proceed in both the directions i.e. forward and backward and are called reversible reactions.	**i.** The reactions that virtually go to completion i.e., reactants are completely consumed and converted into the products. Such reactions are called irreversible reactions.
ii. The reactants are not completely consumed.	**ii.** The limiting reactant is consumed completely.
iii. In reversible reactions the reaction never goes to completion.	**iii.** The reaction virtually goes to completion in irreversible reactions.
iv. These reactions reach at a stage called chemical equilibrium. At this stage the concentration of reactants and products become constant. But the reaction continues to proceed in both the directions without any change in concentrations of reactants and products under existing conditions.	**iv.** The concept of chemical equilibrium is not applicable on irreversible reactions.
v. It is represented by $\rightleftharpoons$ double arrow.	**v.** It is represented by $\longrightarrow$ single arrow.
vi. Examples: i. $2NO_2(g) \rightleftharpoons N_2O_4(g)$ ii. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ iii. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	**vi. Examples:** i. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ ii. $C + O_2 \longrightarrow CO_2$ iii. $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

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 reaction 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 the 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:

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

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:

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

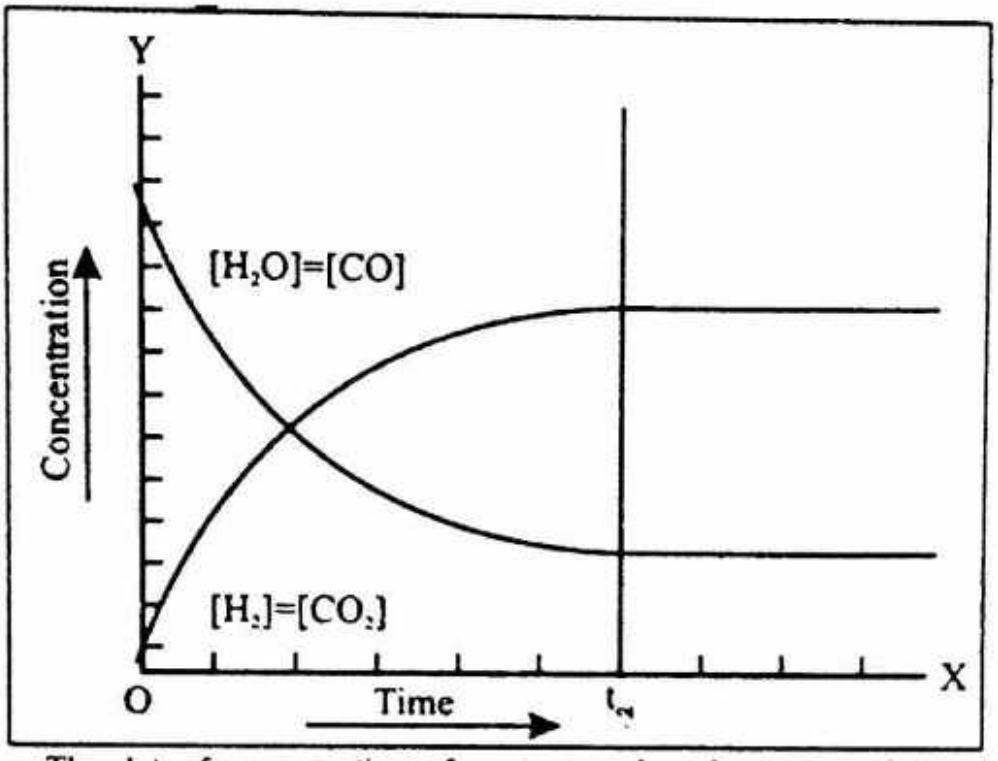
Eventually a time comes when both reactions proceed at the same speed. The reaction at this stage is said to be in chemical equilibrium. The concentrations of reactants and products become constant.

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

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 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 C.M 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^{-3} 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, $R_f \alpha [A]^a [B]^b = k_f [A]^a [B]^b$ ..... **(i)**

Where k_f 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_r is the rate constant for the reverse reaction.

At equilibrium state

Rate of forward reaction = Rate of reverse reaction

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

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

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:

$$CO(g) + \frac{1}{2} O_2(g) \rightleftharpoons CO_2(g)$$

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

SELF-CHECK EXERCISE 7.1

i. The following equations represent various industrial reactions 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: (i) $SO_3(g) + O_2(g) \rightleftharpoons SO_3(g)$

Balancing the equation is

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

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

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

Balancing the equation is

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

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

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

Balancing the equation is

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

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

ii. Give the balanced equations that correspond to following equilibrium expressions.

(i) $K_c = \dfrac{[CH_3OH]}{[CO][H_2]^2}$

(ii) $K_C = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$

Solution:

i. $CO + H_2 \rightleftharpoons CH_3OH$

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 number of moles of the reactants are equal to the number of moles of the products.

For instance K_C for the following reaction has no units.

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

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

$$K_C = \frac{(\text{mol dm}^{-3})(\text{mole dm}^{-3})}{(\text{mole dm}^{-3})(\text{mole dm}^{-3})} = \text{No units}$$

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

Example:

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

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

$K_C = \text{mole dm}^{-3}$

In this way we 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 reactions:

(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:

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

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

$$K_C = \frac{(mole\ dm^{-3})(mole\ dm^{-3})}{(mole\ dm^{-3})} = mole\ dm^{-3}$$

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

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

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

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

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

$$K_C = \frac{(mole\ dm^{-3})^2}{(mole\ dm^{-3})(mole\ dm^{-3})} = No\ units$$

Example 7.3:

The following equilibrium concentrations were observed for the reaction at 500°C.

$$A(g) + 3B(g) \rightleftharpoons 2AB(g)$$

[A] = 0.399M, [B] = 1.197M, [AB] = 0.203M

Calculate K_C

Solution:

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

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

$$= 6 \times 10^{-2}\ dm^6\ mole^{-2}$$

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 is often expressed in terms of partial pressure of each gas

According to **Henry's Law**

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

Equilibrium constant K_p (For partial pressure):

Equilibrium constant K_p 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 K_p 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

$P_{NOCl} = 1.2$ atm

$P_{NO} = 5.0 \times 10^{-2}$ atm

$PCl_2 = 3.0 \times 10^{-1}$ atm

$$K_P = \frac{(P_{NOCl})^2}{(P_{NO})(P_{Cl2})}$$

$$K_P = \frac{(1.2)^2}{(5.0\times10^{-2})(3.0\times10^{-1})}$$

$K_P = 1.9 \times 10^3$

Now

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

$\Delta n = 2 - (2 + 1) = -1$

$R = 0.0820 dm^3\ atm K^{-1}\ mole^{-1}$

$T = 25°C + 273 = 298K$

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

$1.9 \times 10^3 = K_C (0.08205 \times 298)^{-1}$

$$1.9 \times 10^3 = \frac{K_C}{(0.08205 \times 298)}$$

$K_C = 1.9 \times 10^3\ 0.08205 \times 298$

$K_C = 4.65 \times 10^4$

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

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

$R = 0.0821\ atm\ dm^3\ K^{-1}\ mole^{-1}$

$\Delta n = 2 - (2 + 1) = -1$

$T = 25\ °C + 273 = 298\ K$

$K_C = 3.85$

Putting values in equation (i)

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

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

Q8. Define and explain the following terms.

i. Homogenecus 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.

i. Homogeneous Equilibria:

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

Example:

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

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

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

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

ii. Heterogeneous Equilibria:

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

Example:

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

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

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

Note:

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

This is 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 $K_P = p_{H_2}^2 \times p_{O_2}$

