

IPUC: CHEMICAL EQUILIBRIUM & IONIC EQUILIBRIUM

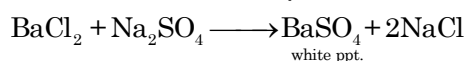
In a chemical reaction, reactants are consumed to form products. It has been observed that reactants are not consumed cent percent and the resulting mixture contains both reactants and products.

On the basis of the above observation, chemical reactions are broadly classified into two types,

1. Irreversible reactions
2. Reversible reactions

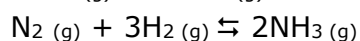
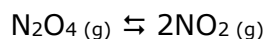
Irreversible Reactions

The reactions which move in forward direction only are called irreversible reactions. For example,



Reversible Reactions

The chemical reactions which take place in both directions under similar conditions are called reversible reactions. For example,



Rate of a reaction

Rate of a reaction is the change in the molar concentration of one of the reactants or products in unit time.

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

For the reaction

A + 2B \rightleftharpoons 3C + 4D, reaction rates are related as

$$-\frac{dA}{dt} = -\frac{1}{2} \frac{dB}{dt} = +\frac{1}{3} \frac{dC}{dt} = +\frac{1}{4} \frac{dD}{dt}$$

Law of mass action

At constant temperature the rate of chemical reaction is directly proportional to the product of the active masses of the reactants.

Active mass is the molar concentration (moles per dm^{-3}) or partial pressure expressed in Nm^{-2}

For a reaction **2A + 3B \rightleftharpoons C + D**

the rate of the reaction, **V = k [A]² [B]³**

Rate equation relates velocity of a reaction to its molar concentration.

The rate of reaction is continuously decreasing with time since the reactants are being consumed continuously.

Reversible reaction is one where the products of the reactants react back to give the reactants.

Chemical Equilibrium

Chemical equilibrium is a state in a reversible reaction when the rate of the forward reaction becomes equal to the reverse reaction.

In the equilibrium state the concentration of the reactants and product do not change with time

Chemical equilibrium is a dynamic equilibrium.

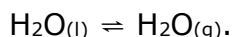
At equilibrium, rate of forward reaction = rate of backward reaction.

- Equilibrium may be classified as:
- Physical equilibrium
- Chemical equilibrium

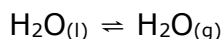
EQUILIBRIUM INVOLVING PHYSICAL CHANGES.

- **Equilibrium state :** When a reversible reaction is carried out in a closed vessel, then both reactions (forward and backward) occur simultaneously and before whole of the reactants are converted into products a state of equilibrium is established. In the state of equilibrium, the reaction appears to be stopped even though the reactants are still present. Therefore, reversible reactions do not proceed to completion.
- State of equilibrium represents a state in which the observable properties (such as pressure, concentration, temperature or intensity of color) of the system do not undergo any noticeable change under a particular set of conditions.

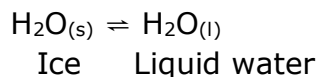
- **Physical equilibrium:** If the opposing processes involve only changes in physical state, then the equilibrium is called physical equilibrium, e.g., liquid water and steam are in physical equilibrium in a closed vessel,



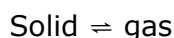
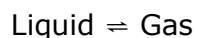
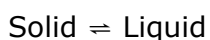
- **Dynamic equilibrium.** Equilibrium is dynamic in nature i.e. both the processes continue even after equilibrium has reached but their rates are equal. e.g., when water (liquid) is in equilibrium with water vapours, the rate of evaporation is equal to the rate of condensation.



- **Solid-liquid equilibrium:** When solid is in equilibrium with liquid in a perfectly insulated thermos flask, it is called solid-liquid equilibrium. e.g.,



- Types of equilibria which exist in the three states of matter are



- The temperature at which the solid-liquid equilibrium is reached for a pure substance under 1 atm pressure is called normal melting or freezing point of the substance.
- The liquid-gas equilibrium can be shown as



Rate evaporation = rate of condensation

- The temperature at which liquid-gas equilibrium is attained for a pure substance under 1 atm pressure is called the normal boiling point of the substance.
- Dissolution of solids in liquids: After the attainment of saturation point, the amount of undissolved solid solute and the concentration of solid solute in the solution remains constant.

