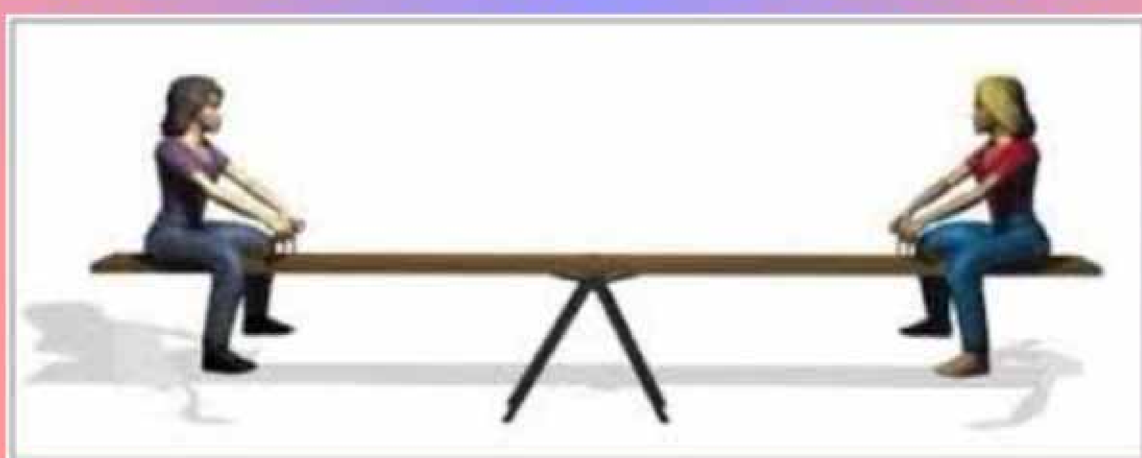
Reversible Reactions, Dynamic Equilibrium and Law of Mass Action



Learning Outcomes

Students will be able to:

1. define irreversible reactions;
2. define reversible reactions;
3. define chemical equilibrium in terms of reversible reactions;
4. write forward and reverse reactions;
5. define law of mass action.

Introduction

When a sample of liquid water is placed in a closed container at constant temperature, part of the liquid vaporizes. As water begins to vaporize, the vapour also begin to condense, although the rate of vaporization is more than the rate of condensation. As time passes the concentration of molecules in the vapour state increases, so does the rate of condensation, eventually it becomes equal to the rate of vaporization. When this happens we may say that the liquid and vapour are in a state of dynamic equilibrium.

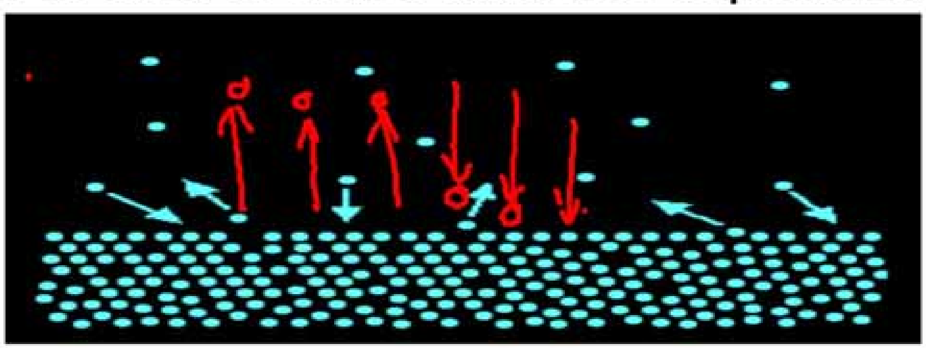
Equilibrium State

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

H_2O $\quad$ H_2O

The double arrow implies that at the equilibrium state the forward process and reverse process are occurring at the same rate. As a result of dynamic equilibrium, concentration of water vapour becomes constant and does not change with time, so long as the temperature remains constant.

Chemical reactions carried out in closed containers show some resemblance to phase changes as described above. It is well established that many reactions do not go to completion. They proceed to a certain extent and then apparently stop. The reactants are not completely consumed. Instead we obtain an equilibruim mixture containing both reactants and products. Under any given set of conditions of temperature, pressure and concentration, the point at which any reaction seems to stop is always the same i.e. there exist a quantitative relationship among the concentrations of various reactants and products which is definitely fixed. When a reaction reaches this stage, it is said to have attained equilibrium.