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

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

and $$K_p = \frac{P^4_{H_2}}{P^4_{H_2O}}$$

SELF-CHECK EXERCISE 7.4

Write K_c and K_p 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) $CH_4(g) + 4Cl_2(g) \rightleftharpoons CCl_4(l) + 4HCl(g)$

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) $CH_4(g) + 4Cl_2(g) \rightleftharpoons CCl_4(l) + 4HCl(g)$

$$K_c = \frac{[HCl]^4}{[CH_4][Cl_2]^2}$$

$$K_P = \frac{P_{HCl}^4}{P_{CH_4} \times P_{HCl}^4}$$

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

$2x = 0.12$

$$x = \frac{0.12}{2}$$

$x = 0.06$

$[N_2O_4] = 0.1 - 0.06$

$= 0.04$ mole

	N_2O_4 (g) $\rightleftharpoons$	$2NO_2$(g)
Initial Conc (in moles)	0.1	zero
Eq. Conc (in moles)	$0.1 - x$	$2x = 0.12$
Eq.con C. (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

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_C = 0.1$ at 2000°C

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

$$0\ 32 = \frac{2x}{0.1-x}$$

$x = 0.014M$

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

$= 0.1 - 0.014$

$= 0.086M$ each

$[NO] = 2x$

$= 2 \times 0.014$

$= 0.028\ M$

SELF-CHECK EXERCISE 7.5

For the reaction

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

K_c = 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:

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

K_C is given as

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

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

Taking square root of both the sides

$$\sqrt{0\ 60} = \sqrt{\frac{x^2}{(0.3-x)^2}}$$

$$0.775 = \frac{x}{(0.3-x)}$$

$$x = 0.775\,(0.3-x)$$

$$x = 0.233 - 0.775x$$

$$x + 0\ 775x = 0.233$$

$$1.775x = 0.233$$

$$x = \frac{0.233}{1\ 775}$$

$x = 0.131$

Thus

$[CO] = x = 0.131\ moles$

Example7.7:

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_c for the reaction.

Solution:

Initial moles of $CH_3COOH = \frac{60g}{60g/mole} = 1$ mole

Initial moles of $C_2H_5OH = \frac{46g}{46g/mole}$ = mole

At equilibrium

Moles of $CH_3COOC_2H_5 = \frac{58.7g}{88g/moles} = 0.666$moles.

Moles of $H_2O = \frac{12g}{18g/moles} = 0.666$mole

$$CH_3COOH\ (1) + C_2H_5OH\ (1) \rightleftharpoons CH_3COOC_2H_5\ (1) + H_2O\ (1)$$

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

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

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

$$K_C = 4$$

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_c for the reaction. **(Ans: 0.179)**

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,
$x = 0.038$
$|Fructose| = 0.25 - x$
$= 0.25 - 0.038\,M$
$= 0.212\,M$
$|Glucose| = x = 0.038M$
$K_C = \frac{|Glucose|}{|Fructose|} = \frac{|0.038|}{|0.212|} = 0.179$

- **When 3.88 moles of NO and 0.88 moles of CO_2 were heated in a flask at a certain temperature. At equilibrium 0.11 moles of each of the product were present. Calculate K_c for the reaction.**

$CO_2(g) + NO(g) \rightleftharpoons CO(g) + NO_2(g)$ (Ans: 0,0042)

Solution:

	$CO_2(g)$ +	NO (g) $\rightleftharpoons$	CO(g) +	$NO_2(g)$
Initial Concentration. (in moles)	0.88	3.88	*zero*	*zero*
Equation Concenitration. (in moles)	$0.88 - x$	$3.88 - x$	x	x

Given that 0.11 *moles of each of the product are present at equilibrium,*
Thus, $x = 0.11$
$|CO_2| = x = 0.11\ moles$
$|NO| = x = 0.11\ moles$
$|CO_2| = 0.88 - x = 0.88 - 0.11 = 0.77\ moles$
$|NO| = 3.88 - x = 3.88 - 0.11 = 3.77\ moles$

$$K_C = \frac{|CO||NO_2|}{|CO_2||NO|}$$

$$0.60 = \frac{(0.11)(0.11)}{(0.77)(3.77)} = 0.0042$$

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_c help us to determine.

i. The Direction of a Reaction.

ii. The Extent of Chemical Reaction.

Ans: i. 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.

$$Q = \frac{[\text{Products}]}{[\text{reactant}]}$$

The value Q leads to one of the following possibilities.

a. **$Q < K_c$**

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

b. **$Q > K_c$**

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. **$Q = K_c$**

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. **K_c is very large:**

Many reactions have very large equilibrium constant.

Example:

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ **$K_c = 5.4\times10^{18}$ at 25°C**

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

$$\frac{[HBr]^2}{1\times1} = 5.4 \times 10^{18}$$

$$[HBr] = \sqrt{5.4\times10^{18}}$$

$$= 2.32 \times 10^{9} M$$

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 K_c indicates that the reaction goes virtually to completion.**

b. **K_c is very small:**

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

Example:

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ **$K_c = 1.0\times10^{-30}$ at 25°C**

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

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

$$\frac{[NO]^2}{1\times 1} = 1 \times 10^{-30}$$

$$[NO] = \sqrt{1\times 10^{-30}}$$

$[NO] = 1 \times 10^{-15}$ moles

Conclusion:

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

c. K_C is neither very small nor very large:

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

Example:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 0.36 \text{ at } 25^\circ C$$

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

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, $K_C = 6.0 \times 10^{-1}$

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

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 $Q > K_C$. 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.

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ $K_c = 8.3\times10^{-4}$ **at 350°C**

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

$[COCl_2] = 0.5$ M

$[CO] = 2.5\times10^{-2}$ M

$[Cl_2] = 2.5\times10^{-2}$ M **(Ans: Towards left)**

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 $Q > K_c$

Hence the system will shift towards left

SELF-CHECK EXERCISE 7.8

White phosphorus P_4 is produced by the reaction of phosphorite rock, $Ca_3(PO_4)_2$ with coke. When exposed to air it bursts into smoke and fumes and releases a large amount of heat. Predict whether K_c 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_c **will be very large** and the reaction will go in forward direction.

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

Ans: Le Chatelier's principle

"It states that if 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 Chatelier'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 Chatelier'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_2O are 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 reduced 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 SO_2 and one of O_2) 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:

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

Whenever the pressure is changed on such a system, neither forward nor the reverse reaction is favoured 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 reactions, it is placed on **the left side of the equation.**

We can use Le Chatelier'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 favours the endothermic reaction.

Example:

Now consider the following reaction

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

Because the reaction is endothermic, we can write heat on left side of equation.

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

Conclusion:

As the temperature is 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_c

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

$[NO_2]^2$ ⟵ increases

$[N_2O_4]$ ⟵ decreases

That is why Kc for this reaction is 7.7×10^{-5} 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 same way as an actual reactant or product is added or removed.

Example:

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

Consider the following reaction

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

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 Chatelier's Principle an increase in temperature will shift reaction from right to left in order to absorb the added heat and to counteract the temperature increase. As a result of this change concentration of SO_3 will decrease and concentrations of SO_2 and O_2 will increase. As a result, the value of equilibrium constant will decrease.

