Unit **09**

Chemical Equilibrium

Long Answer Questions

Q.1 Describe a reversible reaction with the help of an example and graph.

Ans. Reversible Reaction

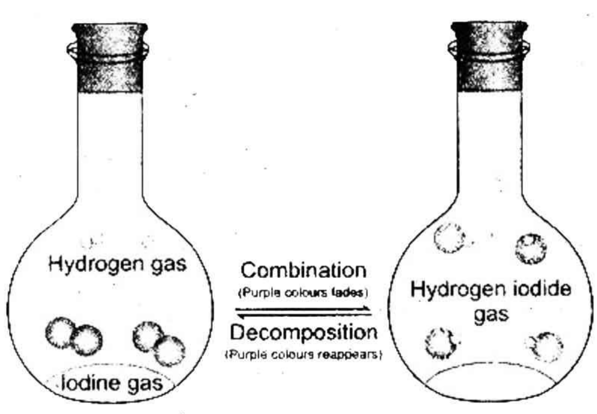
The reaction in which the products can recombine to form reactants, are called reversible reactions. These reactions never go to completion. They are represented by a double arrow ($\rightleftharpoons$) between reactants and products. These reactions proceed in both ways, i.e., they consist of two reactions; forward and reverse. So, a reversible reaction is one which can be made to proceed in either direction depending upon the conditions.

Example:

The reaction between hydrogen and iodinc. Because one of the reactant, iodine is purple, while the product hydrogen iodide is colourless, proceedings of the reaction are easily observable. On heating hydrogen and iodine vapours in a closed flask, hydrogen iodide is formed. As a result purple colour of iodide fades as it reacts to form colourless hydrogen iodide, as shown in figure.

$$H_{2(g)} + \underset{\text{Purple}}{I_{2(g)}} \xrightarrow{\Delta} \underset{\text{Colourless}}{2HI}$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$



This reaction is called as forward reaction.

On the other hand, when only hydrogen iodide is heated in a closed flask, purple colour appears because of formation of iodine vapours. Such as

$$2HI_{(g)} \xrightarrow{\Delta} H_{2(g)} + I_{2(g)}$$

Colourless — Purple

In this case hydrogen iodide acts as reactant and produces hydrogen and iodine vapours. This reaction is reverse of the above. Therefore, it is called as reverse reaction.

When both of these reactions are written together as a reversible reaction, they are represented as:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Chemical Equilibrium State

When we think of the term equilibrium, the first word that usually comes to mind is "balance". However, the balance may be achieved in a variety of ways.

Thus, when the rate of the forward reaction takes place at the rate of reverse reaction, the composition of the reaction mixture remains constant, it is called a chemical equilibrium state. At equilibrium state there are two possibilities

(i) When reaction ceases to proceed, it is called static equilibrium. This happens mostly in physical phenomenon. For example a building remains standing rather than falling down because all the forces acting on it are balanced. This is an example of static equilibrium.

(ii) When reaction does not stop, only the rates of forward and reverse reactions become equal to each other but take place in opposite directions. This is called dynamic equilibrium state. Dynamic means reaction is still continuing. At dynamic equilibrium state:

Rate of forward reaction = Rate of reverse reaction

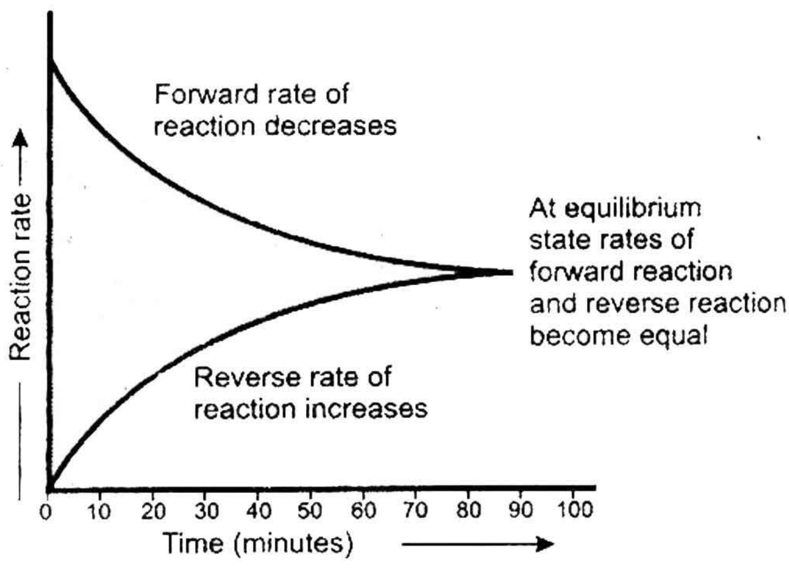
In a reversible reaction, dynamic equilibrium is established before the completion of reaction. It is represented graphically in figure.

At initial stage:

At initial stage the rate of forward reaction is very fast and reverse reaction is taking place at a negligible rate..

By passing time:

But gradually forward reaction slows down and reverse reaction speeds up. Eventually, both reactions attain the same rate, it is called a dynamic equilibrium state.



Q.2 Define chemical equilibrium state. Describe it with examples.

Ans. Chemical Equilibrium state:

When the rate of the forward reaction takes place at the rate of reverse reaction, then the composition of the reaction mixture remains constant, it is called a chemical equilibrium state.

At equilibrium state:

$$\text{Rate of forward reaction} = \text{Rate of reverse reaction}$$

Example 1:

Our existence based on the equilibrium phenomenon taking place in atmosphere. We inhale oxygen and exhale carbon dioxide, while plants consume carbon dioxide and release oxygen. This natural process is responsible for the existence of life on the Earth.

Many other environmental systems depend for their existence on delicate equilibrium phenomenon.

Other examples from nature:

- The lives of aquatic plants and animals are indirectly related to concentration of dissolved oxygen in water.
- Concentration of gases in lake water is governed by the principles of equilibrium.

Example 2:

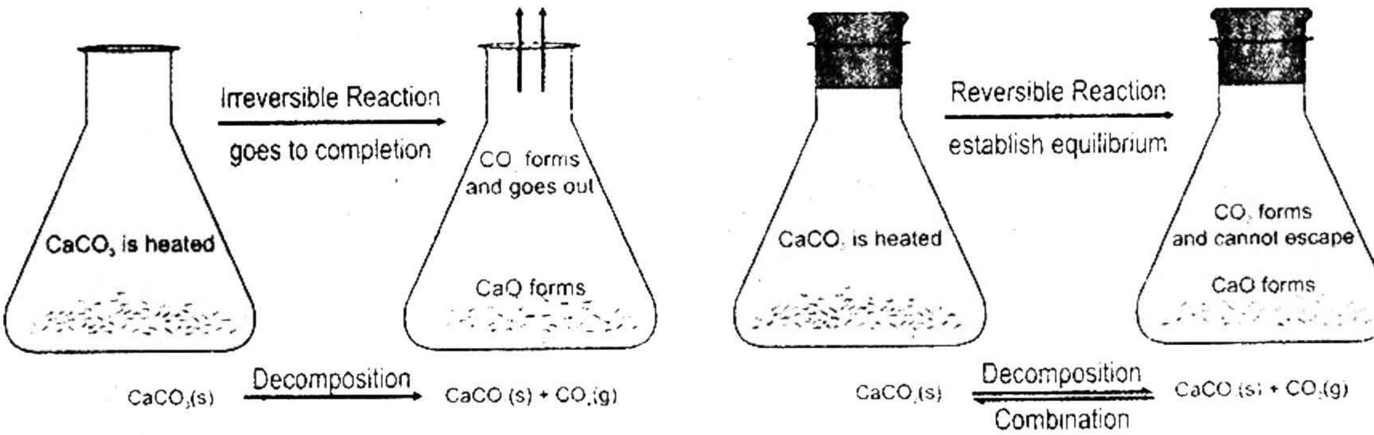
When calcium oxide and carbon dioxide react, they produce calcium carbonate.

