

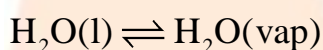
Revision Notes

Class 11 Chemistry

Chapter 7 – Equilibrium

Introduction:

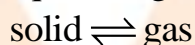
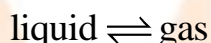
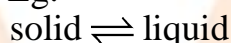
An important in numerical and biological process is meant to be chemical equilibrium. When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an **equilibrium** in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. Then the system has reached equilibrium state at this stage. Thus, at **equilibrium**, the rate of evaporation is equal to the rate of condensation. It may be represented by



The above double arrow indicates that the process simultaneously going in both directions. The equilibrium mixture means the mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**.

Equilibrium in physical process:

we observe some physical process then the characteristics of system at equilibrium are better understand. The most important and familiar examples are **phase transformation process**. Eg.



a) Solid-liquid equilibrium:

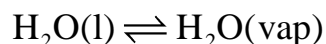
At particular temperature and pressure the ice and water are in equilibrium. The normal melting point or normal freezing point of the substance is the temperature at which the solid phase and liquid phases are equilibrium for any pure substance at atmospheric pressure. When the system at dynamic equilibrium will follow the conditions:

- Both the opposing processes occur simultaneously
- Both the process occurs at the same rate then the amount of ice and water remains constant.

b) Liquid-vapour equilibrium:

The number of water molecules from the gaseous state into liquid state increases until the equilibrium reached.

i.e rate of evaporation = rate of condensation



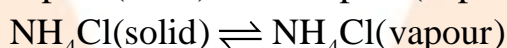
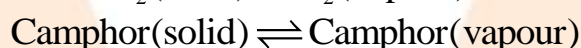
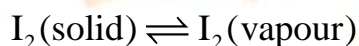
The equilibrium water pressure means at which pressure the water molecules remains constant at given temperature and vapour pressure of water increase with temperature. The evaporation of liquid depends on,

- The nature of the liquid
- The amount of liquid
- The applied temperature

For example in a closed vessel water and water vapour are in equilibrium position at atmospheric pressure (1.031 bar) and at 100⁰C . Which means that for any pure liquid at one atmospheric pressure (1.0301 bar), then the normal boiling point is said to be the temperature at which liquid and vapours are at equilibrium.

c) Solid – vapour equilibrium:

The examples of this type system considered when solids sublime to vapour phase.

**General characteristics of Equilibrium involving physical processes:**

Following characteristics are common to the system at equilibrium for which the physical processes are discussed above:

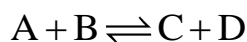
- At a given temperature, the equilibrium possible only in closed systems
- If both the opposing processes occur at the same rate then the system is dynamic at stable condition.
- In a system, all measurable properties are remains constant.
- Equilibrium is characterized by constant value of one of its parameters given, and then it is attained for a physical process.

Equilibrium in chemical processes:

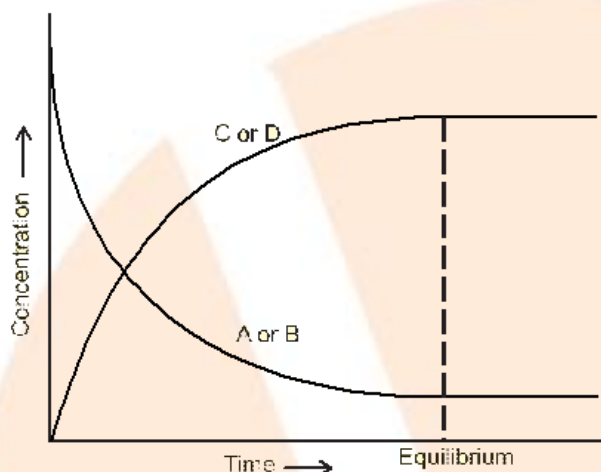
Compared to physical systems chemical reactions also attain a state of equilibrium. Those chemical reactions can occur both in forward and backward directions. The chemical equilibrium is **dynamic** in nature when the rates of forward and backward become equal with the concentrations and products are remains constant.

- **Reversible reactions**

Consider a general case of a reversible reaction



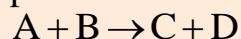
With passing time, there is decrease in the concentration of reactants A and B, the increase in the concentration of products C and D which leads to a decrease in the rate of forward reaction and an increase in the rate of backward reaction.



When the two reactions occur at the same rate and system will reach a state of equilibrium.