Irreversible Reactions:

All the chemical reactions do not proceed to the same extent, some proceed to completion and some never go to completion. ("The reactions which proceed to completion in a definite direction are called Irreversible or One-way reactions.")

For example:

- $NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow NaNO_{3(aq)} + AgCl_{(s)}$
- $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O$
- $Ba(NO_3)_{2(aq)} + SO_4{}^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)} + 2NO_3{}^{1-}{}_{(aq)}$

$2Na_{(s)} + 2H_2O \rightarrow 2NaOH_{(aq)} + H_{2(g)}$

In these reactions, the reactants are completely converted into products.

Reversible Reactions:

So far, most of the reactions we have considered proceed quite definitely in a certain direction. However, the direction of a chemical change can be easily reversed by changing the conditions under which the reaction is taking place. *"Chemical reactions which proceed in both direction forward and backward simultaneously are known as reversible reactions."* These reactions never go to completion but always continue in both directions. For example, when hydrated copper(II) sulphate is heated the blue colour of the crystals changes to the white appearance of the anhydrous salt. The change may be represented by the following equation:

Heat

$$CuSO_4.5H_2O_{(S)} \rightarrow CuSO_{4(s)} + 5H_2O_{(g)}$$

hydrated salt (blue) → **anhydrous salt** (colourless)

However, anhydrous copper(II) sulphate may be changed to the blue hydrated form simply by taking a sample of the anhydrous salt and adding water to it (this is the familiar test for the presence of water).

$$CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CUSO_4.5H_2O_{(S)}$$

anhydrous salt (colourless) → **hydrated salt** (blue)

It is clear that we have managed to carry out the reaction which is the reverse of the one stated above . Because the reaction can be easily reversed it is known as a reversible reaction and this is designated as;

$$CuSO_4.5H_2O_{(s)} \rightleftharpoons CuSO_{4(s)} + 5H_2O(g)$$

Blue colourless.

The symbol $\rightleftharpoons$, two half-arrows, indicates that the reaction may proceed in one direction or the other according to the conditions under which it is carried out.

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

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

- $$PCl_{5(s)} \rightleftharpoons PCl_3 + Cl_2$$

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

Ethyl acetate   Water   Acetic acid   Ethyl alcoho animation

Chemical Equilibrium:

In a reversible reaction, both the changes, forward and the reverse occur simultaneously. Under these circumtances, a reaction might come to some kind of 'balance' in which the forward and the reverse reactions occur at the same rate.

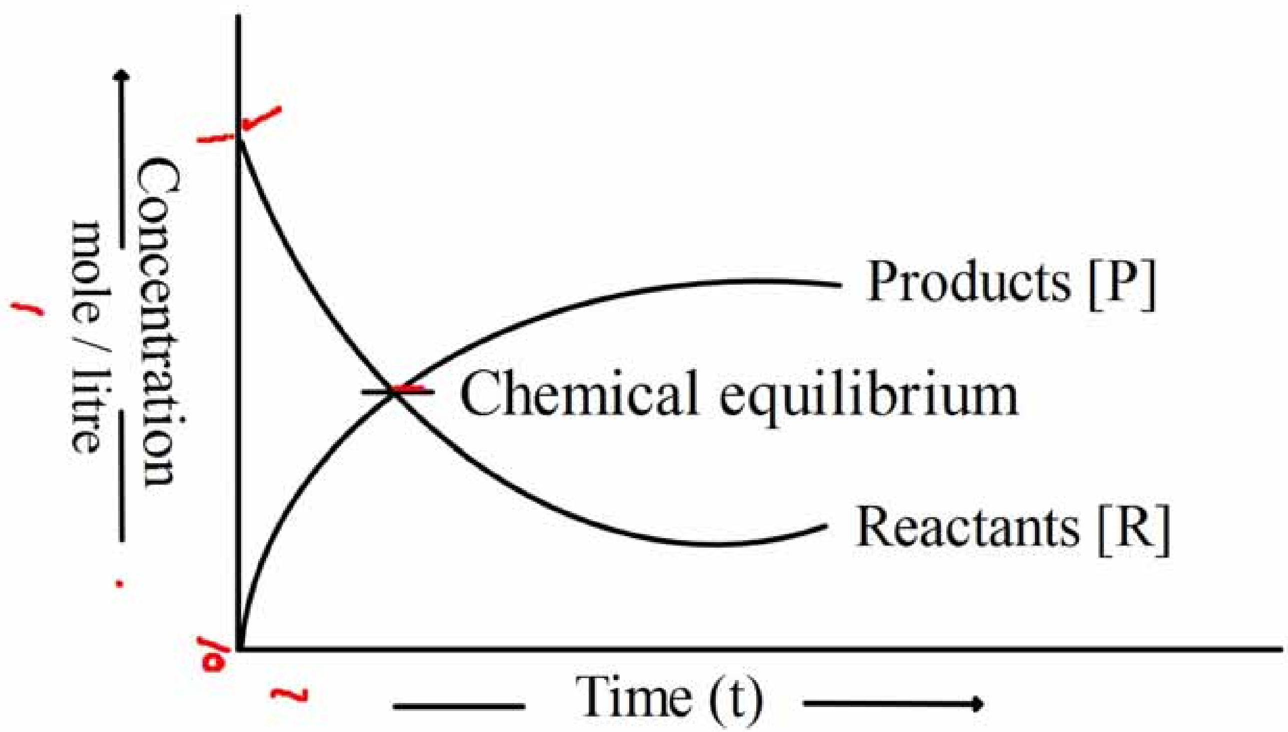
Consider, for example, the following homogeneous reaction (i.e. entirely liquid or entirely gaseous).