At equilibrium, Rate of dissolution = rate of crystallisation

- Dissolution of gases in liquids: The solubility of a gas in liquid depends on the pressure. This dependence is explained on the basis of Henry's law, which states that, the mass of gas dissolved in the given mass of a solvent at a particular temperature is proportional to the pressure of the gas above the solvent.

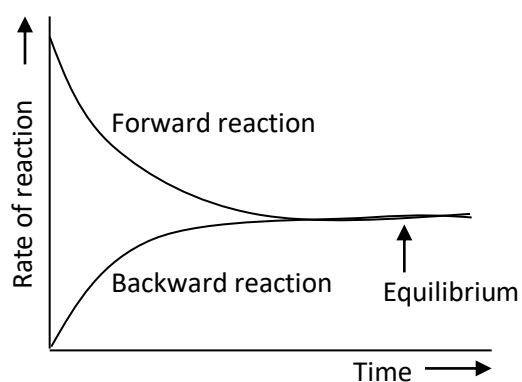
i.e., $m \propto p$ or $m = kp$.

- **Characteristics of physical equilibria**

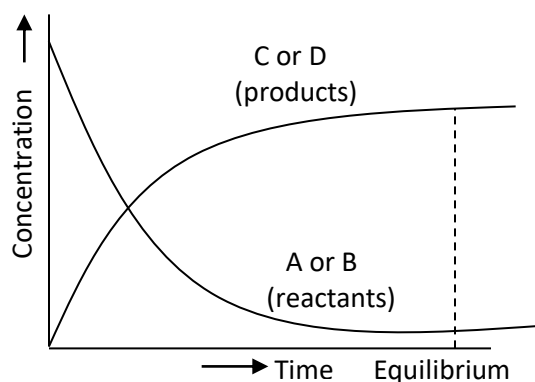
- The measurable properties of the system become constant at equilibrium.
- Equilibrium can be established only in case of closed systems.
- Equilibrium is always dynamic in nature.
- The magnitude of the constant value of the concentration related expression gives an indication of the extent to which the reaction proceeds before attaining equilibrium.

Equilibrium in chemical processes

- Reactions in which the products can react with one another under suitable conditions to give back the reactants are known as reversible reactions.
- Chemical reactions in which products do not react to give back the reactants are known as irreversible reactions.
- Chemical equilibrium is said to be attained when rate of forward and backward reaction of a reversible system are equal. This state is dynamic in nature as the opposing reactions continue to occur with same speed but appear to be static.



(a) Rate of forward reaction becomes equal to rate of backward reaction

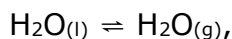


(b) Concentration of reactants and products become constant

Attainment of equilibrium in a reversible reaction

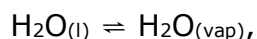
- **Characteristics of chemical equilibrium**

- It is dynamic in nature.
- The properties of system become constant at equilibrium and remain unchanged thereafter.
- Equilibrium can be attained only if the system is closed.
- The equilibrium can be approached from either directions.
- A catalyst does not alter the equilibrium point.
- Law of mass action states that the rate of a chemical reaction at any particular temperature is proportional to the product of molar concentrations of reactants with each concentration term being raised to the power equal to the number of molecules of the respective reactants taking part in the reaction. i.e., if $aA + bB \rightarrow cC$, then $\text{rate} = k[A]^a [B]^b$
- The masses of ice and water do not change and the temperature remain constant (273 K at 1 atm pressure).
- The equilibrium is not static as we could observe the individual molecules of ice and water are colliding with each other and some of them change into liquid, whereas some liquid molecule change into solid (ice) and the rates are equal at 273 K and 1 atm pressure.
- **Liquid-vapour equilibrium:** When there is an equilibrium between liquid and vapours, it is called liquid-vapour equilibrium. It is also dynamic in nature because at equilibrium



$H_2O_{(l)}$ changes into vapours whereas vapours convert into liquid but the rate of evaporation (i.e. conversion of liquid to vapours) and rate condensation (i.e. conversion of vapours to liquid) are equal.

