B.Sc. Semester – I
Subject: - CHE - 101: Ionic Equilibrium
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➢ Contents:

- ✓ Degree of ionization
- ✓ Ostwald dilution law and its limitations
- ✓ pH scale
    - ▪ Definition of pH and importance of pH scale,
    - ▪ Relation between pH and concentration of H^+ in solution,
    - ▪ pH range of acidic, basic solution,
    - ▪ Introduction about pOH, relation between pH and pOH, ionic product of water (K_w),
- ✓ Hydrolysis of salts (from weak acid [HA] and strong base [BOH]) including derivation of

$$K_h = \frac{[HA][OH^-]}{[A^-]}, \qquad K_h = \frac{K_w}{K_a}, \qquad h = \sqrt{\frac{K_h}{C}}, \qquad pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

- ✓ Hydrolysis of salts (from weak base [BOH] and strong acid [HA]) including derivation of

$$K_h = \frac{[BOH][H^+]}{[B^+]}, \qquad K_h = \frac{K_w}{K_b}, \qquad h = \sqrt{\frac{K_h}{C}}, \qquad pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

- ✓ Hydrolysis of salts (from weak acid [HA] and weak base [BOH]) including derivation of

$$K_h = \frac{[HA][BOH]}{[A^-][B^+]}, \qquad K_h = \frac{K_w}{K_a \times K_b}, \qquad h = \sqrt{K_h}, \qquad pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$

- ✓ Buffer solution
    - ▪ Properties of buffer solutions,
    - ▪ Buffer capacity and buffer limit of buffer solution,
    - ▪ pH of buffer formed from weak acid and its salt including derivation of Henderson-Hasselbach equation,
    - ▪ Action of buffer solutions in adjustment of pH during addition of acid or Base,
    - ▪ Buffer standards,
    - ▪ Importance of buffer solutions,
- ✓ Numerical

In this unit we will discuss some important theories of acids and bases. Before going further into lets first revise the concept of electrolytes that will provide the base to construct the unit well ahead.

Water soluble substances are separated by electrolytes or non-electrolytes.

Definition of electrolytes: Substances which dissociate into ions in aqueous solutions are called electrolytes.

Electrolytes	Non Electrolytes
➢ Electrolytes are electrovalent substances that form ions in solutions which conduct an electric current.	➢ Nonelectrolytes are covalent substances which form neutral molecules in solution.
➢ Their solutions conduct an electric current.	➢ Their solutions do not conduct an electric current.
➢ E.g. NaCl, $CuSO_4$ & KNO_3.	➢ E.g. Sugar, Alcohol & Glycerol.

- ➢ An Electrolyte undergoes chemical decomposition as a result of passage of electric current through its solutions. The process of decomposition of an electrolyte by passing electric current through its solution is known as electrolysis.
- ➢ The process of electrolysis is carried out in an apparatus is known as the electrochemical cell. The cell contains water-solution of an electrolyte in which two metallic rods (electrodes) are dipped.
- ➢ These rods are connected to the two terminals of a battery (source of electricity). The electrode connected to the positive terminals of the battery attracts the negative ions (anions) and is known as anode, where as other electrode connected to the negative end of the battery attracts the positive ions (cations) is called cathode.

- ✓ **Types of Electrolytes**
  - ➢ Electrolytes are classified as Weak Electrolytes, Strong Electrolytes and Non Electrolytes on the basis of their relative conductance.
- ✓ **Non Electrolytes**
  - These substances are non-conducting that possessing molecular type of crystalline structure.
  - E.g. Ethers and Hydrocarbon
- ✓ **Weak Electrolytes**
  - Electrolytes that do not dissociate or ionize completely into the aqueous solution is called strong electrolyte. Mostly polar covalent compounds weakly ionize in water.
  - These substances are low conducting in dissolved or molten state and possess polar compounds.
  - Weak electrolytes contain both ions as well as undissociated molecules in its aqueous solution and equilibrium exists between them, so the equation is represented with double headed arrows.
  - E.g. RCOOH, H_2CO_3. Some of them have ionic to molecular structure, Halides of Pb^{+2}, Hg^{+2}, Cu^{+2}
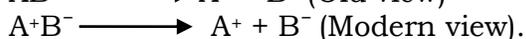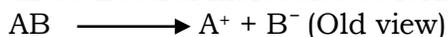
- ✓ **Strong Electrolytes**
  - Electrolytes that dissociate or ionize completely into the aqueous solution is called strong electrolyte.
  - These substances are ionic and polar or Hydrogen bonded molecular structure.
  - E.g. Halides, Hydroxides, acetates of Group IA, IIA elements, Nitrates, Sulphates and chlorates of monovalent and Divalent cations HCl, HBr, HI, H_2SO_4, $HClO_4$, HNO_3.
  - Thus if we have 0.1 mole KCl dissolved in water it contains 0.1 mole K^+ ions and 0.1 mole Cl^- ions. Since there are very negligible unionized molecules at equilibrium the equations for ionization reaction is written with single arrow directed towards right.

- ▶ **Dissociation or Ionization**
- On the basis of behavior of electrolytes in solution such as current carrying capacity, Electrolysis, instantaneous formation of products on mixing solutions of electrolytes, hydrolysis and abnormal behavior of electrolytes in showing their higher values of colligative properties was satisfactory.
  - Svante Arrhenius studied the conduction of current through water suctions of electrolytes. He came to believe that the conductivity of solutions was due to the presence of ions.
  - In 1884, Arrhenius put forward his theory of ionization. According to this theory of ionization…
    - [1] When dissolved in water, neutral electrolyte molecules are split up into two types of charged particles. These particles are known as ions and this process is known as ionization. The positive charge particles are called cations and those having the negative charge were called anions.
      In its modern form, the theory assumes that the ions are already present in the solid electrolyte and these are held together by electrostatic force. When placed in water, these neutral molecules to form separate anions and cations.
      AB $\longrightarrow$ $A^+ + B^-$ (Old view)
      $A^+B^- \longrightarrow$ $A^+ + B^-$ (Modern view).
      Therefore, this this theory is known as theory of electrolytic dissociations.
    - [2] The ions present in solution constantly reunite to form neutral molecules. Thus there is a state of equilibrium between the undissociated molecules and the ions.
      AB $\rightleftharpoons$ $A^+ + B^-$
      Applying the law of Mass and action to the ionic equilibrium we have….

$$K = \frac{[A^+][B^-]}{[AB]}$$

Where K is called Dissociation constant.

- [3] The charged ions are free to move through the solution to the oppositely charged electrode. This movement of the ions constitutes the electric current through

electrolytes. This explains the conductivity of electrolytes as well as phenomenon of electrolysis.

