Chemical Equilibrium

In a chemical reaction chemical equilibrium is defined as the state at which there is no further change in concentration of reactants and products.

For example,

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

At equilibrium the rate of forward reaction is equal to the rate of backward reaction.

Equilibrium **mixture:** The mixture of reactants and products in the equilibrium state is called an equilibrium mixtures.

Based on the extent to which the reactions proceed to reach the state of equilibrium, these may be classified in three groups:

(i) The reactions which proceed almost to completion and the concentrations of the reactants left are negligible.

(ii) The reactions in which most of the reactants remains unchanged, i.e. only small amounts of products are formed.

(iii) The reactions in which the concentrations of both the reactants and products are comparable when the system is in equilibrium.

• Equilibrium in Physical Processes

(i) Solid-Liquid Equilibrium: The equilibrium is represented as

$$H_2O\ (s) \rightleftharpoons H_2O(l)$$

Rate of melting of ice = Rate of freezing of water.

The system here is in dynamic equilibriums and following can be inferred.

(a) Both the opposing processes occur simultaneously

(b) Both the processes occur at the same rate so that the amount of ice and water – remains constant.

(ii) Liquid-Vapour Equilibrium

The equilibrium can be represented as

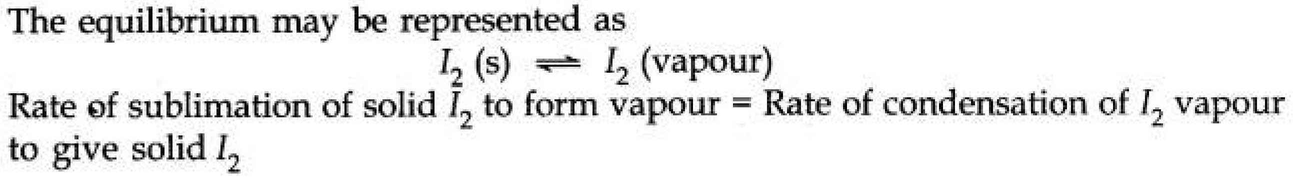
$$H_2O\ (l) \rightleftharpoons H_2O\ (vap)$$

Rate of evaporation = Rate of condensation

When there is an equilibrium between liquid and vapours, it is called liquid-vapour equilibrium.

(iii) Solid-Vapour Equilibrium

This type of equilibrium is attained where solids sublime to vapour phase. For example, when solid iodine is placed in a closed vessel, violet vapours start appearing in the vessel whose intensity increases with time and ultimately, it becomes constant.



The equilibrium may be represented as

$$I_2\ (s) \rightleftharpoons I_2\ (vapour)$$

Rate of sublimation of solid I_2 to form vapour = Rate of condensation of I_2 vapour to give solid I_2

• Equilibrium involving Dissolution of Solid in Liquid

Solution: When a limited amount of salt or sugar or any solute dissolves in a given amount of water solution is formed.

At a given temperature state is reached when no more solute can be dissolved then the solution is called saturated solution.

The equilibrium between a solid and its solution is indicated by the saturated solution and may be represented as

$$\text{Sugar (in solution)} \rightleftharpoons \text{Sugar (solid).}$$

Here dissolution and precipitation takes place with the same speed.
On adding a small amount of radioactive sugar to the saturated solution it will be found that the sugar present in the solution as well as in the solid state is radioactive.

• Equilibrium between a Gas and its Solution in Liquid

This type of equilibrium can be seen by the following example:
Let us consider a sealed soda water bottle in which C02 gas is dissolved under high pressure. A state of equilibrium is attained between CO2 present in the solution and vapours of the gas.

$$CO_2\ (g) \rightleftharpoons CO_2\ \text{(present in solution)}$$

Henry's law: The solubility of a gas in a liquid at a certain temperature is governed by Henry's law. It states that the mass of a gas that dissolves in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the surface of the solvent.