- **Equilibrium vapour pressure:** it is the vapour pressure of water molecule, when water in liquid state is in equilibrium with water in vapour state



It is constant at equilibrium.

- **Boiling point :** It is the temperature at which the vapour pressure of a liquid becomes equal to atmospheric pressure e.g. boiling point of water at 1 atm is 373 K.
- **Normal freezing point or normal melting point:** It is the temperature at which the solid and liquid phases of a pure substance are in equilibrium at 1.0 atmospheric pressure i.e. freezing point of water is 273 K.

Equilibrium constant

- Equilibrium constant is the ratio between the products of molar concentrations of the products to that of the reactants with each concentration term raised to the power equal to the stoichiometric coefficient in the balanced chemical equation at a constant temperature.

i.e., if $A + B \rightleftharpoons C + D$

$$R_f = k_f [A] [B]; R_b = k_b [C] [D]$$

$$\text{At equilibrium, } k_f [A] [B] = k_b [C] [D] \Rightarrow K = \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} = Q$$

where K = equilibrium constant and

Q = concentration quotient.

- Equilibrium constant in gaseous systems can be expressed in terms of partial pressure (K_P) and concentration (K_C).

$$K_P = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \quad \because p = \frac{n}{V} RT \Rightarrow K_P = K_C (RT)^{\Delta n}$$

where, $\Delta n = \sum n_g (\text{product}) - \sum n_g (\text{reactant})$

Value of Δn	Relation between K_P and K_C
0	$K_P = K_C$
+ve	$K_P > K_C$
-ve	$K_P < K_C$

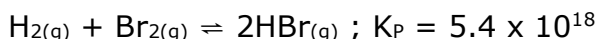
- Effect of temperature on equilibrium constant is

$$\log \left(\frac{K_2}{K_1} \right) = \frac{-\Delta H}{2.303 R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]; (T_2 > T_1)$$

- When $\Delta H = 0$, $K_2 = K_1$
- When $\Delta H = +ve$, $K_2 > K_1$
- When $\Delta H = -ve$, $K_2 < K_1$
- There are two types of chemical equilibrium
- Homogeneous equilibrium: The equilibrium reactions in which all the reactants and products are in the same phase are called homogeneous equilibrium reactions.
- Heterogeneous equilibrium: The equilibrium reactions in which the reactants and products are present in different phases are called heterogeneous equilibrium reactions.
- Characteristics of equilibrium constant
 - Value of equilibrium constant is independent of the original concentration of reactants.
 - The equilibrium constant has a definite value for every reaction at a particular temperature.
- For a reversible reaction, the equilibrium constant for the forward reaction is inverse of that of the backward reaction.
- The value of an equilibrium constant tells the extent to which a reaction proceeds in the forward or reverse direction.
- Its value is independent of the presence of catalyst.

Applications of Equilibrium Constant :

- (i) **Predicting the extent of reaction:** Higher the value of K more will be the extent of reaction which will take place. The magnitude of 'K' is very especially in reactions of industrial importance e.g.



The small value of K shows the reactants N₂ and O₂ will be predominant products.

- (ii) **Predicting the direction of reaction:** For this, we calculate reaction quotient 'Q'.

Reaction quotient : It is defined as ratio of product of molar concentration of products to product of molar concentration of reactants at any stage of reaction.

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

for the reaction $aA + bB \rightleftharpoons cC + dD$

Q_c is reaction quotient in terms of concentration.

If $Q_c > K_c$, the reaction will proceed in backward direction (reverse reaction).

If $Q_c = K_c$, the reaction will be in equilibrium.

If $Q_c < K_c$, the reaction will proceed in forward direction

$$Q_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Q_p is reaction quotient in terms of partial pressure of reactants and products.