[4] The electrical conductivity of an electrolytes solution depends on the number of ions present in solution. Thus the dissociation of an electrolyte determines whether it is a strong electrolyte or weak electrolyte.

✓ **Dissociation Constants or Ionization Constant of Weak Acids**

Let us consider dissociation of weak monobasic acid HA. The equation for equilibrium is
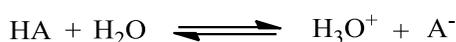
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Applying, law of equilibrium constant to above equation we have:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]}$$

$$K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Because only a very small fraction of water molecules are ionized, the concentration of water, [H₂O], remains virtually unchanged.

So $K[H_2O] = K_a$ = **ionization constant of weak acid**

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Concentration of the acid almost remains unaltered as a smaller portion of it ionize, so [HA] remains constant symbolized by C₀ (initial concentration of acid).

Substituting [HA] = C₀.

$$K_a = \frac{[H_3O^+][A^-]}{C_o}$$

Now during dissociation there will be equal number of positive and negative ions dissociate.

Thus, $[H_3O^+] = [A^-]$

$$K_a = \frac{[H_3O^+][H_3O^+]}{C_o}$$

$$\therefore [H_3O^+]^2 = K_a C_o$$

$$\therefore [H_3O^+] = \sqrt{K_a C_o} - - - - - - - - - -(A)$$

This is the required equation for finding concentration of H_3O^+ ions in the solution of weak acid.

✓ **Ionization Constants of Weak Bases**

Let us consider dissociation of weak base B. The equation for equilibrium is

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Applying, law of equilibrium constant to above equation we have:

$$K = \frac{[BH^+][OH^-]}{[H_2O][B]}$$

$$K[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

Because only a very small fraction of water molecules are ionized, the concentration of water, [H₂O], remains virtually unchanged.

So $K[H_2O] = K_b$ = **ionization constant of weak base**

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Concentration of the base almost remains unaltered as a smaller portion of it ionize, so [B] remains constant symbolized by C₀ (initial concentration of base).

Substituting [B] = C₀.

$$K_b = \frac{[BH^+][OH^-]}{C_o}$$

Now during dissociation there will be equal number of positive and negative ions dissociate.

Thus, $[BH^+] = [OH^-]$

$$K_b = \frac{[OH^-][OH^-]}{C_o}$$

$$\therefore [OH^-]^2 = K_b C_o$$

$$\therefore [OH^-] = \sqrt{K_b C_o} \; -------- (B)$$

This is the required equation for finding concentration of OH^- ions in the solution of weak base.

From equations (A) & (B), it is clear that $[H_3O^+] \propto K_a$ and $[OH^-] \propto K_b$, concluding that with higher the value of K_a & K_b more will be the concentration of $[H_3O^+]$&$[OH^-]$ so stronger will the acid and base respectively.
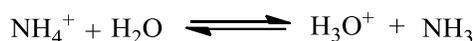
✓ **Relation between K_a and K_b**

K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be presumed.

Considering the example of NH_4^+ and NH_3,

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Now, get multiply both the equilibrium coefficient,

$$K_a \, X \, K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} X \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$= [H_3O^+][OH^-] = K_w$$

$$\therefore \mathbf{K_a \, X \, K_b = K_w}$$

Where, K_a represents the strength of NH_4^+ as an acid and K_b represents the strength of NH_3 as a base.

This can be prove that, equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions.

▶ **Degree of Dissociation or Ionization (α)**

Degree of dissociation is the amount of solute dissociated into ions or radicals per mole or fraction of the total number of molecules which are present as ions in the solution. In case of very strong acids and bases, degree of dissociation will be close to 1 while weak acids or bases will have degree of dissociation less than 1. It is denoted by α.

$$\text{Degree of Dissociation } (\alpha) = \frac{\text{Number of molecules present as ions}}{\text{Total number of molecules dissolved}}$$

✓ **Factors affecting the degree of dissociation:** The extent of degree of dissociation depends upon the following factors.
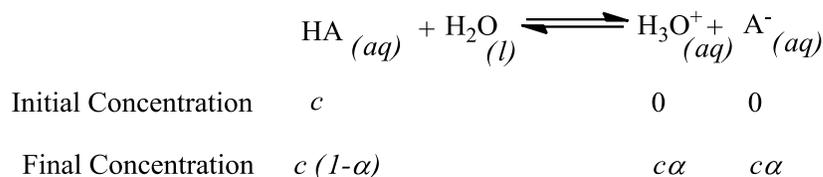
- **Nature of the electrolytes:** Solution of different electrolytes (strong or weak) of some concentration at constant temperature ionize to different extent. Hence, at normal dilution, value of α is nearly one for strong electrolytes, while it is very less than one for weak electrolytes. However, conductance depends on the number of ions per unit volume, speed and charge on the ion.

- **Nature of the solvent:** Dielectric constant of a solvent is a measure of its tendency to weaken the forces of attraction between oppositely charged ions of the electrolytes. Higher the dielectric constant of a solvent more is its ionizing power. Water is the most powerful ionizing solvent as its dielectric constant is highest (82).

- **Concentration:** Degree of ionization is inversely proportional to the concentration. It increase with dilution and at infinite dilution it approaches unity and dissociation is said to be complete.

- **Temperature:** The higher the temperature, the greater is the ionization.

- **Presence of other ions:** The degree of ionization of an electrolyte decrease in presence of strong electrolyte having a common ion.

* Strong electrolyte like HCl, NaOH, NaCl are almost fully dissociated so that the whole of the electrolyte exists in the form of ionic species.

* In case of weak electrolyte, there exists equilibrium between the free ions and the undissociated molecules.

➢ Degree of dissociation of weak acid

Degree of dissociation of weak acid and concentration of H_3O^+ ions (i.e H^+ ions) present in solution can be calculated using its ionization constant K_a.

