Unit-8

Equilibrium

Rate of reaction:

Consider the following chemical reactions:

1. The solution of sodium chloride and silver nitrate when mixed, there is an instantaneous formation of a precipitate of silver chloride. This reaction is very fast.

   $$NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl\downarrow$$

2. Nitrogen pentoxide decomposes on heating to give nitrogen dioxide and oxygen. The rate of this reaction can be measured.

   $$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

3. A piece of iron when exposed to moist air a brown layer of iron oxide is formed over a period of time.

   $$Fe \xrightarrow{\text{moist air}} Fe_2O_3 \,.\, xH_2O \quad \text{(rust)}$$

It is important to notice in the above three reactions that, the first reaction is very fast, the second one proceeds at a measurable rate and the last reaction is very slow. So it can be generalized that the various chemical reactions take place at different rates or speeds or velocities.

The rate of a chemical reaction means the speed with which a chemical reaction takes place. As a reaction progresses the reactants are consumed and the products are formed. As time changes during a chemical reaction, molar concentration of a reactant decreases and the molar concentration of a product increases.

Consider a general reaction

$$\mathbf{A \rightarrow B}$$

During the course of the above reaction, molecules of the reactant 'A' are consumed and the molecules of the product 'B' are formed. The rate of this reaction can be determined by measuring either the decrease in the concentration of reactant or increase in the concentration of product with time.

The concentration of product 'B' is zero initially, But with the time, the concentration of 'B' increases and that of 'A' decreases.
A plot of change in concentration against time is shown in ***Fig 1.***

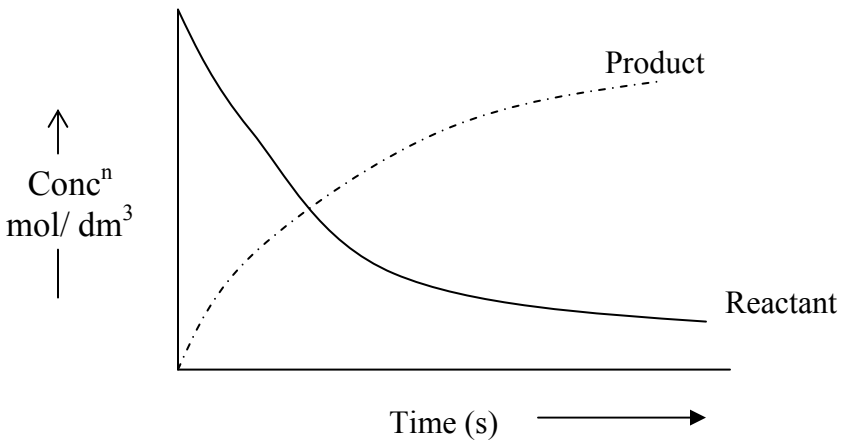

Fig. 1. Plot of change in concentration against time.

The rate of a reaction is defined as the decrease in the concentration of a reactant per unit time or the increase in the concentration of a product per unit time.

It is also defined as the ratio of the change in the concentration of any one of reactant or product with time.
Thus,

Rate of reaction = rate of disappearance of 'A'
= rate of appearance of 'B'

Rate of reaction with respect to (w.r.t) reactant

$$= \frac{\text{decrease in molar conc}^n \text{ of reactant}}{\text{Time}}$$

$$= -\frac{dc}{dt}$$ (-ve sign indicates a decrease in the concentration)

Or

$$\text{rate} = \frac{-d[A]}{dt}$$

Where '[ ]' represents the concentration in mole / dm^3
Rate of reaction w. r. t product

$$= \frac{\text{increase in molar conc}^n \text{ of reactant}}{\text{Time}}$$

$$= + \frac{dc}{dt}$$ (+ve sign indicates an increase in the concentration)

Or

$$\text{rate} = \frac{+d[B]}{dt}$$

$$\text{Rate} = \pm \frac{dc}{dt}$$

Unit = mol $dm^{-3}s^{-1}$

Rate of reaction is also called velocity of reaction.

Factors affecting rate of reaction:

The rate of a given reaction is affected by the following factors.

1. Concentration of reactants :

The rate of a reaction increases with increase in concentration of reactants. The collisions between the reacting molecules increase with increase in concentration.

2. Temperature :

Usually the rate of a reaction increases with increase in temperature. With the increase of temperature, large number of reacting molecules will collide each other due to increase in their kinetic energy. This will result in increase in reaction rate.

3. Catalyst :

A catalyst by its mere presence in the reaction increases its rate. A positive catalyst increases the rate of a reaction. A negative catalyst decreases the rate.

Ex. 1. MnO_2 acts as positive catalyst in the thermal decomposition of KClO3

2. Glycerine acts as negative catalyst in the decomposition of H_2O_2 at room temperature

4. Nature of reactants

In general reactions involving ionic (inorganic) compounds are fast, while those involving covalent (organic) compounds are slow.

Reversible reactions

The reactions in which the products formed during the reaction combine to give back the reactants are called reversible relations.

A Reversible reaction is indicated by writing two half headed arrow marks. The arrow head pointing to the right represents the forward reaction and the one pointing to the left represents the backward reaction.

At any stages of the reversible reaction , the reaction mixture contains both the reactants and products.

Example :

The reversible nature of a chemical reaction can be illustrated by a reaction between H_2 and I_2 to form Hydrogen Iodide (HI)

It is represented as

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

Few more examples are :

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

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

$$2\,SO_{2(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3(g)}$$

$$PCl_{5\,(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2\,(g)}$$

Conditions for a reversible reaction

1. The reaction should be carried out in a closed vessel.
2. The products should not be removed from vessel.
3. Temperature and pressure should be kept constant.