Mathematically, $m \propto p$

$$m = K_H p \text{ (where } K_H = \text{Henry's Constant)}$$

• Characteristics of Equilibria Involving Physical Processes

(i) The equilibrium can be attained only in closed systems at a given temperature.
(ii) At the equilibrium the measurable properties of the system remain constant.
(iii) The equilibrium is dynamic since both the forward and backward processes occur at same rate.
(iv) At equilibrium, the concentrations of substances become constant at constant temperature.
(v) The value of equilibrium constant represents the extent to which the process proceeds before equilibrium is achieved.

• Equilibrium in Chemical Processes

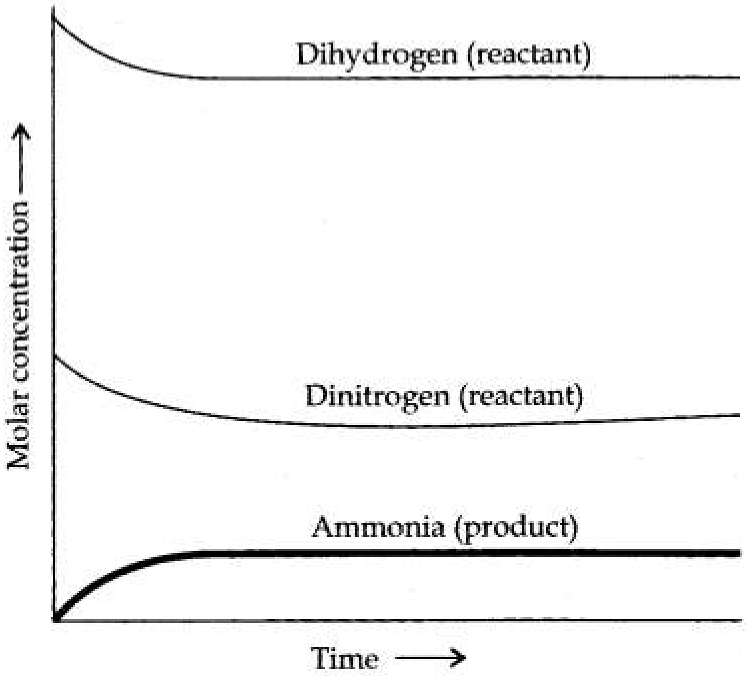
Like equilibria in physical systems it can also be achieved in chemical process involving reversible chemical reactions carried in closed container.

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

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. Haber started his experiment with the known amounts of N2 and H2 at high temperature and pressure. At regular intervals of time he determined the amount of ammonia present. He also found out concentration of unreacted N2 and H2. After a certain time he found that the composition of mixture remains the same even though some of the reactants are still present. This constancy indicates the attainment of equilibrium. In general, for a reversible reaction the chemical equilibria can be shown by

$$A + B \rightleftharpoons C + D$$

After a certain time the two reactions occur at the same rate and the system reaches a state of equilibrium. This can be shown by the given figure.



Depiction of equilibrium for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

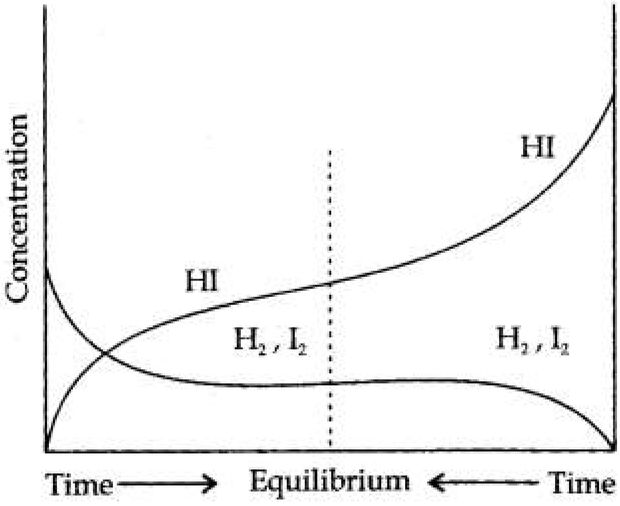
- **Equilibrium in Homogeneous System**

When in a system involving reversible reaction, reactants and products are in the same phase, then the system is called as homogeneous system.