$$CaO_{(s)} + CO_{2(g)} \longrightarrow CaCO_{3(g)}$$

On the other hand, when $CaCO_3$ is heated in an open flask, it decomposes to form calcium oxide and carbon dioxide. CO_2 escapes out and reaction goes to completion.

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + O_{2(g)}$$

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}\uparrow \quad \text{(decomposition)}$$



In these two reactions, decomposition is reverse to combination or vice versa. When calcium carbonate is heated in a closed flask, so that CO_2 can't escape out as shown in figure. For some time only decomposition goes on (forward reaction) but after a while CO_2 starts combining with CaO to form $CaCO_3$.

In the beginning, forward reaction is fast and reverse reaction is slow. But eventually the reverse reaction speeds up and both reactions go on at the same rate. At this stage decomposition and combination take place at the same rate but in opposite directions, as result amounts of $CaCO_3$, CaO and CO_2 do not change. It is written as:

$$CaCO_{3(s)} \overset{\Delta}{\rightleftharpoons} CaO_{(s)} + CO_{2(g)}$$

This is the chemical equilibrium state of this reaction.

Q.3 Write macroscopic characteristics of forward and reverse reactions.

Ans. Macroscopic characteristics of forward and reverse reactions:

Forward Reaction	Reverse Reaction
i) It is a reaction in which reactants react to form products.	It is reaction in which products react to produce reactants.
ii) It takes place from left to right	It takes place from right to left.
iii) At initial stage the rate of forward reaction is very fast.	In the beginning the rate of reverse reaction is negligible.
iv) It slows down gradually.	It speeds up gradually.

Q.4 Write down macroscopic characteristics of dynamic equilibrium.

Ans. Macroscopic characteristics of dynamic equilibrium:

A few important characteristic features of dynamic equilibrium are given below:

(i) An equilibrium is achievable only in a closed system (in which substances can neither leave nor enter)

(ii) At equilibrium state a reaction does not stop. Forward and reverse reactions keep on taking place at the same rate but in opposite direction.

(iii) At equilibrium state, the amount (concentration) of reactants and products do not change. Even physical properties like colour, density, etc. remain the same.

(iv) An equilibrium state is attainable from either way, i.e. starting from reactants or from products.

(v) An equilibrium state can be disturbed and again achieved under the given conditions of concentration, pressure and temperature.

Q.5 State the law of mass action and derive the expression for equilibrium constant for a general reaction

Ans. Law of mass action:

Guldberg and Waage in 1869 put forward this low. According to this law "The rate at which a substance reacts is directly proportional to its active mass and the rate of reaction is directly proportional to the product of the active masses of the reacting substances". Generally an active mass is considered as the molar concentration in units of mol dm^{-3}, expressed as square brackets [ ].

Derivation of the expression for equilibrium constant for general reaction

Let us apply the law of Mass Action for a general reaction. According to this law, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of its reactants raised to power equal to their number of moles in the balanced chemical equation of the reaction.

Let us first discuss the forward reaction. A and B are the reactants whereas 'a' and 'b' are their number of moles.

The rate of forward reaction according to law of Mass Action is

$$R_f \propto [A]^a [B]^b$$
$$R_f = K_f [A]^a [B]^b$$

Where K_f is the rate constant for the forward reaction. Similarly, the rate of the reverse reaction R_r, is directly proportional to the product of $[C]^c [D]^d$, where 'c' and 'd' are the number of moles as given in the balanced equation. Thus,

$$R_r \propto [C]^c [D]^d$$
$$R_r = k_r [C]^c [D]^d$$

Where Kr is the rate constant for the reverse reaction. We know that at equilibrium state the rate of both the reactions are equal to each other.