- It helps to predict the extent of reaction on the basis of its magnitude.
Min. $\frac{\text{Value of } K_c}{10^{-3} \ 1 \ 10^3} \rightarrow \text{very large}$
Slow $\xrightarrow{\text{Rate of reaction}}$ Almost complete
- Relation between K, Q, and ΔG
 $\Delta G = \Delta G^0 + RT \ln Q$
Since at equilibrium, $\Delta G = 0$ and $Q = K_c$.
 $\Rightarrow \Delta G^0 = -RT \ln K_c = -2.303 RT \log K_c$ or $K = e^{-\Delta G^0 / RT}$
- When $\Delta G^0 < 0$, then $K > 1$. The reaction is spontaneous and proceeds in forward direction.
- When $\Delta G^0 > 0$, then $K < 1$. The reaction is non-spontaneous and proceeds in backward direction.
 $\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K$
 - For endothermic reaction ($\Delta H = +ve$), $K \ll 1$
 - For exothermic reaction ($\Delta H = -ve$), $K \gg 1$.

The value of the equilibrium constant does not depend on the initial concentration, pressure or volume of the container.

Under the same conditions of temperature and pressure the same state of equilibrium is attained from whichever side the reaction is started.

Variation of K with Temperature (van't Hoff Equation)

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

where K_2 and K_1 are equilibrium constants at temperatures T_2 and T_1 respectively, R = gas constant, ΔH = enthalpy change

Increase of temperature favours endothermic reaction.

Let K_1 be the equilibrium constant for the reaction **A + 2B \rightleftharpoons 4C**

For the reverse reaction, **4C \rightleftharpoons A + 2B**: $K_2 = \frac{1}{K_1}$.

For the reaction **2A + 4B \rightleftharpoons 8C**, which is obtained by doubling the first equation, equilibrium constant K_3 is $(K_1)^2$

For the reaction $\frac{1}{2}A + B \rightleftharpoons 2C$, which is obtained by dividing the first equation by 2, the equilibrium constant $K_4 = \sqrt{K_1}$

Higher value of K indicates that the equilibrium lies more to the right.

- Le-Chatelier's principle states that any change in the factors that determine the equilibrium conditions of a system will shift the equilibrium in a direction to reduce the effect of the change.
- Factors affecting equilibrium

	Factor	Nature of change of factor	Effect on equilibrium towards
(i)	Temperature	Increase	Endothermic
		Decrease	exothermic
(ii)	Pressure	Increase	Lower n
		Decrease	Higher n
(iii)	Concentration	Increase	Consumption of that species
		Decrease	Production of that species
(iv)	Addition of an inert gas	At const. P	Higher n
		AT const. V	No effect
(v)	Addition of catalyst	-	No effect
		-	No effect

When forward reaction is favoured, the equilibrium shifts to the right and more product is formed.

For the reaction **N₂ + O₂ \rightleftharpoons 2NO $\Delta H = +Q$ kJ**

since Δn is zero, $K_p = K_c$ Pressure has no effect

forward reaction is endothermic. Hence, higher temperature favours the formation of nitric oxide



For the synthesis of ammonia forward reaction is exothermic. Hence, lower temperature favours the formation of ammonia.

The reaction involves in the reduction in the number of moles.

So increase in pressure also favours the formation of more of ammonia



For the dissociation of phosphorous pentachloride, forward reaction is endothermic. Hence, higher temperature favours the dissociation of phosphorous pentachloride.

The reaction involves in the increase in the number of moles.

So decrease in pressure also favours the dissociation of phosphorous pentachloride.

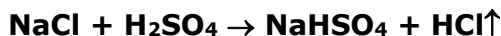
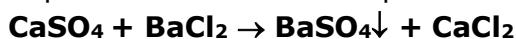


For the synthesis of sulphur trioxide forward reaction is exothermic. Hence, lower temperature favours the formation of sulphur trioxide.

The reaction involves in the reduction in the number of moles.

So increase in pressure also favours the formation of more of sulphur trioxide

If during a reaction a precipitate is formed or a gas is evolved, then such reaction go to completion since one of the product is lost from the system.