For Example,

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

After some time it can be observed that an equilibrium is formed. The equilibrium can be seen by constancy in the colour of the reaction mixture.



Chemical equilibrium in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ can be attained from either direction

- **Law of Chemical Equilibrium**

At a constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants each raised to a power equal to the corresponding stoichiometric coefficients as represented by the balanced chemical equation.

Let us consider the reaction,

$$aA + bB \rightarrow \text{products}$$

By the law, rate of reaction $\alpha[A]^a\,[B]^b = K[A]^a\,[B]^b$

Here a and b are stoichiometric coefficients. K is the rate constant.

Let us consider a general reversible reaction

$$A + B \rightleftharpoons C + D$$

Applying Law of Mass Action,

Rate of the forward reaction $\alpha[A]\,[B] = Kf[A]\,[B]$

Where kf is a constant of proportionality and is called velocity constant for the forw reaction.

Rate of backward reaction $\alpha[C]\,[D] = kb[C]\,[D]$.

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$Kf\,[A]\,[B] = kb\,[C]\,[D]$$

or, $$\frac{[C][D]}{[A][B]} = \frac{Kf}{kb} = K$$

At constant temperatures K is also constant and is called Equilibrium constant.

Now let us consider a more general reversible reaction in a state of equilibrium. By apply law of mass action.

$$aA + bB \rightleftharpoons cC + dD$$

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

Equilibrium constant for the reaction

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

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

- Relationship between Equilibrium constant K, reaction Quotient Q and Gibbs energy G.

A mathematical expression of thermodynamic view of equilibrium can be described by tine equation.

$$\Delta G = \Delta G^{\ominus} + RT \text{ In } Q$$

where $G^{\ominus}$ is standard Gibbs energy.

At equilibrium when $\Delta G = 0$

$$Q = K_c$$

$$\Delta G = \Delta G^{\ominus} + RT \text{ In } K = 0$$

$$\Delta G^{\ominus} = -RT \text{ In } K$$

$$\ln K = \frac{-\Delta G^{\ominus}}{RT}$$

Taking antilog on both sides

$$K = e^{-\Delta G^{\ominus}/RT}$$

- **Factors Affecting Equilibria**

Le Chatelier’s principle: If a system under equilibrium is subjected to a change in temperature, pressure or concentration, then the equilibrium shifts in such a manner as to reduce or to counteract the effect of change.

Effect of Change of Concentration: When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium changes so as to minimise the effect.

Effect of Pressure Change

If the number of moles of gaseous reactants and products are equal, there is no effect of pressure.

When the total number of moles of gaseous reactants and total number of moles of gaseous products are different.

On increasing pressure, total number of moles per unit volume increases, thus the equilibrium will shift in direction in which number of moles per unit volume will be less.

If the total number of moles of products are more than the total number of moles of reactants, low pressure will favour forward reaction.

If total number of moles of reactants are more than total number of moles of products, high pressure is favourable to forward reaction.

Effect of Inert Gas Addition

If the volume is kept constant there is no effect on equilibrium after the addition of an inert gas.

Reason: This is because the addition of an inert gas at constant volume does not change the partial pressure or the molar concentration.

The reaction quotient changes only if the added gas is involved in the reaction.

Effect of Temperature Change

When the temperature of the system is changed (increased or decreased), the equilibrium shifts in opposite direction in order to neutralize the effect of change. In exothermic reaction low temperature favours forward reaction e.g.,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$\Delta H = -92.38 \text{ kJ mol}^{-1}$$

but practically very low temperature slows down the reaction and thus a catalyst is used. In case of endothermic reaction, the increase in temperature will shift the equilibrium in the direction of the endothermic reaction.

Effect of a Catalyst

Catalyst has no effect on the equilibrium composition of a reaction mixture.

Reason: Since catalyst increases the speed of both the forward and backward reactions to the same extent in a reversible reaction.