$$A + B \underset{R_r}{\overset{R_f}{\rightleftharpoons}} C + D \qquad R_f = R_r$$

In the beginning, forward reaction predominates, but as soon as C and D are formed, the reverse reaction 'builds up' until equilibrium position is reached where the forward as well as the reverse changes proceed with the same rate.

The equilibrium state of a chemical reaction, however, differs from these physical examples. The children on a see saw or a note book on a table are in a state of 'Static equilibrium', but the chemical equilibrium is 'dynamic' that is, it is an equilibrium involving the constant inter change of particles in motion (as it involves the balancing of two reactions occurring simultaneously). In static equilibrium, we can observe the fact that the children or the book are in equilibrium, but in dynamic equilibrium we can't observe the individual particles involved.

Although the idea of reactants and products is confusing in a reversible reaction, at a equilibrium point, all the substances involved are present. That is to say that an equilibrium mixture is formed. The composition of this mixture remains constant due to the same rate of forward and backward change. At this point, it apparently appears as if the reaction has stopped because we don't see an increase in the amount of products. But as mentioned earlier, a reversible reaction never stops. It is dynamic! The equilibrium state do not change with the lapse of time.



Graph of concentration ⇨ time

Characteristics of a Dynamic Equilibrium:

The important features of dynamic equilibrium are:

1. At equilibrium, macroscopic properties are constant under the given conditions of temperature, pressure and initial amounts of substances.

2. At equilibrium, microscopic (molecular scale) processes continue but these are in balance. This means that no overall macroscopic (large scale) changes occur. The particles participate in both forward and reverse processes. The rate of the forward process is equal to the rate of the reverse process so that no net change results.

3. The equilibrium can be attained from either direction beginning with only the materials on one side of the change. Changes of this kind are described as reversible.

4. Equilibrium can only be achieved in a closed system. A closed system represents no loss or gain of materials to or from the surrounding. An open system may allow matter to escape or to enter. This cannot reach equilibrium.

The Law of Mass Action (Law of equilibrium):

In 1864-79, the Norwegian scientists, Guldberg and Waage formulated a generalization regarding the effect of concentration on reversible reactions in equilibrium. It is known as the law of mass action or law of equilibrium. It states that:

"The rate at which a substance reacts, is directly proportional to its active mass and the rate of a reaction is directly proportional to the product of the active masses of the reacting substances."

Multiple Choice Questions

1. A reversible reaction is the one which

A. proceeds in backward direction only.
B. proceeds in forward direction only.
C. proceeds in both forward and backward directions.
D. do not proceed in any direction.

2. The equilibrium established between a liquid and its vapour at constant temperature is an example of

A. static equilibrium.
B. dynamic equilibrium.
C. chemical equilibrium.
D. imaginary equilibrium.

3. For the given reaction

$$A + B \rightarrow C + D$$

The rate of the reaction depends on the concentration of

A. A only.
B. B only.
C. both A and B.
D. C and D.