The rate of forward reaction = The rate of reverse reaction

$$R_f = R_r$$

And putting the values of R_f and R_r

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

By taking the constants on one side and the variable on other side of the equation, the above equation turns into;

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

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

Where, K_c $\left(K_c = \frac{k_f}{k_r} \right)$ is called equilibrium constant. So

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

Q.6 Define equilibrium constant. Also describe its unit.

Ans. Equilibrium constant is a ratio of the product of concentration of products raised to the power of coefficient to the product of concentration of reactants raised to the power of coefficient as expressed in the balanced chemical equation.

Formula:

$$K_c = \frac{\text{Product of concentration of products raised to the power of coefficients}}{\text{Product of concentration of reactants raised to the power of coefficients}}$$

It is conventional to write the product side numerator and the substances on the reactant side as denominator. By knowing the balanced chemical equation for a reversible reaction we can write the equilibrium expression. Thus we can calculate the numerical value of K_c by putting actual equilibrium concentrations of the reactants and products into equilibrium expression. The value of K_c depends only on temperature, it does not depend on the initial concentrations of the reactants and products. A few problems have been solved to make the concept understandable.

K_c has no units in reactions with equal number of moles on both sides of the equation. This is because concentration units cancel out in the expression for K_c, e.g., for the reaction

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$Kc = \frac{[HI_{(g)}]^2}{[H_{2(g)}][I_{2(g)}]} \qquad \text{Units} = \frac{(\cancel{mol\,dm^{-3}})^2}{(\cancel{mol\,dm^{-3}})\,(\cancel{mol\,dm^{-3}})} = \text{no units}$$

For reactions in which the number of moles of reactants and product are not equal in the balanced chemical equation, K_c of course, have units, e.g., for the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$Kc = \frac{[NH_3]^2}{[N_{2(g)}][H_{2(g)}]^3} = \frac{(mol\,dm^{-3})^2}{(mol\,dm^{-3})\,(mol\,dm^{-3})^3} = \frac{1}{(mol\,dm^{-3})^2} = mol^{-2}\,dm^6$$

Q.7 How can you predict the direction of a reaction by using the equilibrium constant?

Ans. Knowing the numerical value of equilibrium constant of a chemical reaction, direction as well as extent of the reaction can be predicted.

(i) Predicting Direction of Reaction

Direction of a reaction at a particular moment can be predicted by inserting the concentration of the reactants and products at that particular moment in the equilibrium expression. Consider the gaseous reaction of hydrogen with iodine.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_c = 57.0 \text{ at } 700\,K$$

We withdraw the samples from the reaction mixture and determine the concentrations of $H_{2(g)}$, $I_{2(g)}$ and $HI_{(g)}$. Suppose concentrations of the components of the mixture are:

$$[H_2]_t = 0.10\,mol\,dm^{-3},\ [I_2]_t = 0.20\,mol\,dm^{-3} \text{ and } [HI]_t = 0.40\,mol\,dm^{-3}$$

The subscript 't' with the concentration symbols means that the concentrations are measured at some time t, not necessarily at equilibrium. When we put these concentrations into the equilibrium constant expression, we obtain a value called the reaction quotient Qc. The reaction quotient for this reaction is calculated as:

$$Q_c = \frac{[HI]_t^2}{[H_2]_t[I_2]_t} = \frac{(0.40)^2}{(0.10)(0.20)} = 8.0$$

As the numerical value of Qc (8.0) is less than Kc(57.0), the reaction is not at equilibrium. It requires more concentration of product. Therefore, reaction will move in the forward direction.

The reaction quotient Q_c is useful because it predicts the direction of the reaction by comparing the value of Q_c with K_c.

Thus, we can make the following generalization about the direction of the reaction.