- **Ionic Equilibrium in Solution**

Electrolytes: Substances which conduct electricity in their aqueous solution.

Strong Electrolytes: Those electrolytes which on dissolution in water are ionized almost completely are called strong electrolytes.

Weak electrolyte: Those electrolytes which on dissolution in water partially dissociated are called weak electrolyte.

Ionic Equilibrium: The equilibrium formed between ions and unionised substance is called ionic equilibrium, e.g.,

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Acids: Acids are the substances which turn blue litmus paper to red and liberate dihydrogen on reacting with some metals.

Bases: Bases are the substances which turn red litmus paper blue. It is bitter in taste. Common Example: NaOH, Na_2C0_3.

• Arrhenius Concept of Acids and Bases

Acids: According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$.

Bases: Bases are substances that produce $OH^-(aq)$ after dissociation in water.

The ionization of an acid can be represented as

$$HX(aq) \rightarrow H^+(aq) + X^-(aq)$$

$$HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq)$$

Dissociation of Base molecule in aqueous solution:

$$MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$$

• Limitations of the Arrhenius Concept

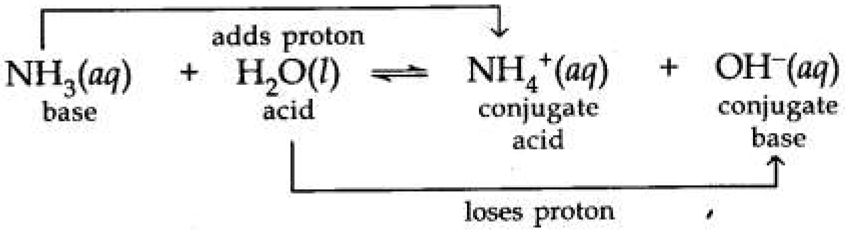
(i) According to the Arrhenius concept, an acid gives H^+ ions in water but the H+ ions does not exist independently because of its very small size (~H^{-18} m radius) and intense electric field.

(ii) It does not account for the basicity of substances like, ammonia which does not possess a hydroxyl group.

• The Bronsted-Lowry Acids and Bases

According to Bronsted-Lowry, an acid is a substance which is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion H^+.

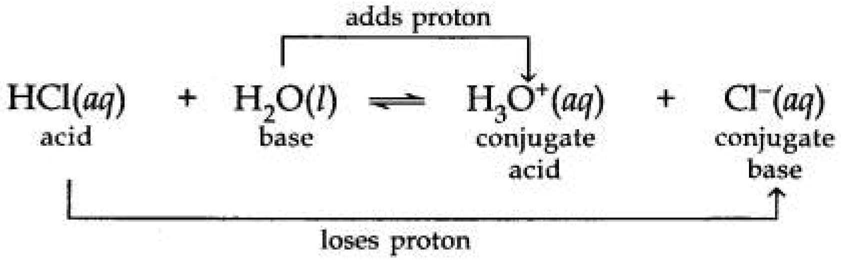
In other words, acids are proton donors and bases are proton acceptors. This can be explained by the following example.



• Acid and Base as Conjugate Pairs

The acid-base pair that differs only by one proton is called a conjugate acid-base pair.

Let us consider the example of ionization of HCl in water.



Here water acts as a base because it accepts the proton.
CL is a conjugate base of HCl and HCl is the conjugate acid of base CL. Similarly, H_20 is conjugate base of an acid H_30^+ and H_30^+ is a conjugate acid of base H_2O.

• Lewis Acids and Bases

According to Lewis, acid is a substance which accepts electron pair and base is a substance with donates an electron pair.
Electron deficient species like $AlCl_3$, BH_3, H^+ etc. can act as Lewis acids while species like H_20, NH_3 etc. can donate a pair of electrons, can act as Lewis bases.