Consider a weak acid **HA**, **c** -- initial concentration and **α**---- degree of dissociation.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Initial Concentration	c	0	0
Final Concentration	$c(1-\alpha)$	$c\alpha$	$c\alpha$

So we have $[HA] = c(1-\alpha), [A^-] = c\alpha, [H_3O^+] = c\alpha$

Substitution these values in equation

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)}$$

When **α** is small for weak acids, considering $(1-\alpha) \approx 1$

$$K_a = \frac{c\alpha \cdot c\alpha}{c} = c\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{c}}$$

Above is the required equation for finding. We can also find pH from, $[H_3O^+] = c\alpha$

$$\therefore [H_3O^+] = c\sqrt{\frac{K_a}{c}} = \sqrt{K_a \cdot c}$$

We know that pH = –log [H_3O^+], so applying –log to above equation.

$$-\log[H^+] = -\log_{10}\sqrt{K_a \cdot c}$$
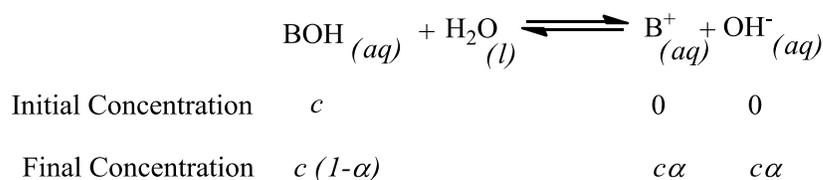
$$-\log[H^+] = \frac{1}{2}[-\log_{10} K_a + (-\log_{10} c)]$$

$$pH = \frac{1}{2}[pK_a - \log_{10} c]$$

➢ Degree of dissociation of weak base

Degree of dissociation of weak base and concentration of OH^- ions present in solution can be calculated using its ionization constant K_b.

Consider a weak acid **BOH**, **c** -- initial concentration and **α**---- degree of dissociation.

$$BOH_{(aq)} + H_2O_{(l)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$$

Initial Concentration	c	0	0
Final Concentration	$c(1-\alpha)$	$c\alpha$	$c\alpha$

So we have $[BOH] = c(1-\alpha), [OH^-] = c\alpha, [B^+] = c\alpha$

Substitution these values in equation

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$K_b = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)}$$

When **α** is small for weak acids, considering $(1-\alpha) \approx 1$

$$K_b = \frac{c\alpha \cdot c\alpha}{c} = c\alpha^2$$

$$\alpha = \sqrt{\frac{K_b}{c}}$$

Above is the required equation for finding. We can also find pH from, $[OH^-] = c\alpha$

$$\therefore [OH^-] = c\sqrt{\frac{K_b}{c}} = \sqrt{K_b \cdot c}$$

We know that pOH = –log $[OH^-]$, so applying –log to above equation.

$$-\log[OH^-] = -\log_{10}\sqrt{K_b \cdot c}$$

$$-\log[OH^-] = \frac{1}{2}[-\log_{10} K_b + (-\log_{10} c)]$$

$$pOH = \frac{1}{2}[pK_b - \log_{10} c]$$

▶ **Ostwald's Dilution Law and its limitation**

Ostwald's dilution law is a relationship between the dissociation constant and the degree of dissociation of a weak electrolyte (acids, bases).

In case of weak electrolytes (AB), the concentration of ion is very less and there exists an equilibrium between the ions and unionized molecules in solution.

	AB	⇌	A$^+$	+	B$^-$	in a v liter of solution
Initial mol	1		0		0	
Mole at equilibrium	1 - α		α		α	
Conc. at equilbrium	$\frac{1-\alpha}{V}$		$\frac{\alpha}{V}$		$\frac{\alpha}{V}$	in mole dm^{-3}

So we have, $[AB] = \frac{(1-\alpha)}{V}, [B^-] = \frac{\alpha}{V}, [A^+] = \frac{\alpha}{V}$

$$K = \frac{[A^+][B^-]}{[AB]}$$

$$K = \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{1-\alpha}{V}}$$

$$K = \frac{\alpha^2}{(1-\alpha)V} \quad --------(1)$$

Thus this equation represents the variation of degree of dissociation with dilution. In case of weak electrolytes, the value of α is very small as compared to unity and hence may be neglected in the denominator. Thus,

$$K = \frac{\alpha^2}{V} \quad \text{or} \quad \alpha = \sqrt{K \cdot V} \quad \text{or} \quad \alpha = \sqrt{\frac{K}{C}} \quad (\because C = \frac{1}{V})$$

So, at a given concentration of a weak electrolyte the degree of dissociation α is directly proportional to the square root of dilution and inversely proportional to the square roots of its concentration.

If you are increasing the volume decrease the concentration so α value nearest to 1. So infinite dilution weak electrolytes works as strong electrolytes it's called Oswald's dilution low.

✓ **Limitation of Oswald's dilution law**

[i] The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula λ/λ_∞. The value of 'α' determined at various dilutions of an electrolyte when substituted in Eq. (1) gives a constant value of K only in the case of weak electrolytes like CH_3COOH, NH_4OH, etc. the cause of failure of Ostwald's dilution law in the case of strong electrolytes is due to the following factors"

[ii] The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilutions and λ/λ_∞ does not give accurate value of 'α'.

[iii] When concentration of the ions is very high, the presence of charges on the ions appreciably effects the equilibrium. Hence, law of mass action in its simple form cannot be strictly applied in the case of strong electrolytes.

► **pH Scale**

If we express the concentration of hydronium ion $[H_3O^+]$ in molarity then values like 10^{-12} and 10^{-2} are possible. It is difficult to express these values on simple graph paper. Hence, scientist Sorensen found scale which is called pH scale. pH is the abbreviation of the pondus hydrogenii (potential of hydrogen). It is a numeric scale used to specify the acidity or basicity of an aqueous solution.

✓ **Definition of pH:** The pH of solution is the negative logarithm of its hydrogen ion (H^+) concentration. or
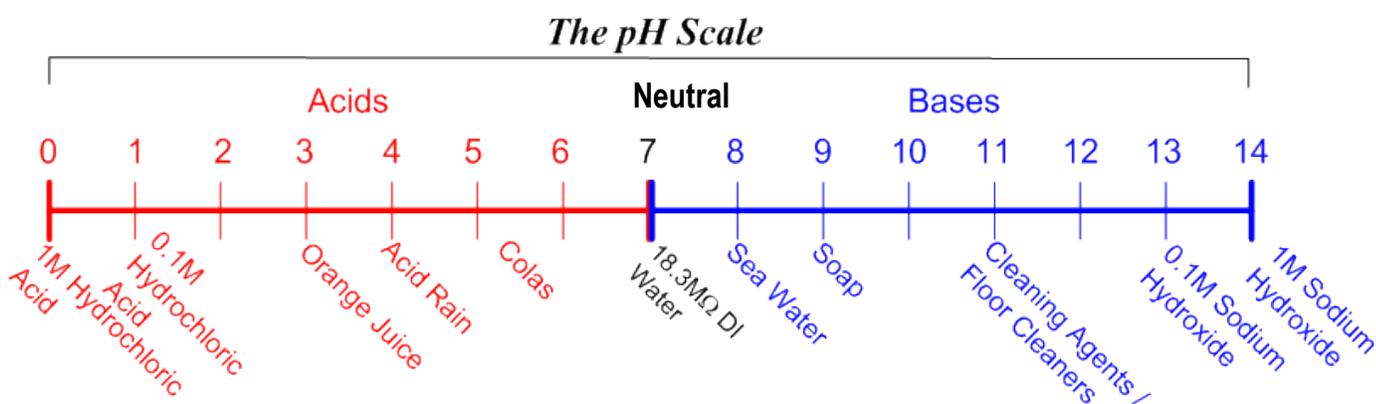The pH of a solution is logarithm of the reciprocal of hydrogen ion (H^+) concentration.