Ionic equilibrium

- When a substance (ionic compound) is dissolved in water, it gets split up into its constituent ions. This process is known as ionization.
- Those substances which completely ionise in aqueous solutions are called strong electrolytes, e.g., NaCl, KNO₃, etc.
- Those substances which ionise only to a limited extent in aqueous solutions are called weak electrolytes, e.g. CH₃COOH, NH₄OH, etc.
- Ionic equilibrium may be defined as the equilibrium which is established between the un-ionised molecules and ions in solution of weak electrolytes.

$$\text{Degree of dissociation, } \alpha = \frac{\text{No. of moles dissociated}}{\text{Total no. of moles}}$$

- Ostwald's dilution law is applicable to only weak electrolytes and it gives the relation between degree of dissociation (α) and concentration of the electrolyte (C).

$$\alpha = \sqrt{\frac{K}{C}} = \sqrt{K \times V}$$

Concepts of acids and bases

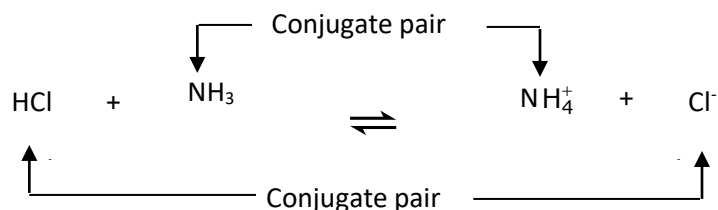
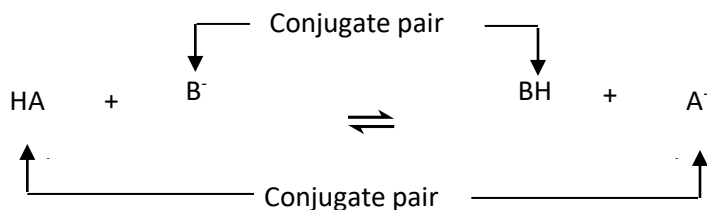
- According to **Arrhenius concept**, an acid is a proton donor in aqueous solution and a base is hydroxyl ion donor in aqueous solution, e.g. HCl, HNO₃, etc. are acids and NH₄OH, Ca(OH)₂, etc. are bases.
- According to the **Bronsted-Lowry concept**, an acid is a proton donor and a base is a proton acceptor, e.g. HCl, NH₄⁺, etc. are acids while NH₃, Cl⁻, etc. are bases.
- All Arrhenius acids are Bronsted acids but all Arrhenius bases are not Bronsted bases.

- The pairs of acids and bases which are formed from each other by the gain or loss of a proton are conjugate acid-base pairs.



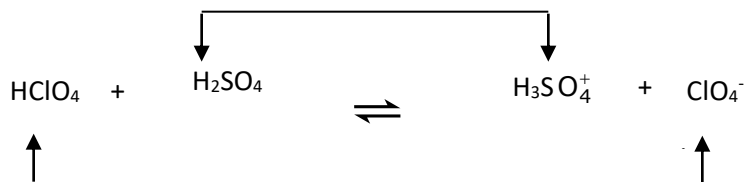
- Conjugate acid-base pair: In case of acid-base reaction, the reverse reaction is also an acid-base reaction. Every acid forms a conjugate base by the loss of a proton while every base forms a conjugate acid by the gain of a proton (H^+).

For example,

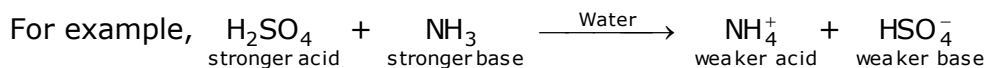


- A conjugate pair of acid and base differ by a proton only.
Acid = Base + H^+
- If two acids (with respect to water) are mixed together then the weaker acid will act as a base with respect to the stronger acid.

For example,



- Acid base reactions always proceed in the direction from the stronger to weaker acid-base combination.