• Ionization of Acids and Bases

Strength of acid or base is determined with the help of extent of ionization in aqueous solution.

pH Scale: Hydrogen-ion concentration are measured as the number of gram ions of hydrogen ions present per litre of solution. Since these concentrations are usually small, the concentration is generally expressed as the pH of the solution. pH being the logarithm of the reciprocal of the hydrogen ion concentration.

$$\mathrm{pH} = -\log\{[\mathrm{H}^+]/\mathrm{mol}\ L^{-1}\}$$

pH of pure water at 25°C is given as

$$\mathrm{pH} = -\log(10^{-7}) = 7$$

$$\begin{aligned} \text{Acidic solution has pH} &< 7 \\ \text{Basic solution has pH} &> 7 \\ \text{Neutral solution has pH} &= 7 \\ K_w &= [\mathrm{H_3O^+}][\mathrm{OH^-}] = 10^{-14} \\ \mathrm{p}K_w &= \mathrm{pH} + \mathrm{pOH} = 14 \end{aligned}$$

• Di and Polybasic Acids

Acids which contain more than one ionizable proton per molecule are called Dibasic acids or polybasic acids or polyprotic acids.
Common examples are oxalic acid, sulphuric acid, phosphoric acid etc.

The ionization reactions for a dibasic acid can be represented as.

$$\begin{aligned} \mathrm{H_2X}(aq) &\rightleftharpoons \mathrm{H^+}(aq) + \mathrm{HX^-}(aq) \\ \mathrm{HX^-}(aq) &\rightleftharpoons \mathrm{H^+}(aq) + \mathrm{X^{2-}}(aq) \end{aligned}$$

Their equilibrium constants can be written as

$$K_{a_1} = \frac{[\mathrm{H^+}][\mathrm{HX^-}]}{[\mathrm{H_2X}]};\ K_{a_2} = \frac{[\mathrm{H^+}][\mathrm{X^{2-}}]}{[\mathrm{HX^-}]},$$

K_{a_1} and K_{a_2} are called first and second ionization constants respectively.

$$K_{a_1} > K_{a_2} \text{ for dibasic acid.}$$

Factors Affecting Acid Strength

When the strength of H-A bond decreases

$$\xrightarrow{\text{Size increases}}$$
$$\text{HF} << \text{HCl} << \text{HBr} << \text{HI}$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

The energy required to break the bond decreases, H-A becomes a stronger acid.

As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases.

In a period, as the electronegativity of A increases, the strength of the acid increases.

$$\xrightarrow{\text{Electronegativity of A increases}}$$
$$CH_4 < NH_3 < H_2O < HF$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

- **Common Ion Effect**

If in a aqueous solution of a weak electrolyte, a strong electrolyte is added having an ion common with the weak electrolyte, then the dissociation of the weak electrolyte is decreased or suppressed. The effect by which the dissociation of weak electrolyte is suppresed is known as common ion effect.

For example: In an aqueous solution of CH_3COOH, a small amount of CH_3COONa (stro electrolyte) has been added.

Due to the presence of common $CH_3\ COO^-$ (*aq*) ions, the equilibrium will be shifted to left.

$$CH_3\ COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^-\ (aq)$$
$$CH_3COONa\ (aq) \rightleftharpoons CH_3COO^-(aq) + Na^+\ (aq)$$

Common ion

Thus, the dissociation of CH_3COOH will get decreased or suppressed.

- Hydrolysis of Salts and the pH of their Solutions

Salt Hydrolysis: Salt + water ⇌ Acid + Base

Hydrolysis is a process which is reverse of neutralization reaction.

Hydrolysis of Salts of Strong Acids and Weak Base

e.g., NH_4Cl, NH_4NO_3 etc.

$$NH_4\ NO_3 + H_2O \rightleftharpoons NH_4\ OH + HNO_3$$
$$NH_4^+ + NO_3^- + H_2O \rightleftharpoons NH_4\ OH + H^+\ NO_3^-$$

or
$$NH_4^+ + H_2O \rightleftharpoons NH_4\ OH + H^+$$

After hydrolysis solution will be acidic pH < 7.