- **Irreversible reactions**

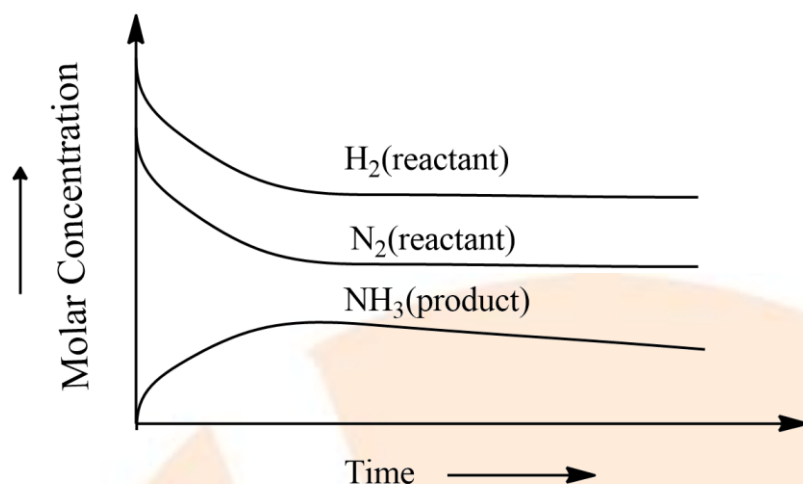
The products formed will not react back the reactants under same conditions; it is called the Irreversible reaction. These reactions cannot take place in the reverse direction.



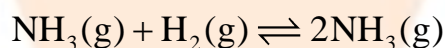
- It is state of minimum Gibb's energy
- $dG = 0$ and $\Delta G = 0$ at this state
- Rate of forward reaction = rate of backward reaction
- This equilibrium is dynamic and stable in nature

Dynamic Nature of Chemical Equilibrium:

This dynamic nature of chemical equilibrium can be explained by the synthesis of ammonia by Haber's process. This process starts with definite amounts of N_2 & H_2 and carrying out reaction when equilibrium is attained at particular temperature. At equilibrium the concentrations of N_2 , H_2 & NH_3 are remains constant.



Representing the attainment of equilibrium for the reaction,



Characteristics of Chemical Equilibrium:

- The concentration of each of the reactants and the products becomes constant at equilibrium.
- The rate of forward reaction becomes equal to the rate of backward reaction at equilibrium and hence equilibrium is dynamic in nature.
- None of the products is allowed to escape out or separate out as a solid then only chemical equilibrium can be established.

Equilibrium constant:

An equilibrium mixture is a mixture of reactants and products in the equilibrium state.

Consider a general reversible reaction,



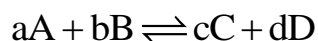
Where A and B are reactants, C and D are products in the above balanced equation.

$$K_c = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

Where K_c is Equilibrium constant and expressed in concentrations of molL^{-1} .

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

The equilibrium constant for general reaction,



Equilibrium constant expressed as,

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

Where [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products.

The product of the molar concentrations of the products, each raised to the power equal to its stoichiometric coefficient is divided by the product of the molar concentrations of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature is called **Equilibrium Constant**.

Characteristics of Equilibrium Constant:

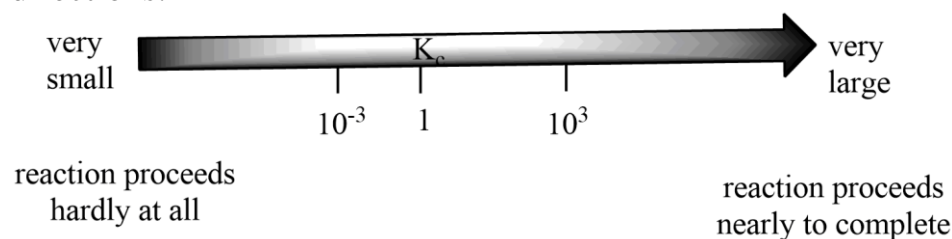
- The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium approached.
- The value of equilibrium constant is inverted when the reaction is reversed.
- The equilibrium constant for the new equation is square root of K. (i.e., \sqrt{K}), when the equation is divided by 2.
- The equilibrium constant for new equation is the square of K (i.e., K^2), when the equation is multiplied by 2.
- By the addition of catalyst to the reaction will not affect the value of the equilibrium.

Predicting the Extent of reaction:

If the value of $K_c > 10^3$ will be high, then the equilibrium reaction is forward dominant.

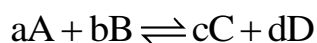
If the value of $K_c < 10^{-3}$ will be low, then the equilibrium reaction is backward dominant.

Moderate value of K_c (between 10^3 and 10^{-3}) dominates equilibrium neither directions.



Predicting the Direction of the Reaction- Reaction Quotient:

We can predict the direction in which reaction will proceed at any stage with the help of the equilibrium constant. Reaction Quotient Q will calculate for this purpose. The same way as the equilibrium constant K_c , Reaction Quotient will define are not necessarily equilibrium values.