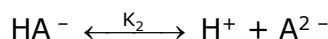
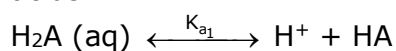
- Strong acids have weak conjugate bases and weak acids have strong conjugate bases.
- Strong bases have weak conjugate acids while weak bases have strong conjugate acids.
- According to **Lewis concept**, an acid is a molecule or ion which can accept an electron pair while a base is a molecule or ion which can donate an electron pair, e.g. NH_3 , ROH , etc. are bases while AlCl_3 , BF_3 , etc. are acids.
- Strength of acids and bases can be measured in terms of the number of H^+ and OH^- ions produced by them in aqueous solution respectively.

$$\therefore K_a \propto [\text{H}^+] \text{ and } K_b \propto [\text{OH}^-]$$

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \sqrt{\frac{K_{aI}}{K_{aII}}}$$

$$\frac{\text{Strength of base I}}{\text{Strength of base II}} = \sqrt{\frac{K_{bI}}{K_{bII}}}$$

- Acids having more than one ionisable proton per molecule are known as polybasic acids.



- The ionization constants K_{a1} and K_{a2} are given as

$$K_{a1} = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]}; K_{a2} = \frac{[\text{H}^+][\text{A}^{2-}]}{[\text{HA}^-]}$$

It has been found that $K_{a1} > K_{a2}$

- Bases which can ionise in more than one step are polyacidic bases. For them, $K_{b1} > K_{b2} > \dots$
- $\text{p}K_a = -\log K_a$, thus larger the value of K_a and lower the value of $\text{p}K_a$, stronger is the acid.
- $\text{p}K_b = -\log K_b$, thus larger the value of K_b and lower the value of $\text{p}K_b$, stronger is the base.

Ionisation of water and pH scale

- Ionic product of water, $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$ (at 298 K)
- $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}$ (at 298 K)
- The value of K_w increases with increase in temperature.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [\text{H}^+] = \log \frac{1}{[\text{H}^+]}$$

$$\text{pOH} = -\log[\text{OH}^-] = \log \frac{1}{[\text{OH}^-]}$$

pH scale

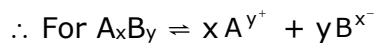
- For neutral solution, $\text{pH} = \text{pOH} = 7$.
- For acidic solution, $\text{pH} < 7$ and $\text{pOH} > 7$.
- For basic solution, $\text{pH} > 7$ and $\text{pOH} < 7$.
- Relationship between pH and pOH
 $\text{pH} + \text{pOH} = \text{p}K_w = 14$.
- $\text{p}K_a + \text{p}K_b = \text{p}K_w$.
- Common ion effect: The ionisation of an acid gives hydrogen ion and the corresponding anion, if hydrogen ions are added to the solution from any other source, they will combine with the anion in the solution and form unionized acid. AS a result, the degree of ionisation of the acid will be reduced. This is known as the common ion effect.

Hydrolysis of salts

Salt	Hydrolysis	Resulting solution	Hydrolysis Constant (K_h)	Degree of Hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$
Strong acid and Weak base	Cationic	Acidic	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$
Weak acid and Weak base	Anionic and Cationic	Neutral (almost)	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$

Solubility and solubility product

- A solution which remains in contact with undissolved solute is said to be saturated.
- Solubility product (K_{sp}) is the product of concentration of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature in a saturated solution.



$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

- For precipitation of an electrolyte, the ionic product of the electrolyte must exceed its solubility product.

Buffer solutions

- The solution which resists a change in the hydrogen ion concentration on the addition of small amount of acid or base is a buffer.
- Buffer solutions are of two types:
- Acidic buffer: It contains equimolar quantities of a weak acid and its salts with a strong base, e.g., $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$.
- Basic buffer: It contains equimolar quantities of weak base and its salt with a strong acid. e.g., $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.
- Henderson-Hasselbalch equation for the pH of any buffer solution is:



$$\text{pH} = \text{p}K_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$

- For acidic buffer, $\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

- For basic buffer, $\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

Buffer capacity

- Number of moles of acid or base added in one litre of solution as to change the pH by unity.

$$\text{Buffer capacity } (\phi) = \frac{\text{No. of moles of acid or base}}{\text{Change in pH}}$$

$$\phi = \frac{\partial b}{\partial \text{pH}}.$$

- Buffer capacity is maximum
- when $[\text{salt}] = [\text{acid}]$
i.e., $\text{pH} = \text{pK}_a$ for acidic buffer
- When $[\text{salt}] = [\text{base}]$, i.e., $\text{pOH} = \text{pK}_b$ for basic buffer.