Irreversible reactions

It is the reaction which proceeds only in one direction.

A reaction in which the products formed do not combine to give back the reactants is called an irreversible reaction.
Few examples of irreversible reactions are:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

$$Mg + 2\,HCl \longrightarrow MgCl_2 + H_2\uparrow$$

$$AgNO_{3(aq)} + KCl_{(aq)} \longrightarrow AgCl\downarrow + KNO_{3(aq)}$$

$$2\,H_2 + O_2 \longrightarrow 2H_2O$$

It is observed that an irreversible reaction can not be made reversible even if it is carried out in a closed vessel.

* The definition and characteristics of chemical equilibrium are dealt in detail in XI standard

Acids :

An acid is a substance which contains one or more replaceable hydrogen atoms and dissociates in solution giving hydrogen ions (H^+).

For example, Hydrochloric acid (HCl) is an acid.

HCl dissociates in solution giving 'H^+' ions.

$$HC1_{(aq)} \longrightarrow H^+ + CI^-$$

Acids contain different number of replaceable hydrogen atoms. It is called basicity.

Basicity of an acid :

The number of replaceable hydrogen atoms present in a molecule of an acid is called basicity of the acid.

Depending on the basicity of the acids, they are classified as:

(i) Monobasic acid:

Monobasic acid contains one replaceable hydrogen atom in a molecule.

Ex: HCl – Basicity of HCl is one.
HNO_3 -- It is also monobasic acid.

Organic acids like Formic acid (HCOOH), Acetic acid (CH_3COOH), Benzoic acid (C_6H_5COOH) are all monobasic.

(ii) Dibasic acid :

Dibasic acid contains two replaceable hydrogen atoms in a molecule.

Ex: Sulphuric acid (H_2SO_4) – It is dibasic acid.
Oxalic acid ($C_2H_2O_4.2H_2O$) – It is also dibasic acid.

(iii) Tribasic acid :

A tribasic acid contains three replaceable hydrogen atoms in a molecule

Ex: Orthophosphoric acid (H_3PO_4)
Its basicity is 3.
So it is tribasic acid.

Almost all the inorganic acids are soluble in water.

Note:

The aqueous solution of acids having different concentrations are prepared in the laboratory for carrying out volumetric analysis. The concentration of acids are expressed in normality during the process of volumetric analysis.

Bases:

A base is a substance which dissociate in solution giving hydroxyl (OH^-) ions.

The oxides and hydroxides of metals are bases or basic in nature.
For Example,
Sodium hydroxide (NaOH) is a base.

NaOH dissociates in solution.

$$NaOH \longrightarrow Na^+ + OH^-$$

Acidity of base :

The number of molecules of a monobasic acid required to neutralize a molecule of a base is called acidity of the base.

Ex: NaOH is monoacidic base because a molecule of NaOH is completely neutralized by a molecule of monobasic acid like HCl.

KOH is also monoacidic base. Its acidity is one.

$Ca(OH)_2$ is diacidic base. Its acidity is two

$Al(OH)_3$ is triacidic base. Its acidity is three

All the bases are not readily soluble in water.

Alkali :

The bases which are readily soluble in water are called alkali.

Note:

The oxides and hydroxides of "group – 1" metals of long form of periodic table are readily soluble in water. They are called alkalies and metals are called alkali metals.

Example:

NaOH is a base and also an alkali.

KOH is also an alkali.

$Mg(OH)_2$, $Ca(OH)_2$ are bases only but not alkalies.

[*All the alkalies are bases*

But not all the bases are alkalies]

Neutralisation:

The reaction between an acid and a base in dilute aqueous solution is called neutralisation reaction.

An acid and a base react in equal proportions. For example, 1 gm equivalent mass of an acid is completely neutralised by 1 gm equivalent mass of base in aqueous solution. The amount of an acid or a base present in a known volume of water (solvent) is the concentration and is expressed in terms of normality (N)

Ex:

A definite volume of 1 N HCl solution is completely neutralised by an equal volume of 1 N NaOH solution and vice versa.

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O$$

Salt :

The chemical substance obtained as a result of neutralization reaction between an acid and a base is called salt.

Ex: Sodium Chloride (NaCl)

Potassium Chloride (KCl)

Sodium nitrate ($NaNO_3$) etc.

Exercises:

1. Define rate of a reaction.
2. How does concentration of a reactant vary with time in a reaction?
3. Give the SI unit of rate of a reaction.
4. What are the significances of the rate expression $\pm \frac{dc}{dt}$
5. How is the rate of reaction expressed for the reaction $A+B \longrightarrow C+D$ with respect to reactants and products ?
6. Name the factors affecting the rate of a reaction.
7. What are reversible reactions? Give an example.
8. Mention the conditions for a reaction to become reversible.
9. What are irreversible reactions? Give an example.
10. HCl is an acid. Give reason.
11. Sulphuric acid is a dibasic acid. Why?
12. What are tribasic acids? Give an example.
13. NaOH is a base and also an alkali. Why?
14. Define acidity of a base.
15. Mention the acidity of alluminium hydroxide.
16. What are salts ? Give examples.
17. What is basicity of an acid?
18. What type of reaction is called as neutralization reaction ? Give an example.
19. The acidity of barium hydroxide is 2. Give reason.
20. Calcium hydroxide is abase but not an acid. Why?