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

- the reaction proceeds in the direction of reactants when $Q_c > K_c$
- the reaction proceeds in the direction of products when $Q_c < K_c$
- the reaction mixture is already at equilibrium when $Q_c = K_c$

Calculating Equilibrium Concentrations:

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

- (a) The initial concentration,
- (b) The change in concentration on going to equilibrium, and
- (c) The equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x .

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x . If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x .

Step 5. Check your results by substituting them into the equilibrium equation.

Relationship between equilibrium constant and Gibbs free energy:

The value of equilibrium constant for a reaction does not depend on the rate of reaction.

- If change in Gibbs free energy ΔG is negative, then the reaction proceeds in the forward reaction with spontaneity.
- If change in Gibbs free energy ΔG is positive, the products of the forward reaction shall be converted to reactants with non-spontaneous process.
- If the change in Gibbs free energy is Zero, then the reaction at equilibrium and there is no longer any free energy left to drive the reaction.

A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation:

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

Where Q is Reaction Quotient. And G^\ominus is standard Gibbs free energy.

At equilibrium, when $\Delta G^\ominus = 0$ and $Q_c = K_c$

$$\Delta G = \Delta G^\ominus + RT \ln K_c = 0$$

$$\Delta G^\ominus = -RT \ln K_c$$

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

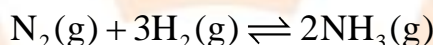
$$K = e^{\frac{\Delta G^\ominus}{RT}}$$

from the above equation, from the values of ΔG^\ominus , the reaction spontaneity can be interpreted.

Homogeneous Equilibria:

In a equilibrium system, all the reactants and products are in same phase is known as Homogenous system.

For example,



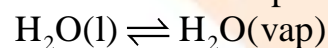
In the above reaction all reactants and products are in gaseous phase.



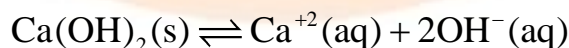
In the above reaction, all reactants and products are homogeneous solution phase.

Heterogeneous Equilibria:

In a equilibrium system having more than one phase is called heterogeneous equilibrium. The familiar example for this type of system is the equilibrium between water vapour and liquid water in a closed container.



Similarly, there is equilibrium between a solid and its saturated solution is a heterogeneous equilibrium.



Le Chatelier's principle:

This principle helps to decide what course of reaction adopts and make a qualitative prediction about the effect of changes in conditions on equilibrium.

It states that, "a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to

reduce or to counteract the effect of the change.”

This principle is applicable for all physical and chemical equilibrium systems.

a) Effect of concentration change:

Generally equilibrium disturbed by addition or removal of any reactant or product. The **Le Chatelier's principle** predicts that:

- The concentration of added reactant or product is relieved by the direction of net reaction that consumes the added substance.
- The concentration of removed reactant or product is relieved by the direction of net reaction that replenishes the added substance.

“When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes”.

b) Effect of temperature change

Because of the Reaction Quotient Q no longer equals to equilibrium constant when equilibrium is disturbed by change in the concentrations, pressure, or volume and further the composition of the equilibrium mixture changes.

The value of the equilibrium constant changed when a change in the temperature observed.

Generally temperature change dependence of equilibrium constant depends on the sign of the ΔH for the reaction.

- If ΔH is negative, then the equilibrium constant of the exothermic reaction decreases because of temperature increases.
- If ΔH is positive, then the equilibrium constant of the endothermic reaction increase because of temperature decreases.

c) Effect of pressure change

When the total number of moles of gaseous products is different, then a pressure change obtained changing the volume can affect the yield of products in case of gaseous reaction. Le-Chatelier's principle is applied to heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume of a solution or liquid is nearly independent of pressure.

d) Effect of volume change

Effect of increase of pressure is equivalent to the effect of decrease of volume.

So the effect of decrease in volume will be shifted towards the equilibrium in the direction in which the number of moles decreases.

e) Effect a catalyst

The chemical substance which increases the rate of chemical reaction by making available a new low energy pathway for the conversion of reactants to products. Catalyst increases the rate of forward and reverse reactions that pass through the transition state which does not affect the equilibrium.

For example: contact process



the oxidation of sulphur di oxide to sulphur trioxide partially very slow.

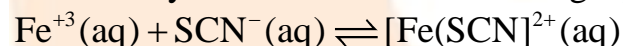
So, Platinum or divanidium pentaoxide (V_2O_5) is used as catalyst to increase the rate of reaction.

f) Effect of inert gas addition

If an inert gas such as argon is added and the volume kept constant this does not take any part in the reaction. Thus, the equilibrium remains undisturbed. Because the addition of inert gas does not change the partial pressures or the molar concentrations of substances involved in the reaction at constant volume.