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

increases ⟵ ⟵ decreases

That is why $K_C = 2.8 \times 10^2$ at 1000K whereas at 298K the value of $K_C = 1 \times 10^{26}$. The equilibrium production of SO_3 is favoured at lower temperature. This is because K_C 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: K_C for, the following reaction is 1.0×10^{-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 $2dm^3$ 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 I_2 and Cl_2 will increase by x whereas concentration of ICl will 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}	$\frac{2.6-2x}{2}$	$\frac{0.05+x}{2}$	$\frac{0.05+x}{2}$

$$K_C = \frac{[Cl_2][I_2]}{[ICl]^2}$$

$$1.0 \times 10^{-3} = \frac{\left(\frac{0.05+x}{2}\right)\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)^2}$$

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 moles dm^{-3}

$[ICl] = 2.6 - 2x$

$= 2.6 - 2x\ 0.029$

$= 2.571$ moles dm^{-3}

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

$= 0.05 + 0.029$

$= 0.079$ moles dm^{-3}

SELF-CHECK EXERCISE 7.9

K_C for, the following reaction is 1.0×10^{-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 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 ICl will decrease while the concentration of I_2 and Cl_2 will increase

	$2ICl\ (g)$	$\rightleftharpoons$	$Cl_2(g) + I_2(g)$	
Initial Concentration (in moles)	1.6 + 1 = 2.6		0.05	0.05
Concentration at new equilibrium. (in moles)	$2.6 - 2x$		$0.05 + x$	$0.05 + x$
Equation concentration (in mole dm^{-3})	$\frac{2.6-2x}{2}$		$\frac{0.05+x}{2}$	$\frac{0.05+x}{2}$

$$K_C = \frac{[Cl_2][I_2]}{[ICl]}$$

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

$$1.0 \times 10^{-3} = \frac{\left(\frac{0.05+x}{2}\right)^2}{\left(\frac{2.6-2x}{2}\right)^2}$$

Taking squar root of both the sides

$$\sqrt{1.0 \times 10^{-3}} = \sqrt{\frac{\left(\frac{0.05+x}{2}\right)^2}{\left(\frac{2.6-2x}{2}\right)^2}}$$

$$\sqrt{1.0 \times 10^{-3}} = \frac{\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)}$$

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

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

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

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

$$1.0632x = 0.0322$$

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

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

$$= 2.6 - 2x \times 0.030 = 2.54\ mole\ dm^{-3}$$

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

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

Do you know?

Cigarette smoke is a major source of CO. Smokers inhale it directly through burning cigarette. even non- smoker also inhale CO when they are exposed to cigarette smoke of others. CO combines with hemoglobin to form carboxy-hemoglobin. Because carboxy-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. Infact, 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

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

A student decreases pressure over the 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_2 on reactant side (total thee molecules), while one molecule of CH_3OH 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**

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

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

Solution:

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

$$2I(g) \rightleftharpoons I_2(g) + \text{heat}$$

According to the Le-Chatelierfe 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.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l) \qquad \text{(exothermic)}$$

Solution:

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

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l) + \text{heat}$$

According to the Le-Chatelier'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 as

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

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 K_{SP} is a constant known as the solubility product constant.

General, K_{SP} expression:

In general, K_{SP} expression of any slightly soluble ionic compound A_mB_n can 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

$$Q' = [\text{Initial conc. of } Ca^{+2}] [\text{Initial conc of } F^-]^2$$

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 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 $MgCl_2$. Will $Mg(OH)_2$ precipitate? K_{SP} for $Mg(OH)_2 = 2\times10^{-11}$.

Solution:

First we will determine the concentrations of the ions present after mixing

Total volume of solution

$= 50cm^3 + 150cm^3$

$= 200\ cm^3$

$= 0.2dm^3$

$NaOH \rightleftharpoons Na^+(aq) + OH^-(aq)$

0.001M 0.001M 0.001M

$50cm^3$ NaOH solution = $0.05dm^3$

$$[OH^-] = \frac{0.05dm^3 \times 0.001M}{0.2dm^3}$$

$= 2.5 \times 10^{-4}M$

$MgCl_2 \rightleftharpoons Mg^{+2}(aq) + 2Cl^-(aq)$

0.01M 0.01M $2 \times 0.01M$

$150cm^3$ $MgCl_2$ solution = $0.15dm^3$

$$[Mg^{+2}] = \frac{0.05dm^3 \times 0.001M}{0.2dm^3}$$

$= 7.5 \times 10^{-3}$ M

Now

$Q' = [Mg^{+2}][OH]^2$

$= (7.5 \times 10^{-3})(2.5 \times 10^{-4})^2$

$= 47 \times 10^{-11}$

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

Example7.11:

The solubility of Ag Br is 7.1×10^{-7}M at 25°C. Calculate its K_{SP}.

Solution:

7.1×10^{-7}M of dissolved Ag Br produces equal moles of Ag^+ and Br^- ions.

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

7.1×10^{-7}M 7.1×10^{-7}M 7.1×10^{-7}M

$K_{SP} = [Ag^+][Br^-]$

$K_{SP} = (7.1 \times 10^{-7})(7.1 \times 10^{-7})$

$K_{SP} = 5.0 \times 10^{-15}$

SELF-CHECK EXERCISE 7.12

i. Write K_{SP} expressions for

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

Solution:

- **Iron(II)Hydroxide**

$$Fe(OH)_2(s) \rightleftharpoons Fe^{+2}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Fe^{+2}][OH^-]^2$$

- **Calcium Sulphate**

$$CaSO_4(s) \rightleftharpoons Ca^{+2}(aq) + SO_4^{-2}(aq)$$

$$K_{sp} = [Ca^{+2}][SO_4^{-2}]$$

ii. Lead(II)Sulphate is used as white pigment. What is the solubility of $PbSO_4$? $K_{SP} = 1.96\times10^{-8}$ at 25°C (Ans: 1.4×10^{-4}M)

Solution:

	$PbSO_4\,(s)$	$\rightleftharpoons$	$Pb^{+2}\,(aq)$ +	$SO_4^{-2}\,(aq)$
Initial Concentration. (in moles)	a		0	0
Concentration at equilibrium. (in moles)	$a-x$		x	x

$$K_{sp} = |Pb^{+2}|\,|SO_4^{-2}|$$
$$K_{sp} = |x\times x| = 1.96\times10^{-8}$$
$$x^2 = 1.96\times10^{-8}$$

Taking square root on both sides

$$\sqrt{x^2} = \sqrt{1.96\times10^{-8}}$$
$$x = 1.40\times10^{-4}M$$

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 1.0×10^{-9}M each. Will calcium phosphate precipitate? $K_{SP} = 1.2\times10^{-29}$ at 25°C (Ans: No)

Solution:

$$K_{sp} = 1.2\times10^{-29}\ at\ 25\ ^\circ C$$
$$Concentration\ of\ Ca^{+2}\ ions = 1.0\times10^{-9}M$$
$$Concentration\ of\ PO_4^{-3}\ ions = 1.0\times10^{-9}M$$

$Ca_3(PO_4)_2$ ionizes in water as

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

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 called common ion effect"

Explanation:

Consider a solution of weak acid, hydrofluoric acid $K_a = 7.2\times10^{-4}$, its salt sodium fluoride produces the common ion

$$HF\,(aq) \overset{H_2O}{\rightleftharpoons} H^+(aq) + F^-(aq)$$
$$NaF\,(s) \overset{H_2O}{\rightleftharpoons} Na^+(aq) + F^-(aq)$$

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 Chatelier's principle, the equilibrium 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 **behaviour of a solution** in which same ion is produced by two different compounds.

i. Precipitation of Potassium per chlorate ($KClO_4$):

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.

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

$$KCl(s) \rightarrow K^+\ (aq) + Cl^-\ (aq)$$

According to the Le Chatelier's principle K^+ ions will react with ClO_4^- 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 HCl gas is passed through the saturated solution of NaCl (Brine), it causes to increases the concentration of Cl^- ion.

$$NaCl(s) \rightleftharpoons Na^+\ (aq) + Cl^-\ (aq)$$

$$HCl\ (aq) \rightleftharpoons H^+\ (aq) + Cl^-\ (aq)$$

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.