$$pH = \log \frac{1}{[H^+]}$$
$$\therefore pH = -\log [H^+]$$

In neutral solution pure water $[H^+] = [OH^-] = 1 \times 10^{-7}$ ∴ pH = 7

In acidic solution: $[H^+] > 10^{-7}$ ∴ pH < 7

In alkaline solution: $[H^+] < 10^{-7}$ ∴ pH > 7

The pH scale can be represented as following:

- Since K_w (ionic product of water) changes with temperature, the pH value also changes with temperature.
- Since dissociation of water is an endothermic process, pH of a solution decreases on heating. Hence, pH of boiling water is 6.5625, although it is neutral.
- pH of solutions of acids, bases and salts of same concentration varies from one another. For examples, pH for 0.1 n solutions of HCl, H_2SO_4, CH_3COOH, NH_3, NaOH and Na_2CO_3 at 25 °C are 1.0, 1.2, 2.9, 11.3, 13.0 and 8.4 respectively.
- Negative pH value is not possible.
- The pH of a solution can be determined by universal indicator or by EMF method using pH meters.

✓ **Importance of pH scale**

- Solutions are considered acidic, neutral or basic according to their pH value. Below 4 is acidic, 7 is perfectly neutral, with distilled water being an example, above 11 is basic.
- Human blood has a pH of 7.3 to 7.5, which is slightly on the basic side of the scale. If blood pH drops below 7.0 or goes higher than 7.8 the body can no longer function and dies.
- Acidic soils must often be treated with lime, which is an alkaline substance, to neutralize the pH before planting. The pH will determine what type of plant will grow and thrive in the soil.
- In a marine environment, including an indoor aquarium, a basic pH of 8.1 to 8.4 makes it easier for fish to maintain their own cleanliness and resist illness. It has a slight antiseptic effect.
- pH describes the balance between hydrogen ions and hydroxide ions. Ions are charged atoms, meaning they have either a negative or positive charge as a result of losing or gaining an electron. Hydrogen ions carry a positive charge while hydroxide atoms carry a negative charge. In a neutral solution the two are evenly balanced.

▶ **pOH Scale**

pOH is the abbreviation of the potential of hydroxyl ion). It is a numeric scale used to specify the acidity or basicity of an aqueous solution.

- **Definition of pOH:** The pOH of solution is the negative logarithm of its hydroxyl ion (OH⁻) concentration. or

  The pOH of a solution is logarithm of the reciprocal of hydroxyl ion (OH⁻) concentration.

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

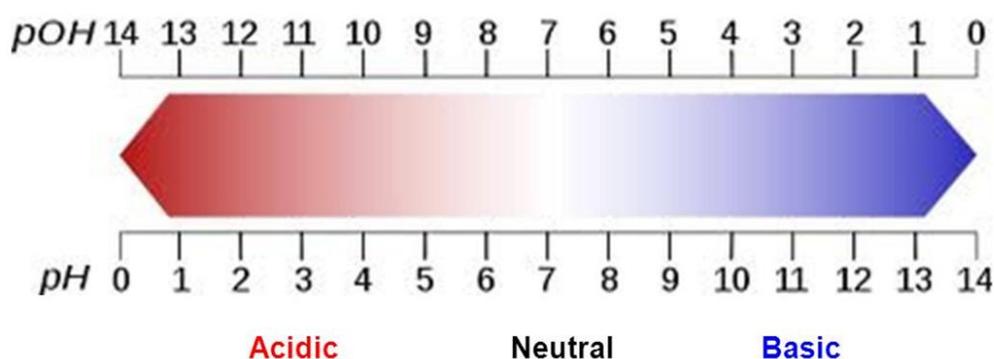$$\therefore pOH = -\log [OH^-]$$

In neutral solution pure water $[H^+] = [OH^-] = 1 \times 10^{-7}$ ∴ pH = 7

In alkaline solution: $[OH^-] > 10^{-7}$ ∴ pOH < 7

In acidic solution: $[OH^-] < 10^{-7}$ ∴ pOH > 7

The pOH scale with pH scale can be represented as following:

> **Ionic product of water**

Water possesses unique property as its ability to act either as an acid or as a base. In reactions with acids such as HCl it functions as base (acceptance of H^+ ions) while and in reactions with bases such as NH_3, it functions as an acid (donation of H^+ ions). Water being very weak electrolyte it does undergo ionization to a small extent protons (H^+) and hydroxyl ions (OH^-).
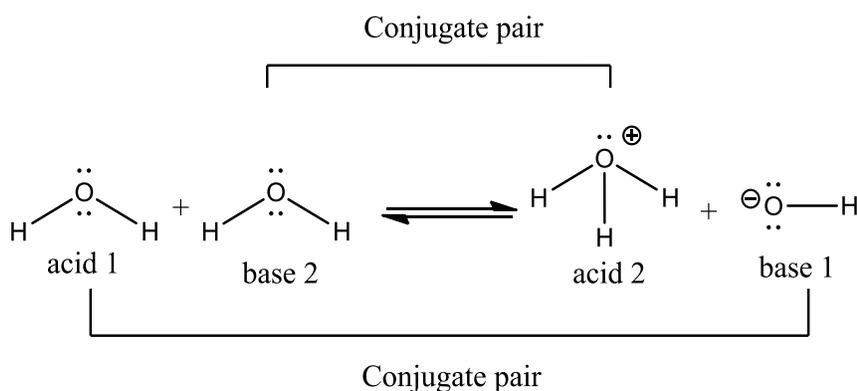
The reaction is sometimes called the auto-ionization of water. To describe the acid-base properties of water in the Brønsted framework, we express its auto-ionization as follows.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The acid-base conjugate pairs are (1) H_2O (acid) and OH^- (base) and (2) H_3O^+ (acid) and H_2O (base). In general representation we symbolize H_3O^+ as H^+.

Applying, law of equilibrium constant to above equation.