Ionic equilibrium in solution:

The effect of change in the concentration on the direction of equilibrium, incidentally come across the following equilibrium which involves ions:



There are equilibria reactions involve ions only. According Micheal Faraday, classified the substances two categories based on their ability to conduct electricity. Those are electrolytes and non-electrolytes. Because of presence the ions, the solution of electrolytes conduct electricity.

For example an aqueous solution of NaCl is dissociated completely into Na^+ and Cl^- ions, because of almost 100% ionization in case of sodium chloride. But in case of acetic acid which is weak electrolyte, 5% ionization takes place. Hence, equilibrium is established between ions and unionized molecules in weak electrolytes. This type of equilibrium involving ions in an aqueous solution is known as **Ionic Equilibrium**.

Classification of electrolytes:

Based on the strength of electrolytes are classified into two categories:

a) Strong electrolytes

The electrolytes which are easily break into ions with complete dissociation are known as strong electrolytes.

Eg: HCl, NaCl, NaOH, HNO_3 , HClO_4 , H_2SO_4

b) Weak electrolytes

The electrolytes which are partially dissociation are known as weak electrolytes. Eg: CH_3COOH , NH_4OH , HCN , $\text{H}_2\text{C}_2\text{O}_4$, and all organic acids and bases.

Acids, Bases and Salts:

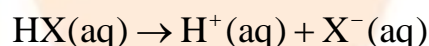
There are various theories from the explanation of acids and bases.

Arrhenius concept of acids and bases:

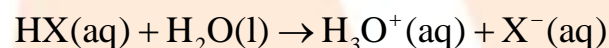
According to this theory, acids are the substances which give H^+ ions dissociates in water and bases which produce hydroxyl ions OH^- in water.

Arrhenius acids: which increases the H^+ ion concentration in water.

The ionization of acids can be represented by the following equations for HX (aq):



Or

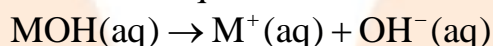


Example: HCl , H_2SO_4 , CH_3COOH etc.

Arrhenius bases: which increases the OH^- ions concentration in water.

For example: NaOH , $\text{Ca}(\text{OH})_2$, NH_4OH etc.

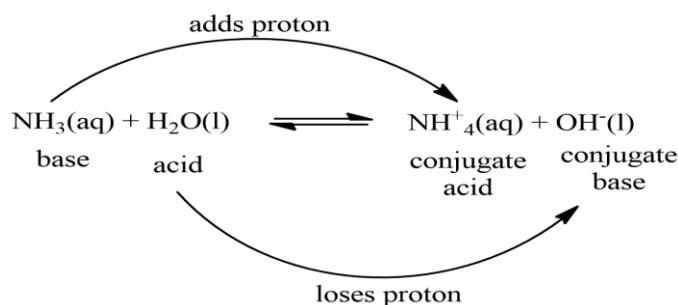
MOH like base molecule ionizes in aqueous solution from the following equation:



The Bronsted-Lowry acids and bases:

According to Brönsted-Lowry theory, acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+ . In short, acids are proton donors and bases are proton acceptors.

For example, consider the dissolution of NH_3 in H_2O represented by the following equation:



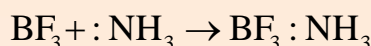
in this reaction, water molecule acts as proton donor is known as Lowry-Bronsted acid and ammonia molecule act as proton acceptor is known as Lowry-Bronsted base.

Lewis Acids and Bases:

According to this theory, acid is a species which accepts electron pair and a base which donates electron pair.

A typical example is reaction of electron deficient species BF_3 with NH_3 .

In this example BF_3 does not have proton but acts as Lewis acid and NH_3 accepting lone pairs from Lewis acid. The reaction can be represented as:



Lewis acids are electron deficient species like $\text{AlCl}_3, \text{Co}^{+3}, \text{Mg}^{+2}$

Lewis bases are electron pair donating species like $\text{H}_2\text{O}, \text{NH}_3, \text{OH}^-$

The ionization constant of water and its ionic product:

Some substances are unique ability of acting acid and base like water molecules.



The dissociation constant is represented by:

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

The concentration of water is neglected from the denominator as water is pure liquid and its concentration remains constant. Then the equilibrium constant is known as **Ionic Product Of Water**, K_w .

$$K_w = [\text{H}^+][\text{OH}^-]$$

The concentration of $\text{H}^+ = 1.0 \times 10^{-7} \text{ M}$ at 298K

As dissociation of water produces equal number of $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M}^2$$

We can distinguish acidic, neutral, and basic solutions by the relative values of the H_3O^+ and OH^- concentrations:

Acidic: $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

Neutral: $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

Basic: $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

The pH Scale:

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the **pH Scale**.