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

Solution:

NH_4Cl ionizes in water as

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

Since, NH_4Cl is highly soluble in water, therefore, it increases the concentration of NH_4^+ ions in the solution. According to the Le Chatelier'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 **thej** concentration of CO_3^{-2} in the solution. According to the Le-Chatelier's principle, CO_3^{-2} 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_c 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 $Q > K_c$, the reaction will proceed from right to left to achieve equilibrium.
  If $Q < K_c$, the reaction will proceed from left to right to achieve equilibrium.
  If $Q = K_c$, 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 Chatelier'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 will 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 on 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.

EXERCISE

MULTIPLE CHOICE QUESTIONS

1. Choose the Correct Answer.

(i) **K_c is independent of**

(a) Temperature (b) Pressure
(c) Both temperature and pressure (d) K_P

(ii) **For which of the following reactions, Kc has units of concentration.**

(a) $2A(g) \rightleftharpoons B(g)$ (b) $A(g) \rightleftharpoons B(g)$
(c) $A(g) \rightleftharpoons 2B(g)$ (d) $3(g) \rightleftharpoons 2C(g)$

(iii) **For the following reaction**

$2A(g) + B(g) \rightleftharpoons 3C(g)$

We can write

(a) $K_c > K_P$ (b) $K_c < K_P$
(c) $K_P - K_c = 0$ (d) $K_P - K_c = -1$

(iv) **When a catalyst is added to an equilibrium mixture, it decreases**

(a) Reverse reaction (b) Forward reaction
(c) Concentrations of reaction mixture (d) Enthalpy of reaction
(e) It has not effect

(v) **If $K_{sp} = [M^{+3}]^2[X^{-1}]^3$, the chemical formula of compound is**

(a) MX_2 (b) M_2X_3
(c) M_3X_2 (d) M_2X_3 (e) None of these

(vi) **NaCl can be purified by passing HCl gas through the _____ solution of NaCl.**

(a) Dilute (b) Concentrated (c) Hot (d) Cold

(vii) **$K_c = K_P$ when Δn is equal to**

(a) Zero (b) +1 (c) -1 (d) -2

(viii) **Consider the following reaction:**

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ ΔH° -198 KJ

Yield of sulphur trixoxide can be increased by

(a) increasing pressure (b) increasing temperature
(c) adding catalyst (d) increasing concentration of oxygen

1 a b

- The addition of catalyst has no effect on 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.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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1 a b

2. a, b, c
3. a, b, c, d
4. a, d

Answers

i. d	ii. c	iii. c	iv. e	v. b	vi. b	vii. a	viii. 4

2. Define chemical equilibrium?

Ans. Chemical Equilibrium:

"It is the state of a reversible reaction at which composition of the reaction mixture do not change and the rate of both forward and reverse reaction is same that stage of reaction is called chemical equilibrium."

3. State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.

Ans: Conditions for Equilibrium:

Important features of equilibration constant expression are as follows:

i. K_c applies only at equilibrium. The subscript c indicates the concentrations of reactants and products are in moles per dm^3 at equilibrium state.

ii. K_c is independent of initial concentrations of reactants and products but depends upon temperature. At a given temperature, it has only one value. Whether we start reaction with pure reactants or pure products or any composition in between, the value of K_c remains unchanged.

iii. K_c is related to the coefficients of the balanced equation. The concentrations of the products are placed in the numerator and those of reactants in the denominator. Each concentration is raised to a power equal to its coefficient in the balanced equation.

iv. The magnitude of K_c indicates the position of equilibrium. When K_c is less then I, the denominator is greater in magnitude than the numerator. This means the concentration of the reactants are greater than those of products when the equilibrium is established. Whereas, when K_c is greater than I, the numerator is greater in magnitude than the denominator. This means the concentrations of the products are greater than those of the reactants at equilibrium.

Ways to Recognize Equilibrium and Determination of Equilibrium Constant:

Equilibrium constant expression can be determined by two methods:

a) Physical Method (spectrometric method)

b) Chemical Method

a) Physical Method (spectrometric method):

This method is based on the measurement of a physical property of the reaction mixture. This physical property is measured during the course of reaction without removing the sample from the reaction mixture.

Explanation:

This method is applicable if a reactant or product absorbs ultraviolet, visible or infrared radiation. The concentration can be determined by measuring the amount of radiation absorbed.

Example:

Equilibrium constant for N_2O_4 – NO_2 system can be determined by the spectrophotometer.

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

N_2O_4 is a colourless gas whereas NO_2 is reddish brown gas. The progress of the reaction can be studied by measuring the absorbance at regular interval Absorbance is proportional to the concentration of NO_2.

At equilibrium spectrometer will show constant value of absorbance Suppose reaction is started with "a" moles of N_2O_4 at 100°C and x moles of it is converted to NO_2. By applying stoichiometery, the amount of NO_2 present in equilibrium will be $2x$, which is measured by the spectrophotometer.

Mathematically:

Suppose the volume of the reaction mixture is V dm^3, then we can write

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

Initial Conc (in moles)	a	zero
Eq. Conc (in moles)	$a - x$	$2x$
Eq. Conc ($mole/dm^3$)	$\frac{a-x}{V}$	$\frac{2x}{V}$

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

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

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

b) Chemical Method:

In this method, the amount of a reactant or product is determined by a suitable chemical reaction

Explanation:

Consider the reaction between acetic acid and ethanol to form ethyl acetate and water It is an example of reversible reaction in the solution state

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

Suppose this reaction is started by taking 'a' moles of acetic acid and 'b' moles of ethanol in a stoppered flask at room temperature. A small amount of mineral acid is added in the mixture to catalyse the reaction

The progress of the reaction can be studied by determining the concentration of acetic acid after regular intervals For this purpose small portion of mixture is withdrawn

The concentration of acetic acid is determined by titrating it against a standard solution of NaOH using phenolphthalein as indicator. Concentration of

acetic acid will decrease until equilibrium is attained. Suppose x moles of acetic acid has been reacted with ethanol. Since one mole of acetic reacts with one mole of ethanol, the amount of ethanol reacted with acetic acid will also be x moles. As one mole of each of the product is formed. At equilibrium x moles of ethyl acetate and x moles of water are produced.

Mathematically:

Reaction	$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$			
Initial Conc (in moles)	a	b	Zero	Zero
Eq. Conc (in moles)	$a - x$	$b - x$	x	x

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

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

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

4. Describe the microscopic events that occur when a chemical system is in equilibrium.

Ans: Microscopic events:

The microscopic events that take place in an equilibrium system are given below.

i. The rate of chemical reaction depends on the numbers of effective collisions between the reacting molecules.

ii. At equilibrium the numbers of effective collisions for the forward and reverse reactions are equal.

Number of effective collisions:

Increase in concentration of reactant increases such collisions for the forward reaction. Thus equilibrium shift towards right with the formation of more molecules of products.

Therefore the **number** of effective collisions for the reverse process also increases. As time passes the effective collisions of reactant molecules decreased, lowering the rate of forward reaction.

Ultimately the number of effective collisions for both the processes again becomes equal and equilibrium is re-established.

5. Define and explain the following terms:

(i) Reaction quotient

(ii) Solubility product

(iii) Common ion effect

(iv) Heterogenous equilibrium

(v) Ion product

Ans. (i) 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.

$$Q = \frac{[\text{Products}]}{[\text{reactant}]}$$

The value Q leads to one of the following possibilities.

a. **$Q < K_c$**

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

b. **$Q > K_c$**

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. **$Q = K_c$**

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

(ii) 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 as

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

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 K_{SP} is a constant known as the solubility product constant.