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Because only a very small fraction of water molecules are ionized, the concentration of water, $[H_2O]$, remains virtually unchanged. So we have:

$$K [H_2O] = [H^+] [OH^-]$$

$$\therefore K_w = [H^+] [OH^-]$$

Where, K_w is called the ionic product of water, which is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature. In pure water at 25°C (298 K), the concentrations of H^+ and OH^- ions are equal and found to be 1.0 x 10^{-7} M (moles/liter).

$$K_w = [H^+][OH^-] = (1.0 \times 10^{-7}) \times (1.0 \times 10^{-7}) = 1.0 \times 10^{-14} \, M^2$$

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

(a) Acidic: $[H^+] > [OH^-]$

(b) Basic: $[H^+] < [OH^-]$

(c) Neutral: $[H^+] = [OH^-]$.

In practice, we can change the concentration of either H^+ or OH^- ions in solution, but we cannot vary both of them independently.

If we adjust the solution so that $[H^+] = 1.0 \times 10^{-8}$M,

Then $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-8}} = 1.0 \times 10^{-6}$ M.

Thus $[H^+] < [OH^-]$ solution is basic.

➢ **Relation Between pH and pOH**

We know the $\qquad$ $K_w = [H^+] \times [OH^-]$

$$\therefore [H^+][OH^-] = K_w$$

In water $K_w = 1.0 \times 10^{-14}$ (at 25 °C)

$$\therefore [H^+][OH^-] = 1.0 \times 10^{-14}$$

Applying –log for the above equation

$$-\log[H^+] + (-\log[OH^-]) = -\log 1.0 \times 10^{-14}$$

$$now, -\log[H^+] = pH \text{ and } -\log[OH^-] = pOH$$

$$\therefore pH + pOH = 14$$

❖ **Hydrolysis of salt and the pH of their solution**

Pure water being weak electrolyte and dissociate to very small extent forming $[H^+]$ (i.e. $[H_3O^+]$) and $[OH^-]$ ions. There exists equilibrium between the undissociated molecules of water and H^+ ion concentration is exactly equal to OH^- ion concentration. Moreover it is neutral in nature. When a salt is dissolved in water the cations or anions may interact with $[H^+]$ or $[OH^-]$ ions of water and disturb the equilibrium as a result concentration decreases of either $[H^+]$ or $[OH^-]$. Thus the solution becomes either acidic (if concentration of $[OH^-]$ ions decreases) or basic (if concentration of either $[H^+]$ ions decreases).

The phenomenon involving the interaction of cation or anion (or both) of a salt with the $[H^+]$ or $[OH^-]$ ions of water leading to the formation of an acidic ($[H^+] > [OH^-]$) or alkaline ($[H^+] < [OH^-]$) or sometimes neutral solution is called **salt hydrolysis**.

As the nature of the cation or anion of the salt determines whether its solution will be acidic, basic or neutral, it is proper to divide the salts into four categories.

    (A) Salt of strong acid and strong base
        Examples: $NaCl$, Na_2SO_4, KCl, $NaNO_3$ etc.

    (B) Salt of weak acid and strong base
        Examples; CH_3COONa. Na_2CO_3, $NaCN$ etc.

    (C) Salt of strong acid and weak base
        Examples: NH_4Cl, $FeSO_4$, $AlCl_3$ etc.

    (D) Salt of weak acid and weak base
        Examples: CH_3COONH_4. NH_4CN, $CuCO_3$ etc.

▶ **Salts of Strong acid and strong base**

Such salts do not undergo hydrolysis when dissolved in water and their solution is neutral.

To understand this lets take the example of NaCl. This is a salt of strong acid HCl (H⁺ is strong acid and its conjugate Cl⁻ is weak base) and strong base NaOH (OH⁻ being strong base and its conjugate Na⁺ is weak acid). Salt NaCl contains weak acid (Na⁺) and weak base (Cl⁻). These ions don't have tendency to take [H⁺] or [OH⁻] from water so the equilibrium of [H⁺] or [OH⁻] remains undisturbed and the solution remains neutral.

▶ **Salts of weak acid and strong base**

These salts hydrolyze in water to form alkaline solutions.

To understand this lets take the example of CH_3COONa. This is a salt of weak acid CH_3COOH (H⁺ is weak acid and its conjugate CH_3COO^- is strong base) and strong base NaOH (OH⁻ being strong base and its conjugate Na⁺ is weak acid).

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

CH_3COO^- is being strong base takes up the H⁺ ions of water to form weakly dissociated CH_3COOH.

$$H_2O + CH_3COO^- \rightleftharpoons CH_3COOH + OH^-$$
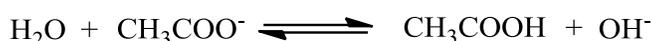
In order to compensate the decrease of H⁺ ions, the undissociated water molecules get further dissociated to maintain the constant value of K_w. Thus increase in the concentration of OH⁻ makes the solution basic.

✓ **Hydrolysis Constant (K_h)**

Hydrolysis of salt (AB) of weak acid (HA) and strong base (BOH) can be represented as:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$
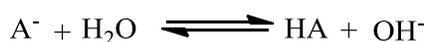
Applying, law of equilibrium constant to above equation we have:

$$K = \frac{[OH^-][HA]}{[H_2O][A^-]}$$

$$K[H_2O] = \frac{[OH^-][HA]}{[A^-]}$$

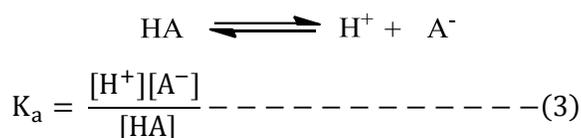Since water is present in large extent its concentration is regarded as constant.

$$K_h = \frac{[OH^-][HA]}{[A^-]} - - - - - - - - - - (1)$$

$K[H_2O] = K_h$ = constant which is called as hydrolysis constant.

✓ **Relation between K_h, K_w & K_a**

Ionic product of water is given by $K_w = [H^+][OH^-] - - - - - - - - (2)$

Dissociation of weak base is represented as

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} - - - - - - - - - - - - (3)$$

Now dividing equation (2) & (3)

$$\frac{K_w}{K_a} = \frac{[H^+][OH^-]}{\frac{[H^+][A^-]}{[HA]}}$$

$$\frac{K_w}{K_a} = \frac{[OH^-][HA]}{[A^-]}$$

From equation (1) we have $\frac{K_w}{K_a} = K_h - - - - - - - - - - - - - (4)$

Above equation (4) represents the relation between K_h, K_w & K_a.