Since only cations of the salt participate in the hydrolysis, it is known as catio hydrolysis.

Hydrolysis of salts of strong base and weak acids

Salts in this category are CH_3COONa, Na_2CO_3, Na_3PO_4 etc.

$$CH_3\ COONa + H_2O \rightleftharpoons CH_3\ COOH + NaOH$$

$$CH_3\,COO^- + Na^+\,H_2O \rightleftharpoons CH_3\,COOH + Na^+ + OH^-$$

or $$CH_3\,COO^- + H_2O \rightleftharpoons CH_3\,COOH + OH^-$$

After hydrolysis, solution will be basic $pH > 7$

In this type of hydrolysis, only anions of salt take part in the hydrolysis, it is known anionic hydrolysis.

Hydrolysis of Weak Acid and Weak Base

Salts belong to this type are: CH_3COONH_4, $(NH_4)_2CO_3$ etc.

$$CH_3\,COONH_4 + H_2O \rightleftharpoons CH_3\,COOH + NH_4OH$$

or $$CH_3\,COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3\,COOH + NH_4OH$$

pH of solution depends upon the relative strengths of acid and base.

- **Buffer Solutions**

The solutions which resist change in pH on dilution or with the addition of small amount acid or alkali, are called Buffer solutions.

e.g., $CH_3\,COOH + CH_3COONa$,
$H_2CO_3 + HCl$

Acidic Buffer: Weak acid and its salt with strong base are known as acidic buffer. PH <
e.g., CH_3COOH and CH_3COONa, H_2CO_3 and HCl

Basic Buffer: Weak base and its salt with strong acid are known as basic buffer.
$pH > 7$ *e.g.,* NH_4Cl and NH_4OH

- **Solubility Products**

It is applicable to sparingly soluble salt. There is equilibrium between ions and unionised solid substance.

Consider an equation

$$BaSO_4\,(s) \underset{\text{in water}}{\overset{\text{Saturated solution}}{\rightleftharpoons}} Ba^{2+}(aq) + SO_4^{2-}\,(aq)$$

$$K = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$$

$$K_{sp} = K[BaSO_4] = [Ba^{2+}]\,[SO_4^{2-}]$$

K_{sp} is called the solubility product constant or simply solubility product.

Under equilibrium conditions

$$K_{sp} = Q_{sp}$$

The solubility of salts of weak acids like, phosphates, increases at lower pH.

- **Equilibrium:** It can be established for both physical and chemical processes. At the state of equilibrium rate of forward and backward reactions are equal.
- **Equilibrium constant:** Kc is expressed as the concentration of products divided by reactants each term raised to the stoichiometric coefficients. For reactions,

$$aA + bB \rightleftharpoons cC + dD$$

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

- **Le Chatelier’s principle:** It states that the change in any factor such as temperature, pressure, concentration etc., will cause the equilibrium to shift in such a direction so as to reduce the effect of the change.
- **Electrolytes:** Substances that conduct electricity in aqueous solutions are called electrolytes.
- **Arrhenius Concept:** According to Arrhenius, acids give hydrogeneous while bases produce hydroxyl ions in their aqueous solution.
- **Bronsted-Lowry concept:** Bronsted-Lowry defined acid as proton donor and a base as a proton acceptor.
- **Conjugate base and Conjugate acid:** When a Bronsted-Lowry acid reacts with a base it produces its conjugate base and conjugate acid.
- **Conjugate pair of acid and base:** Conjugate pair of acid and base differs only by one proton.
- **Lewis acids:** Define acid as an electron pair acceptor and a base as an electron pair donor.
- **pH Scale:** Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the pH scale. The pH of pure water is 7.
- **Buffer solution:** It is the solution whose pH does not change by addition of small amount of strong acid or base.

For example: $CH_3COOH + CH_3COONa$.

- **Solubility product (K_{sp}):** For a sparingly soluble salt, it is defined as the product of molar concentration of the ions raised to the power equal to the number of times each ion occurs in the equation for solubilities.

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+]\,[Cl^-].$$