(iii) Common Ion Effect:

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 called **common ion effect**"

Explanation:

Consider a solution of weak acid, hydrofluoric acid $K_a = 7.2 \times 10^{-4}$, its salt sodium fluoride produces the common ion.

$$HF(aq) \overset{H_2O}{\rightleftharpoons} H^+(aq) + F^-(aq)$$

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

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 Chatelier's principle, the equilibrium 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

(iv) Heterogenous equilibrium:

Equilibria which involve more than one phases are called Heterogeneous equilibria For example

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

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

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

If pure solids or pure liquids are involved in an equilibrium system, their concentrations are not included in the equilibrium constant expression. This is because the change in concentrations of any pure solid or liquid has no effect on the equilibrium system.

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

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

and $K_P = p_{H_2}^2 \times p_{O_2}$

(v) Ion product:

It is the product of the initial concentration of ions each raised to a power equal to the co-efficient of the ion in the balanced chemical equation.

6. Explain industrial application of Le Chatelier's principle using Haber's process as an example.

Ans: Industrial Application of Le Chatelier's Principle (Synthesis of Ammonia by Haber's Process):

The manufacture of ammonia by Haber's process is represented by the following equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ = -92.46KJ$$

This equation provides the following information.

i) The reaction is exothermic.

ii) The reaction proceeds with a decrease in number of molecules or moles.

Le Chatelier's principle suggests three ways to get maximum yield of ammonia.

i. Low Temperature:

The forward reaction is exothermic therefore, low temperature will favour the formation of ammonia. The suitable temperature is 400°C.

ii. High Pressure:

Since four molecules (one of N_2 and three of H_2) react to produce two molecules of NH_3. Thus high pressure will shift the equilibrium to the right side i.e. formation of NH_3. The most suitable pressure is 200 – 300 atm.

Optimum condition:

Thus optimum condition for equilibrium production of ammonia is low temperature and high pressure. Although at low temperature yield of ammonia is high, but the rate of its formation is so slow that the process becomes uneconomical. Therefore, a catalyst is used to increase the rate of reaction. Usually a piece of iron with other metal oxides is used as catalyst. The equilibrium mixture contains 35% NH_3 by volume.

iii. Continual removal of ammonia:

A final factor which greatly increases the production of ammonia is the continuous removal of ammonia as it is formed. This is done by liquefying ammonia.

The equilibrium mixture is cooled by refrigeration coils until ammonia condenses at -33.4°C and is removed. N_2 and H_2 which do not liquefy at this temperature are recycled into the reaction chamber.

The stress caused by the continual removal of ammonia shifts the equilibrium toward the production of more ammonia. In fact the mixture needs not to be allowed to come to equilibrium at all. In this way practically 100% conversion of $N_2$and H_2 to NH_3 is possible.

7. Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.

Ans. Microscopic events:

The microscopic events that take place in an equilibrium system are given below.

i. The rate of chemical reaction depends on the numbers of effective collisions between the reacting molecules.

ii. At equilibrium the numbers of effective collisions for the forward and reverse reactions are equal.

Number of effective collisions:

Increase in concentration of reactant increases such collisions for the forward reaction. Thus equilibrium shift towards right with the formation of more molecules of products.

Therefore the **number** of effective collisions for the reverse process also increases. As time passes the effective collisions of reactant molecules decreased, lowering the rate of forward reaction.

Ultimately the number of effective collisions for both the processes again becomes equal and equilibrium is re-established.

8. 50 cm^3 of acetic acid (d = 1.049 gcm^{-3}) is mixed with 50 cm^3 of ethanol (d=0.789 gcm^{-3}) what is the equilibrium composition of the mixture at 25°C (K_c=4). (Ans:CH_3COOH=31.68 g, C_2H_5OH=32.506 g, $CH_3COOC_2H_5$=30.448 g, H_2O= 6.22 g)

Solution:

$Equilibrium\ constant = K_c = 4\ at\ 25°C$

Volume of acetic acid = 50 cm^3
Density of acetic acid = 1 049 g cm^{-3}
Mass of acetic acid = $density \times Volume$ = 1 049×50 = 52.45 g
Molar mass of acetic acid = 60 $g\ mole^{-1}$

$$\textbf{Number of moles of } CH_3COOH = \frac{52.45}{60} = 0.874\ \textbf{mole}$$

Volume of ethanol = 50 cm^3
Density of ethanol = 0.789 g cm^{-3}
Mass of ethanol = $density \times Volume$ = 0.789 × 50 = 39.45 g
Molar mass of ethanol= 46 $g\ mole^{-1}$

$$\textbf{Number of moles of } C_2H_5OH = \frac{39.45}{46} = 0.858\ \textbf{mole}$$

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

Initial Concentration. (in moles)	**0.874**	**0.858**	***zero***	***zero***
Equation Concentration. (in moles)	$0.874 - x$	$0.858 - x$	x	x

K_C will be

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

$$4 = \frac{(x)(x)}{(0.874 - x)(0.858 - x)}$$

$$x^2 = 4(0.874 - x)(0.858 - x)$$
$$x^2 = 4(0.750 - 0.874x - 0.858x + x^2)$$
$$x^2 = 4(0.750 - 1.732x + x^2)$$
$$x^2 = 3 - 6.928x + 4x^2$$
$$x^2 - 3 + 6.928x + 4x^2 = 0$$
$$-3x^2 + 6.928x - 3 = 0$$

Taking negative sign common on both side

$$3x^2 - 6.928x + 3 = 0$$

Using quadratic formula
a = 3, b = - 6 928 and c = 3

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(-6.928) \pm \sqrt{(-6.928)^2 - 4(4 \times 3 \times 3)}}{2 \times 3}$$

$$x = \frac{6.928 \pm \sqrt{11.997}}{6}$$

Thus,

$$x = \frac{6.928 \pm \sqrt{11.997}}{6} \quad or \quad x = \frac{6.928 - \sqrt{11.997}}{6}$$

$$x = 1.73\ moles \quad or \quad x = 0.577\ moles$$

x = 1.73 moles is not possible because it is greater than the initial concentral of reactants.
Therefore,
x = 0.577 moles

The equilibrium concentrations in moles are as follows.

$[CH_3COOH]$ $= 0.874 - x = 0.874 - 0.577 = 0.297$ moles

Mass of $[CH_3COOH]$ in grams $= 0.297$ moles $\times 60$ g mole$^{-1} = 17.82$ g

$[C_2H_5OH]$ $= 0.858 - x = 0.858 - 0.577 = 0.281$ moles

Mass of $[C_2H_5OH]$ $= 0.281$ moles $\times 46$ g mole$^{-1} = 12.93$ g

$[CH_3COOC_2H_5]$ $= x = 0.577$ *moles*

Mass of $[CH_3COOC_2H_5]$ $= 0.577$ moles $\times 88$ g mole$^{-1} = 50.78$ g

$[H_2O]$ $= x = 0.577$ *moles*

Mass of $[H_2O]$ $= 0.577$ moles $\times 18$ g mole$^{-1} = 10.39$ g

9. Write K_c and K_p expressions for the following reactions

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

(ii) $H_2O(g) + Cl_2O(g) \rightleftharpoons 2HO\,Cl(g)$

(iii) $O_3(g) \rightleftharpoons O_2(g) + O(g)$

(iv) $O_3(g) \rightleftharpoons \frac{3}{2} O_2(g)$

(v) $Fe_3O_4(s) + H_2(g) \rightleftharpoons 3Fe\,O(s) + H_2O(g)$

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

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

(viii) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

Solution:

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

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}} \quad and \quad K_p = \frac{P_{SO_3}}{P_{SO_2} \times P_{O_2}^{\frac{1}{2}}}$$

(ii) $H_2O(g) + Cl_2O(g) \rightleftharpoons 2HO\,Cl(g)$

$$K_C = \frac{[HOCl]^2}{[H_2O][Cl_2O]} \quad and \quad K_p = \frac{P_{HOCl}^2}{P_{H_2O} \times P_{Cl_2O}}$$

(iii) $O_3(g) \rightleftharpoons O_2(g) + O(g)$

$$K_C = \frac{[O_2][O]}{[O_3]} \quad and \quad K_p = \frac{P_{O_2} \times P_O}{P_{O_3}}$$

(iv) $O_3(g) \rightleftharpoons \frac{3}{2} O_2(g)$

$$K_C = \frac{[O_2]^{\frac{3}{2}}}{[O_3]} \quad and \quad K_p = \frac{P_{O_2}^{\frac{3}{2}}}{P_{O_3}}$$

(v) $Fe_3O_4(s) + H_2(g) \rightleftharpoons 3Fe\,O(s) + H_2O(g)$

As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression.