Thus, the hydrolysis of constant of the salt varies inversely to the dissociation constant of the acid, i.e., weaker the acid, greater is the hydrolysis constant of the salt.

✓ **Degree of hydrolysis (h)**

Degree of hydrolysis is the fraction of the mole that undergoes hydrolysis from total moles, during equilibrium is attained. It is symbolized by **h.**

$$h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{Total number of moles of the salt dissolved}}$$

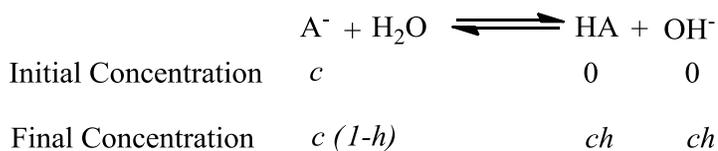If **c is the initial concentration of salt in moles/lit** (i.e. total number of moles per lit.)

Then

$$c \, X \, h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{Total number of moles of the salt dissolved}} \, X \, \frac{\text{Total number of moles of the salt dissolved}}{\text{lit}}$$

$$c \, X \, h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{lit}}$$

= **concentration of ions formed in solution**

Final concentration of salt will be **c-ch (i.e. {c (1-h)}) --- in moles/lit**

Equation for salt (AB) of weak acid (HA) and strong base (BOH) can be represented as

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

Initial Concentration	c	0	0
Final Concentration	$c\,(1\text{-}h)$	ch	ch

So, $[OH^-]$ = ch, [HA] = ch, $[A^-]$ = c(1 – h)

Substitution these values in equation (1)

$$K_h = \frac{[OH^-][HA]}{[A^-]}$$

$$K_h = \frac{ch \cdot ch}{c(1-h)}$$

When h is small, considering $(1 - h) \approx 1$

$$K_h = \frac{ch \cdot ch}{c} = ch^2$$

$$h = \sqrt{\frac{K_h}{c}} - - - - - - - - (5)$$

Thus, the degree of hydrolysis of a salt of a weak acid and a strong base is inversely proportional to the square root of the molar concentration. If V is the volume of the solution in litres containing 1 mole of the solute, then $c = \frac{1}{V}$. Substituting the value of c in equation 5.

$$h = \sqrt{K_h \cdot V}$$

Thus, the degree of hydrolysis is directly proportional to the square root of the volume of the solution in litres containing one mole of the salt, i.e., it increase with dilution.

Hence from equation (4) & (5) $h = \sqrt{\frac{K_w}{K_a \cdot c}} - - - - - - - - - (6)$

✓ **Calculation of pH of the salt solution**

From above equation $[OH^-]$ = ch

From equation (6) $[OH^-] = c \cdot \sqrt{\frac{K_w}{K_a \cdot c}}$

$$[OH^-] = \sqrt{\frac{K_w \cdot c}{K_a}} - - - - - -(7)$$

We know $K_w = [H^+][OH^-]$

So, $[OH^-] = \frac{K_w}{[H^+]}$ put this value in equation (6)

So, $\frac{K_w}{[H^+]} = \sqrt{\frac{K_w \cdot c}{K_a}}$

$$[H^+] = \dfrac{K_w}{\sqrt{\dfrac{K_w \cdot c}{K_a}}}$$

$$[H^+] = \sqrt{\dfrac{K_w \cdot K_a}{c}}$$

Applying –log to above equation.

$$-\log[H^+] = -\log_{10}\sqrt{\dfrac{K_w \cdot K_a}{c}}$$

$$-\log[H^+] = \dfrac{1}{2}[-\log_{10} K_w + (-\log_{10} K_a)-(-\log_{10} c)]$$

$$pH = \dfrac{1}{2}[pK_w + pK_a + \log_{10} c] \ ------(8)$$

Above equation (8) represents the equation for calculating pH of weak acid and strong base.

Thus, in such case, pH will always be grater then 7 and the solution will be alkaline.

▶ **Salts of strong acid and weak base**

These salts hydrolyze in water to form acidic solutions.

To understand this lets take the example of NH_4Cl. This is a salt of strong acid HCl (H^+ is strong acid and its conjugate Cl^- is weak base) and weak base NH_4OH (OH^- being weak base and its conjugate NH_4^+ is strong acid).

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

NH_4^+ being strong acid takes up the OH^- ions of water to form weakly dissociated NH_4OH.

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$
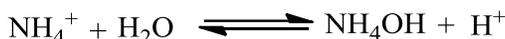
In order to compensate the decrease of OH^- ions, the undissociated water molecules get further dissociated to maintain the constant value of K_w. Thus increase in the concentration of H^+ makes the solution acidic.

✓ **Hydrolysis Constant (K_h)**

Hydrolysis of salt (AB) of strong acid (HA) and weak base (BOH) can be represented as:

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

Applying, law of equilibrium constant to above equation we have:

$$K = \dfrac{[BOH][H^+]}{[H_2O][B^+]}$$

$$K[H_2O] = \dfrac{[BOH][H^+]}{[B^+]}$$

Since water is present in large extent its concentration is regarded as constant.
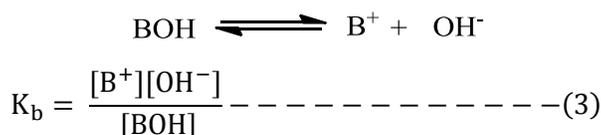
$$K_h = \dfrac{[BOH][H^+]}{[B^+]} \ ----------(1)$$

$K[H_2O] = K_h$ = constant which is called as hydrolysis constant.

✓ **Relation between K_h, K_w & K_b**

Ionic product of water is given by $K_w = [H^+][OH^-] \ --------(2)$

Dissociation of weak base is represented as

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b = \dfrac{[B^+][OH^-]}{[BOH]} \ --------------(3)$$

Now dividing equation (2) & (3)

$$\dfrac{K_w}{K_b} = \dfrac{[H^+][OH^-]}{\dfrac{[B^+][OH^-]}{[BOH]}}$$

$$\dfrac{K_w}{K_b} = \dfrac{[H^+][BOH]}{[B^+]}$$

From equation (1) we have $\frac{K_w}{K_b} = K_h$ − − − − − − − − − − − − − (4)

Above equation (4) represents the relation between K_h, K_w & K_b.

Thus, the hydrolysis of constant of the salt varies inversely to the dissociation constant of the base, i.e., weaker the base, greater is the hydrolysis constant of the salt.