From the definition of pH,

$$\text{pH} = -\log[\text{H}^+]$$

at 25°C pure water has a concentration of hydrogen ions, $[\text{H}^+] = 10^{-7} \text{ M}$

Hence, the pH of pure water is given as:

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

Acidic solutions possess a concentration of hydrogen ions, $[\text{H}^+] > 10^{-7} \text{ M}$, while basic solution possesses a concentration of hydrogen ions, $[\text{H}^+] < 10^{-7} \text{ M}$

Thus, acidic solution has $\text{pH} < 7$

Basic solution has $\text{pH} > 7$

Neutral solution has $\text{pH} = 7$

Then the ionic product of water, $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$

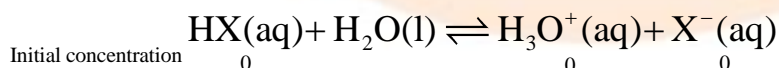
Taking negative logarithms on both sides of equation, we obtain

$$-\log K_w = -\log\{[\text{H}_3\text{O}^+][\text{OH}^-]\} = -\log 10^{-14}$$

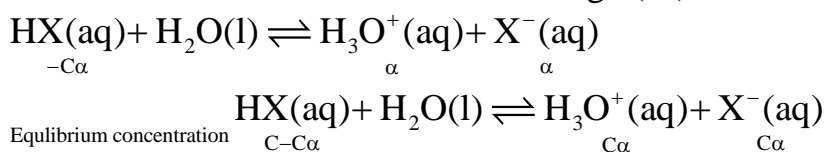
$$\text{p}K_w = \text{pH} + \text{pOH} = 14$$

Ionization constants of weak acids:

Consider a weak acid HX which is partially ionized in the aqueous solution. The equilibrium can be expressed by:



Let α be the extent of ionization change (M)



Here C is the initial concentration of the undissociated acid HX. Then the equilibrium constant for the above discussed acid dissociation equilibrium.

$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

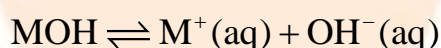
K_a is called **acid dissociation constant or ionization constant**.

the pH scale for the hydrogen ion concentration has been so useful that besides pK_w

$$pK_a = -\log(K_a)$$

Ionization constants of weak bases:

The ionization of base MOH can be represented by the following equation:



In a weak base there is partial ionization of MOH into M^+ and OH^- , the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called base ionization constant and is represented by K_b . It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

$$K_b = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

The pH scale for the hydrogen ion concentration has been extended to get:

$$pK_b = -\log(K_b)$$

Hydrolysis of salts:

The reactions between acids and bases in definite proportions forms salts which undergo ionize in water. The cations or anions formed on ionization of salts either exit as hydrated ions in aqueous solutions ions in aqueous solutions or interact with water to reform corresponding acids or bases depending upon the natural salts.

Consider three types of hydrolysis of the salts:

- Salts of weak acid and strong base. Eg: CH_3COONa

$$\text{pH} = 7 + \frac{1}{2}\text{pK}_a - \frac{1}{2}\log C$$

- Salts of strong acid and weak base. Eg: NH_4Cl

$$\text{pH} = 7 - \frac{1}{2}\text{pK}_b - \frac{1}{2}\log C$$

- Salts of weak acid and weak base. Eg: $\text{CH}_3\text{COONH}_4$

$$\text{pH} = 7 + \frac{1}{2}\text{pK}_a - \frac{1}{2}\text{pK}_b$$

Buffer solutions:

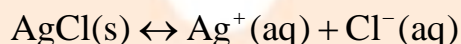
Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.

Solubility Equilibria of Sparingly Soluble Salts:

Each salt has its characteristic solubility which depends on temperature. We classify salts on the basis of their solubility in the following three categories

Category I	Soluble	Solubility $>0.1\text{M}$
Category II	Slightly soluble	$0.01\text{M} < \text{solubility} < 0.1\text{M}$
Category III	Sparingly soluble	Solubility $<0.01\text{M}$

For example,



Solubility product, $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = \text{I.P} = \text{Ionic product}$

If ionic product $< K_{sp}$, more salt can be dissolved through forward reaction.

If ionic product $> K_{sp}$, precipitation of solid salt takes place as backward reaction.

If ionic product $= K_{sp}$ no more salt can be dissolved. This stage is saturation point.