Therefore

$$K_C = \frac{[H_2O]}{[H_2]} \quad and \quad K_p = \frac{P_{H_2O}}{P_{H_2}}$$

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

$$K_C = \frac{[NOCl]^2}{[NO]^2[Cl_2]} \quad and \quad K_p = \frac{P^2_{NOCl}}{P^2_{NO} \times P_{Cl_2}}$$

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

As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression

$$K_C = [CO_2] \quad and \quad K_p = P_{CO_2}$$

(viii) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression

$$K_C = \frac{[CO][H_2]}{[H_2O]} \quad and \quad K_p = \frac{P_{CO} \times P_{H_2}}{P_{H_2O}}$$

10. $K_c = 2.6 \times 10^{-5}$ at 125°C for the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ Calculate K_p at this temperature. (Ans: k_p=284.4078)

Solution:

$T = 125\,°C + 273 = 398\,K$

$K_C = 2.6 \times 10^{-5}\ at 125\,°C$

$\Delta n = (1 + 3) - 2 = 2$

$R = 0.0821\ atm\ dm^3\ K^{-1}\ mole^{-1}$

As we know that

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

Putting values

$K_p = 2.6 \times 10^{-5}(0.0821 \times 398)^2$

$K_p = 2.78 \times 10^{-2}$

11. At a particular temperature K_p = 0.133 atm. Which of the following conditions corresponds to equilibrium position for the reaction.

$A(g) \rightleftharpoons 2B(g)$

(a) P_B = 0.175 atm, P_A = 0.102 atm

(b) P_B = 0.064 atm, P_A = 0.0308 atm

(c) P_B = 0.144 atm, P_A = 0.156 atm (Ans: b and c)

Solution:

$A(g) \rightleftharpoons 2B(g)$

K_p = 0.133 atm

As we know that

$$K_p = \frac{P_B^2}{P_A}$$

(a) P_B = 0.175 atm, P_A = 0.102 atm

$$K_p = \frac{P_B^2}{P_A} = \frac{(0.175)^2}{(0.102)} = 0.30\ atm$$

As this value does not correspond with the given value therefore the reaction is not at equilibrium

(b) P_B = 0.064 atm, P_A = 0.0308 atm

$$K_p = \frac{P_B^2}{P_A} = \frac{(0.064)^2}{(0.0308)} = 0.133\ atm$$

As this value corresponds with the given value therefore the reaction is at equilibrium

(c) **$P_B = 0.144$ atm, $P_A = 0.156$ atm**

$$K_P = \frac{P_B^2}{P_A} = \frac{(0.144)^2}{(0.156)} = 0.133\ atm$$

As this value corresponds with the given value therefore the reaction is at equilibrium.

12. Write the expression for K_c and K_p for the following processes.

(a) Blue vitriol is deep blue solid copper (II) sulphate pentahydrate is heated to drive off water vapours to form white solid copper (II) sulphate.

(b) The decomposition of solid phosphorus pentachloride to gaseous phosphorus trichloride and chlorine gas.

Solution:

(a) The balance chemical equation for process **(a)** is given below.

$$CuSO_4.5H_2O\ (s) \rightleftharpoons CuSO_4\ (s) + 5H_2O\ (g)$$

As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression

$$K_C = [H_2O]^5$$
$$K_p = P_{H_2O}^5$$

(b) The balance chemical equation for process **(b)** is given below

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

As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression.

$$K_C = [PCl_3][Cl_2]$$
$$K_p = P_{PCl_3} \times P_{Cl_2}$$

13. Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

i. $PCl_3(g) + 2NH_3(g) \rightleftharpoons P(NH_2)_3(g) + 3HCl(g)$

ii. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

iii. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

Ans. Principle:

According to Le-Chatlier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.

i. $PCl_3(g) + 2NH_3(g) \rightleftharpoons P(NH_2)_3(g) + 3HCl(g)$

In this reaction three molecules are present on reactant side (PCl_3 , $2NH_3$) while four molecules are present on product side ($P(NH_2)_3$, $3HCl$).

Therefore, when the volume decreases by increasing pressure then the equilibrium will shift in backward direction to reduce the number of molecules and to compensate the change.

ii. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

In this reaction three molecules are present on reactant side ($2NO$, O_2) and two molecules ($2NO_2$)are present on product side

Therefore, when the volume decreases by increasing pressure then the equilibrium will shift in forward direction to reduce the number of molecules, and to compensate the change

iii. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

In this reaction, nine molecules are present on reactant side ($4NH_3$, $5O_2$) and ten molecules are present on product side ($4NO$, $6H_2O$)

Therefore, when the volume decreases by increasing pressure then the equilibrium will shift in backward direction to reduce the number of molecules and to compensate the change

14. For each of the following reactions, predict how the value of K_c changes as the temperature is increased.

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H^\circ = 180$ KJ

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H^\circ = -198$ KJ

(c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^\circ = 58$ KJ

(d) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H^\circ = 256$ KJ

Ans.

Principles:

i. High temperature favours endothermic reactions.

ii. Low temperature favours exothermic reactions.

iii. In exothermic reactions heat is written on the right side of the equation.

iv. In endothermic reactions heat is written on the left side of the equation.

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H^\circ = 180$ KJ

As the reaction is endothermic therefore heat is written on the left side of the equation.

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

According to Le-Chatlier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat. Therefore, concentration of NO will increase while that of N_2 and O_2 will decrease.

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

Hence, in this case the value of K_C will increase with increase in temperature.

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H^\circ = -198$ KJ

As the reaction is exothermic therefore, heat is written on the right side of the equation.

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

According to Le-Chatlier's principle, when temperature is increased this reaction will shift in the reverse direction in order to compensate the added heat. Thus, concentration of SO_2 and O_2 will increase while that of SO_3 will decrease.

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

Hence, in this case the value of K_C will decrease with increase in temperature.

(c) $N_2O_4(g) \rightarrow 2NO_2(g)$ ΔH° **58 KJ**

As the reaction is endothermic therefore heat is written on the left side of the equation.

$$N_2O_4(g) + \text{Heat} \rightleftharpoons 2NO_2(g)$$

According to Le-Chatlier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat. Therefore, concentration of NO_2 will increase while that of N_2O_4 will decrease

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

Hence, in this case the value of K_C will increase with increase in temperature.

(d) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ ΔH° **256 KJ**

As the reaction is endothermic therefore heat is written on the left side of the equation.

$$CH_4(g) + H_2O(g) + \text{heat} \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H^\circ = 256 \text{ KJ}$$

According to Le-Chatlier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat. Therefore, concentration of CO and H_2 will increase while that of CH_4 and H_2O will decrease.

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

Hence, in this case the value of K_C will increase with increase in temperature.

15. What is the difference between an equilibrium with a K_c value larger than one compared with an equilibrium that has a K_c smaller than one.

Ans. **K_C is very large:**

Many reactions have very large equilibrium constant.