If $Q_c < K_c$ the reaction goes from left to right, i.e, in forward direction to attain equilibrium.

If **$Q_c > K_c$** of a reaction is more than K_c, the reaction goes from right to left, i.e. in reverse direction to attain equilibrium.

If **$Q_c = K_c$**: forward and reverse reactions take place at equal rates i.e, equilibrium has been attained

Q.8 How can you predict the extent of reaction by using equilibrium constant?

Ans. Predicting extent of a reaction

Numerical value of the equilibrium constant predicts the extent of a reaction. It indicates to which extent reactants are converted to products. In fact, it measures how far a reaction proceeds before establishing equilibrium state.

In general there are three possibilities of predicting extent of reactions as explained below.

(a) Large numerical value of K_c

The large value of K_c indicates that at equilibrium position the reaction mixture consists of almost all products and reactants are negligible. The reaction has almost gone to completion. For example, oxidation of carbon monoxide goes to completion at 1000 k.

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} \qquad K_c = 2.2\times10^{22}$$

(b) Small numerical value of K_c

When the K_c value of reaction is small it may indicate the equilibrium has established with a very small conversion of reactants to products. At equilibrium position almost all reactants are present but amount of products is negligible. Such type of reaction never goes to completion, for example,

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)} \qquad K_c = 3.0\times10^{-9}$$

(c) Numerical value of K_c is neither small nor large

Such reactions have comparable amounts of reactants and products at equilibrium position. For example:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_c = 0.211$$

Solved Book Examples

Example 1:

When hydrogen reacts with iodine at 25°C to form hydrogen iodide by a reversible reaction as follows:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

The equilibrium concentrations are:

$[H_2]$ = 0.05 mol dm^{-3} ; $[I_2]$ = 0.06 mol dm^{-3} and $[HI]$ = 0.49 mol dm^{-3}

Calculate the equilibrium constant for this reaction?

Solution:

Given equilibrium concentrations are;

$[H_2] = 0.05\ mol\ dm^{-3}$; $[I_2] = 0.06\ mol\ dm^{-3}$ and $[HI] = 0.49\ mol\ dm^{-3}$

Write the equilibrium constant expression as

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

Now put the equilibrium concentration values in the equilibrium expression

$$K_c = \frac{[0.49]^2}{[0.05][0.06]} = \frac{0.2401}{0.0030} = 80$$

Examples 2:

For the formation of ammonia by Haber's process hydrogen and nitrogen react reversibly at 500°C as follows

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

The equilibrium concentrations of these gases are: nitrogen 0.602 mol dm^{-3}; hydrogen 0.420 mol dm^{-3} and ammonia 0.113 mol dm^{-3}. What is value of K_c.

Solution:

The equilibrium concentrations are

$[N_2] = 0.602\ mol\ dm^{-3}$, $[H_2] = 0.420\ mol\ dm^{-3}$ and $[NH_3] = 0.113\ mol\ dm^{-3}$

The equilibrium constant expression for this reaction is:

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

Now put the equilibrium concentration values into the equilibrium expression

$$K_c = \frac{[0.113]^2}{[0.602][0.420]^3} = 0.286\ mol^{-2}\ dm^6$$

Example 3:

For a reaction between PCl_3 and Cl_2 to form PCl_5, the equilibrium constant is 0.13 mol^{-1} dm^3 at a particular temperature. When the equilibrium concentrations of PCl_3 and Cl_2 are 10.0 and 9.0 mol dm^{-3} respectively, what is the equilibrium concentration of PCl_5.

Solution:

$[PCl_3] = 10\ mol\ dm^{-3}$ $\quad$ $[Cl_2] = 9.0\ mol\ dm^{-3}$

$K_c = 0.13\ mol^{-1}\ dm^{-3}$ $\quad$ $[PCl_5] = ?$

Now write the balanced chemical equation and equilibrium constant expression

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_5$$

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

Now put the known values in above equation and rearrange