✓ **Degree of hydrolysis (h)**

Degree of hydrolysis is the fraction of the mole that undergoes hydrolysis from total moles, during equilibrium is attained. It is symbolized by **h.**

$$h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{Total number of moles of the salt dissolved}}$$

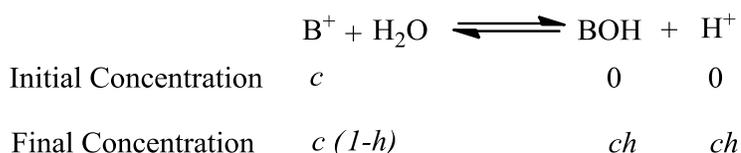If **c is the initial concentration of salt in moles/lit** (i.e. total number of moles per lit.)

Then

$$c \, X \, h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{Total number of moles of the salt dissolved}} \, X \, \frac{\text{Total number of moles of the salt dissolved}}{\text{lit}}$$

$$c \, X \, h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{lit}}$$

= **concentration of ions formed in solution**

Final concentration of salt will be **c-ch (i.e. {c (1-h)}) --- in moles/lit**

Equation for salt (AB) of strong acid (HA) and weak base (BOH) can be represented as

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

Initial Concentration	c	0	0
Final Concentration	$c\,(1\text{-}h)$	ch	ch

So, $[H^+] = ch$, $[BOH] = ch$, $[B^+] = c(1 - h)$

Substitution these values in equation (1)

$$K_h = \frac{[BOH][H^+]}{[B^+]}$$

$$K_h = \frac{ch \cdot ch}{c(1 - h)}$$

When h is small, considering $(1 - h) \approx 1$

$$K_h = \frac{ch \cdot ch}{c} = ch^2$$

$$h = \sqrt{\frac{K_h}{c}} − − − − − −(5)$$

Thus, the degree of hydrolysis of a salt of a strong acid and a weak base is inversely proportional to the square root of the molar concentration. If V is the volume of the solution in litres containing 1 mole of the solute, then $c = \frac{1}{V}$. Substituting the value of c in equation 5.

$$h = \sqrt{K_h \cdot V}$$

Thus, the degree of hydrolysis is directly proportional to the square root of the volume of the solution in letres containing one mole of the salt, i.e., it increase with dilution.

Hence from equation (4) & (5) $\quad h = \sqrt{\frac{K_w}{K_b \cdot c}} − − − − − − − − − (6)$

✓ **Calculation of pH of the salt solution**

From above equation $[H^+] = ch$

From equation (5) $\qquad\qquad\qquad [H^+] = c \cdot \sqrt{\frac{K_w}{K_b \cdot c}}$

$$[H^+] = \sqrt{\frac{K_w \cdot c}{K_b}} − − − − − −(7)$$

Applying −log to above equation.

$$-\log[H^+] = -\log_{10} \sqrt{\frac{K_w \cdot c}{K_b}}$$

$$-\log[H^+] = \frac{1}{2}[-\log_{10} K_w + (-\log_{10} c) - (-\log_{10} K_b)]$$

$$pH = \frac{1}{2}[pK_w - pK_b - \log_{10} c] \ - - - - - -(8)$$

Above equation (8) represents the equation for calculating pH of strong acid and weak base. Thus, in such case, pH will always be less than 7 and the solution will be acidic.

▶ **Salts of weak acid and weak base**

When dissolved in water these salts undergo hydrolyze to a greater extent resulting in either acid, alkaline or neutral solution depending upon the relative hydrolysis of the constituent ions present in it.

To understand this lets take the example of CH_3COONH_4. This is a salt of weak acid CH_3COOH (H^+ is weak acid and its conjugate CH_3COO^- is strong base) and weak base NH_4OH (OH^- being weak base and its conjugate NH_4^+ is strong acid).

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

CH_3COO^- is being strong base takes up the H^+ ions of water to form weakly dissociated CH_3COOH while NH_4^+ being strong acid take up the OH^- ions of water to form weakly dissociated NH_4OH.

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

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$
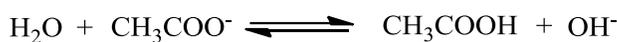
Overall reaction is represented as

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Particularly in this case the extent of hydrolysis of CH_3COO^- is same as that of NH_4^+ hence consumption of H^+ & OH^- ions will be same resulting in neutral solution.

But when the extent of hydrolysis of anion is relatively more than cation, resulting solution will be alkaline (e.g. NH_4CN) and if the extent of hydrolysis of cation is relatively more than anion, resulting solution will be acidic (e.g. $(NH_4)_2C_2O_4$).

✓ **Hydrolysis Constant (K_h)**

Hydrolysis of salt (AB) of weak acid (HA) and weak base (BOH) can be represented as:

$$B^+ + A^- + H_2O \rightleftharpoons HA + BOH$$

Applying, law of equilibrium constant to above equation we have:

$$K = \frac{[HA][BOH]}{[H_2O][A^-][B^+]}$$

$$K[H_2O] = \frac{[HA][BOH]}{[A^-][B^+]}$$

Since water is present in large extent its concentration is regarded as constant.

$$K_h = \frac{[HA][BOH]}{[A^-][B^+]} - - - - - - - - - -(1)$$

$K[H_2O] = K_h$ = constant which is called as hydrolysis constant.

✓ **Relation between K_h, K_w, K_a & K_b**

Ionic product of water is given by $K_w = [H^+][OH^-] - - - - - - - - (2)$

Dissociation of weak base is represented as

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} - - - - - - - - - - - -(3)$$

Dissociation of weak base is represented as

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} - - - - - - - - - - - -(4)$$

Now dividing equation (2) by (3) & (4)

$$\frac{K_w}{K_a \cdot K_b} = \frac{[H^+][OH^-]}{\frac{[H^+][A^-]}{[HA]} \cdot \frac{[B^+][OH^-]}{[BOH]}}$$

$$\frac{K_w}{K_a \cdot K_b} = \frac{[HA][BOH]}{[A^-][B^+]}$$

From equation (1) we have $\quad \frac{K_w}{K_a \cdot K_b} = K_h$ – – – – – – – – – – – – (5)

Above equation (5) represents the relation between K_h, K_w, K_a & K_b.

✓ Degree of hydrolysis (h)

Degree of hydrolysis is the fraction of the mole that undergoes hydrolysis from total moles, during equilibrium is attained. It is symbolized by **h.**

$$h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{Total number of moles of the salt dissolved}}$$

If **c is the initial concentration of salt in moles/lit** (i.e. total number of moles per lit.)