Example:

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ **$K_c = 5.4\times10^{18}$ at 25°C**

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

$$\frac{[HBr]^2}{1\times1} = 5.4 \times 10^{18}$$

$$[HBr] = \sqrt{5.4\times10^{18}}$$

$$= 2.32 \times 10^{9} M$$

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 K_C indicates that the reaction goes virtually to completion.**

b. K_C is very small:

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

Example:

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ **$K_c = 1.0\times10^{-30}$ at 25°C**

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

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

$\frac{[NO]^2}{1 \times 1} = 1 \times 10^{-30}$

$[NO] = \sqrt{1 \times 10^{-30}}$

$[NO] = 1 \times 10^{-15}$ moles

Conclusion:

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

16. Describe the behaviour of the following equilibria with the stated changes

(a) Increasing pressure on

$C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$

(b) Adding $I_2(g)$ to $2HI(g) \rightleftharpoons I_2(g) + H_2(g)$

(c) Removing heat from

$CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$ $\Delta H^\circ = 284KJ$

(d) Decreasing pressure on

$C_2H_6(g) \rightleftharpoons H_2(g) + C_2H_4(g)$

Ans. (a) Increasing pressure on

$C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$

According to Le-Chatlier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.

According to the given reaction, six molecules are present on reactant side (C_3H_8 , $5O_2$) and seven molecules ($3CO_2$, $4H_2O$)are present on product side.

Therefore, when the pressure increases the volume must decreases and the equilibrium will shift in backward direction to reduce the number of molecules and to compensate the change.

(b) Adding $I_2(g)$ to $2HI(g) \rightleftharpoons I_2(g) + H_2(g)$

According to Le-Chatlier's principle, the addition of I_2 increase the concentration of products and to compensate it the equilibrium will shift in the backward direction.

(c) Removing heat from

$CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$ $\Delta H^\circ = 284KJ$

As the reaction is endothermic therefore heat is written on the left side of the equation.

$$CO_2(g) + \text{heat} \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$$

According to Le-Chatlier's principle, when temperature is decreased this reaction will shift in backward direction in order to compensate the decrease in heat. Therefore, the concentration of CO_2 will decrease while that of CO and O_2 will decrease

$$K_c = \frac{[CO][O_2]^{\frac{1}{2}} \cdot \text{---} \; decrease}{[CO_2] \; \text{---} \; increase}$$

(d) Decreasing pressure on

$$C_2H_6(g) \rightleftharpoons H_2(g) + C_2H_4(g)$$

In the given reaction one molecule is present on reactant side (C_2H_6) and two molecules are present on product side (H_2, C_2H_4). So, when pressure is decreased, the equilibrium will shift in forward direction to compensate the change

17. A solution is prepared by mixing 50 cm^3 of 5×10^{-3}M NaCl with 50 cm^3 of 2×10^{-2}M $Pb(NO_3)_2$. Will a precipitate of $PbCl_2$ form? K_{SP} for $PbCl_2$ is 1.7×10^{-5}. (Ans: No)

Solution:

Molarity of $Pb(NO_3)_2$ solution $= 2 \times 10^{-2}$ M
Molarity of NaCl solution $= 5 \times 10^{-3}$ M
Precipitate of $PbCl_2$ = ?
K_{SP} for $PbCl_2 = 1.7 \times 10^{-5}$.
Volume of NaCl solution = 50cm^3 = 0.05dm^3
Volume of $Pb(NO_3)_2$ solution = 50cm^3 = 0.05dm^3
Total volume of solution = 0.05dm^3 + 0.05dm^3 = 0.1dm^3

Concentration of Cl^-:

NaCl $\rightleftharpoons$ **Na^+(aq) + Cl^- (aq)**
5×10^{-3} M **5×10^{-3} M** **5×10^{-3} M**

1 dm^3 of NaCl solution contains Cl^- ions = 5×10^{-3} M moles
0.05 dm^3 of NaCl solution contains Cl^- ions = $5 \times 10^{-3} \times 0.05$
= 2.5×10^{-4} moles

Now total volume is 0.1 dm^3 therefore
0.1 dm^3 of total solution contains Cl^- ions = 2.5×10^{-4} moles
1 dm^3 of total solution contains Cl^- ions = $\frac{2.5 \times 10^{-4}}{0.1} = 2.5 \times 10^{-3}$ moles
$[Cl^-] = 2.5 \times 10^{-3}$ M

Concentration of Pb^{+2}:

$Pb(NO_3)_2$ $\rightleftharpoons$ **Pb^{+2}(aq) + $2NO_3^-$ (aq)**
2×10^{-2} M **2×10^{-2} M** **$2 \times 2 \times 10^{-2}$ M**

1 dm^3 of $Pb(NO_3)_2$ solution contains Pb^{+2} ions = 2×10^{-2} moles
0.05 dm^3 of $Pb(NO_3)_2$ solution contains Pb^{+2} ions = $2 \times 10^{-2} \times 0.05$
= 1.0×10^{-3} moles

Now total volume is 0.1 dm^3 therefore
0.1 dm^3 of total solution contains Pb^{+2} ions = 1.0×10^{-3} moles

1 dm^3 of total solution contains Pb^{+2} ions $= \frac{1.0 \times 10^{-3}}{0.1} = 1.0 \times 10^{-2}$ moles

$[Pb^{+2}] = 1.0 \times 10^{-2}$ M

Precipitate of $PbCl_2$

Now for ionization of $PbCl_2$

$$PbCl_2 \rightleftharpoons Pb^{+2}(aq) + 2Cl^-(aq)$$

So

$Q' = [Pb^{+2}][Cl^-]^2$

$= (1.0 \times 10^{-2})(2.5 \times 10^{-3})^2 = 6.25 \times 10^{-8}$

$K_{SP} = 1.7 \times 10^{-5}$

Since, $Q' < K_{SP}$, therefore precipitation will not occur.

18. When solid $PbCl_2$ is added to pure water at 25°C, the salt dissolves until the concentration of Pb^{+2} reaches 1.6×10^{-2}M. After this concentration is reached, excess solid remains undissolved. What is K_{SP} for this salt? (Ans: 1.6384×10^{-5})

Solution: $PbCl_2(s) \rightleftharpoons Pb^{+2}(aq) + 2Cl^-(aq)$

$[Pb^{+2}] = 1.6 \times 10^{-2}$ M

$[Cl^-] = 2 \times 1.6 \times 10^{-2}$ M $= 3.2 \times 10^{-2}$

$K_{SP} = [Pb^{2+}][Cl^-]^2$

$K_{SP} = (1.6 \times 10^{-2})(3.2 \times 10^{-2})^2$

$K_{SP} = 1.6384 \times 10^{-5}$

19. The equilibrium constant for the following reaction is 1.6×10^5 at 1000K $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$
Find the equilibrium pressures of all the gases if 10.0 atm of HBr is introduced into a sealed container at 1000K.

Solution:

	$H_2(g)$	+ $Br_2(g)$	$\rightleftharpoons$	$2HBr(g)$
Initial Concentration.	*zero*	*zero*		10
Equation Concentration.	x	x		$10 - 2x$

$$K_p = \frac{P^2_{HBr}}{P_{H_2} \times P_{I_2}}$$

$$1.6 \times 10^5 = \frac{(10-2x)^2}{(x)(x)}$$

$$1.6 \times 10^5 = \frac{(10-2x)^2}{x^2}$$

Taking square root of both the sides

$$\sqrt{1.6 \times 10^5} = \frac{10 - 2x}{x}$$

$$400 = \frac{10 - 2x}{x}$$

$$10 - 2x = 400x$$

$$10 = 400x + 2x$$

$$10 = 402x$$

$$or\ x = \frac{10}{402}$$

$x = 0.0249$

$$P_{H_2} = P_{Br_2} = x = 0.0249 \text{ atm}$$

$$P_{HBr} = 10 - 2x = 10 - 2 \times 0.0249 = 9.9502 \text{ atm}$$

20. Consider the following gas phase reaction.
Describe four changes that would derive the equilibrium to left (backward direction).

$$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g) + Heat$$

Ans. According to Le-Chatlier's Principle following are the four changes that will drive the equilibrium in the reverse direction.

(i) Continual removal of reactants:

When any of the reactant is removed the equilibrium will shift in the reverse direction to compensate the change

(ii) Low Pressure:

According to the given equation two molecules are present on reactant side (SO_2 , Cl_2) and one molecule is present on product side (SO_2Cl_2) Thus when pressure decreased, the equilibrium will shift in the reverse direction to compensate the change.

(iii) High Temperature:

As the reaction is exothermic therefore, high temperature will not favour it and hence the reaction will proceed in the reverse direction with the increase in temperature.

(iv) Addition of products:

Addition of products increases their concentration and the reaction will shift in the reverse direction to compensate this change i e from right to left

21. How would you change the volume of the following reactions to increase the yield of products?

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

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

Ans. (i) $Cl_2(g) + I_2(g) \rightleftharpoons 2ICl(g)$

According to Le-Chatlier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.

According to the given reaction, two molecules are present on both the reactant and the product side (Cl_2, I_2, 2ICl)

Thus the change in volume will not affect the equilibrium position

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

According to Le-Chatlier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.

According to the given equation, two molecules are present on reactant side ($2NO_2$) and one molecule is present on product side (N_2O_4)

When we reduce volume by increasing pressure then the equilibrium will shift in forward direction and thus the yield increases

Think Tank

22. A figurine device used to predict weather condition is blue on dry, sunny days and pink on damp, rainy days. These figurines are coated with substances containing chemical species that undergo following equilibrium. $2[Co(H_2O)_6]^{+2} + 4Cl^- \rightleftharpoons Co[CoCl_4]^{-2} + 12H_2O$

(a) Identify the blue substance

(b) Identify the pink substance

(c) How is Le Chatelier's Principle applied here.

Ans. (a) Blue substance = $Co[CoCl_4]^{-2}$

(b) Pink substance = $[Co(H_2O)_6]^{+2}$

Appling Le Chatelier's Principle

Rainy days:

According to the reaction water is the product. On damp, rainy days the concentration of water is more in the surrounding and hence according to Le-Chatlier's principle, the equilibrium will shift in the reverse direction. Thus the concentration of $[Co(H_2O)_6]^{+2}$ Increases and the colour of figurine becomes pink.

Sunny days:

According to the reaction water is the product. On a sunny day the concentration of water is low in the surrounding and therefore according to Le-Chatlier's principle, the equilibrium will shift in forward direction. Thus the formation of $Co[CoCl_4]^{-2}$ increases and the colour of figurine become blue.

23. The combination of oxygen with hemoglobin (Hb) molecule, which carries oxygen through the blood, is a complex reaction. For our purpose it can be represented by the simplified equation.

$Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq)$ where HbO_2 is oxyhaemoglobin that actually transport oxygen to tissues. The equilibrium constant expression is $K_C = \frac{[HbO_2]}{[Hb][O_2]}$

Scaling a 3km mountain can cause headache, nausea, extreme fatigue and other discomforts. Give possible explanation for it.

Ans: $Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq)$

External pressure low on high mountains and thus the concentration of O_2 in the atmosphere also decreases. Hence, according to Le-Chatlier's principle, the given equilibrium will shift in reverse direction.

As a result, the concentration of HbO_2 decreases in order to give Hb and O_2 and to compensate the change. Therefore, supply of oxygen to body is also decreased. This can cause headache, nausea, extreme fatigue and other discomforts.

24. Baking Soda undergoes thermal decomposition as follows

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Would we obtain more CO_2 by adding extra baking soda to the reaction mixture in (a) a closed vessel (b) an open vessel.

Ans. As pressure has very little effect on volume of solids so they almost remain same but pressure can affect the volume of gases.

(a) Closed vessel:

In close vessel volume does not change and therefore we can not obtain more carbon dioxide gas by adding extra baking soda to the reaction mixture.

(b) Open vessel:

According to the reaction, there are two gaseous molecules on the product side (CO_2 and H_2O). Thus in this case according to Le-Chatlier's principle, when the volume increases then the equilibrium will shift in forward direction. Therefore, by adding baking soda more CO_2 will produce in an open vessel.

25. Potassium dichromate solution has beautiful clear orange colour. This is due to the colour of dichromate ion, $Cr_2O_7^{-2}$. When a salt is dissolved in water, the following equilibrium is setup, on heating solution. $Cr_2O_7^{-2}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{-2}(aq) + 2H^+(aq)$

(orange) (yellow)

What will happen if:

i. dilute Sodium hydroxide is added to this solution.

ii. this is followed by dilute hydrochloric acid addition.

Ans.

i. Dilute Sodium hydroxide is added to this solution.

NaOH is a base and it produces OH^- ions which will react with H^+ ion to form water.

Therefore the concentration of H^+ ions decreases and according to Le-Chatlier's principle, to compensate that change the dichromate/chromate equilibrium will shift in forward direction. As a result more orange $Cr_2O_7^{-2}$ ions react with H_2O to give yellow CrO_4^{-2} ions and the colour of solution changes from orange to yellow.

ii. This is followed by dilute hydrochloric acid addition.

HCl is a strong acid and it produces H^+ ions in the solution due to which a concentration of H^+ ion increases. Thus, according to Le-Chatliers' principle, to compensate this change the equilibrium will shift in backward direction. Thus, more yellow CrO_4^{-2} ions react with H^+ ions to give orange CrO_4^{-2} ions and the colour of solution changes from yellow to orange.

26. If 0.350 moles of SO_3 is placed in a 1.00 dm^3 flask and allowed to come to equilibrium at a high temperature, 0.207 mole of SO_3 remains. Calculate K_c for the reaction. (Ans: 14.64)

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

Solution:

	$2SO_3(g)$	$\rightleftharpoons$	$2SO_2(g)$	+	$O_2(g)$
Initial Concentration. (*in moles* dm^{-3})	0.350		*zero*		*zero*
Equation Concentration. (*in moles* dm^{-3})	$0.350 - 2x$		$2x$		x

Given that at equilibrium, 0.207 *moles of* SO_3 *remains*

$$0.350 - 2x = 0.207$$
$$-2x = 0.207 - 0.350$$
$$-2x = -0.143$$

$$Or \quad x = \frac{0.143}{2} = 0.0715$$

Equilibrium concentrations:

$$[SO_3] = 0.207 \ moles\, dm^{-3}$$
$$[O_2] = x = 0.0715 \ moles\, dm^{-3}$$
$$[SO_2] = 2x = 2 \times 0.0715 = 0.143 \ moles\, dm^{-3}$$
$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

Putting values

$$K_c = \frac{(0.143)^2(0.0715)}{(0.207)^2} = 0.0341$$

27. For the reaction between hydrogen and Iodine to form hydrogen Iodide, the value of K_c is 794 at 298K but 54 at 700K what can you deduce from this information?

Ans.

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

Given that the value of K_C decreased with the increase in temperature from 794 at 298K to 54 at 700K.

Conclusion:

Thus this indicates that the reaction is **exothermic** and is not favoured by high temperature. Therefore the concentration of HI is decreased and that of H_2 and I_2 is increased by increase in temperature.

$$K_C = \frac{[HI]^2 \longleftarrow decrease}{[H_2][I_2] \longleftarrow increase}$$