Then

$$c \times h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{Total number of moles of the salt dissolved}} \times \frac{\text{Total number of moles of the salt dissolved}}{\text{lit}}$$

$$c \times h = \frac{\text{Number of moles of salt undergoing hydrolysis}}{\text{lit}}$$

= **concentration of ions formed in solution**

Final concentration of salt will be **c-ch (i.e. {c (1-h)}) --- in moles/lit**

Equation for salt (AB) of weak acid (HA) and weak base (BOH) can be represented as

$$B^+ + A^- + H_2O \rightleftharpoons HA + BOH$$

Initial Concentration	c	c	0	0
Final Concentration	$c(1-h)$	$c(1-h)$	ch	ch
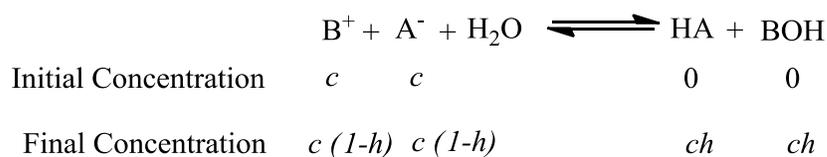
So, $[HA] = ch$, $[BOH] = ch$, $[B^+] = c(1-h)$, $[A^-] = c(1-h)$

Substitution these values in equation (1)

$$K_h = \frac{[HA][BOH]}{[A^-][B^+]}$$

$$K_h = \frac{ch \cdot ch}{c(1-h) \cdot c(1-h)}$$

When h is small, considering $(1-h) \approx 1$

$$K_h = \frac{ch \cdot ch}{c^2} = h^2$$

$$h = \sqrt{K_h}$$

Thus, degree of hydrolysis is independent of the concentration (i.e., dilution of the salt).

From equation (5) $\quad h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$ – – – – – – – – – (6)

✓ Calculation of pH of the salt solution

Dissociation of weak base is represented as

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = \frac{K_a [HA]}{[A^-]}$$

We know, $[A^-] = c(1-h)$, $[HA] = ch$

$$[H^+] = \frac{K_a \, ch}{c(1-h)}$$

When h is small, considering $(1-h) \approx 1$

$$[H^+] = K_a \cdot h$$

From equation (6)
$$[H^+] = K_a \cdot \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

$$[H^+] = \sqrt{\frac{K_a \cdot K_w}{K_b}}$$

Applying –log to above equation

$$-\log[H^+] = -\log_{10} \sqrt{\frac{K_a \cdot K_w}{K_b}}$$

$$pH = \frac{1}{2}[-\log_{10} K_a + (-\log_{10} K_w) - (-\log_{10} K_b)]$$

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b] - - - -(7)$$

Above equation (7) represents the equation for calculating pH of weak acid and weak base.

Case 1: $pK_a = pK_b$ Strength of acid is same that of base

$$\therefore pH = \frac{1}{2}pK_w = 7$$

Solution will be neutral although the salt has undergoing hydrolysis

Case 2: $pK_a > pK_b$ Strength of acid is relatively weaker than base

$$\therefore pH > \frac{1}{2}pK_w > 7$$

Solution will be alkaline

Case 3: $pK_a < pK_b$ Strength of base is relatively weaker than acid

$$\therefore pH < \frac{1}{2}pK_w < 7$$

Solution will be acidic

Important characteristics of salts

No.	Type of Salt	Examples	Hydrolysis constant K_h	Degree of Hydrolysis h	pH	Nature of solution
1.	Salts of strong acid strong base	NaCl K_2SO_4	No Hydrolysis			Neutral
2.	Salts of weak acid strong base	CH_3COONa KCN	$\frac{K_w}{K_a} = K_h$	$h = \sqrt{\frac{K_w}{K_a \cdot c}}$	$pH = \frac{1}{2}[pK_w + pK_a + \log_{10} c]$	Alkaline
3.	Salts of strong acid weak base	NH_4Cl NH_4NO_3	$\frac{K_w}{K_b} = K_h$	$h = \sqrt{\frac{K_w}{K_b \cdot c}}$	$pH = \frac{1}{2}[pK_w - pK_b - \log_{10} c]$	Acidic
4.	Salts of weak acid weak base	NH_4CN $(NH_4)C_2O_4$	$\frac{K_w}{K_a \cdot K_b} = K_h$	$h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$	$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$	$pK_a = pK_b, pH = 7$ $pK_a > pK_b, pH > 7$ $pK_a < pK_b, pH < 7$

▶ **Buffer Solutions**

The pH of water and most solutions changes drastically when a small amount of acid or base is added. However, if a solution is buffered, there is little change in pH.

A buffer solution is the solution which maintains its pH fairly constant and is capable of resisting the change in pH on addition of small amounts of acid or base.

The ability of a buffer solution is to resist any change in pH on addition of acid or base is called buffer action.

✓ **Characteristics of buffer solution:**

(A) Buffer solution possess a definite pH value.

(B) The pH value remains steady on keeping or on dilution.

(C) The pH value is not changed on the addition of a strong in acidic buffer and a strong base

in basic buffer.

✓ **Types of Buffer Solution**

[1] Acidic buffer solution: The solution of weak acid and its salt with a strong base is called acidic buffer.

Example: Solution containing equimolar quantities of acetic acid (weak acid) and sodium acetate (salt of acetic acid with strong base NaOH) pH of this solution is around 4.74.

[2] Basic buffer solution: The solution of a weak base and its salt with a strong acid is called a basic buffer.

Example: Solution containing equimolar quantities of ammonium hydroxide (weak base) and ammonium chloride (salt of ammonium hydroxide with strong acid HCl) pH of this solution is around 9.25.

✓ **Mechanism of buffer solution**

[1] Acidic buffer solutions

To understand the buffer action considers the example of acetic acid (weak acid) and sodium acetate (salt of acetic acid with strong base NaOH). Acetic acid is weak electrolyte, it will not ionize completely. Sodium acetate is a strong electrolyte, it will ionize completely.

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

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$
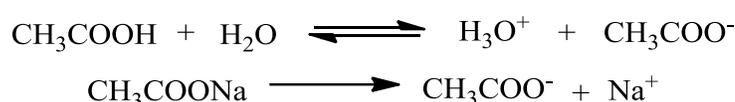
The dissociation of acetic acid further decreases in presence of sodium acetate due to common ion effect.

This solution contains large number of CH_3COO^- ions due to dissociation of sodium acetate.

➢ **Adding an acid to this buffer solution,**

Added HCl increases the concentration of H_3O^+ ions concentration in the solution, which will decrease the pH of the solution. The excess acetate ions present will combine with the H_3O^+ ions to form weakly ionized CH_3COOH solution.

$$CH_3COO^-_{(aq)} + H_3O^+_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + H_2O_{(l)}$$

(from buffer) (from added HCl)
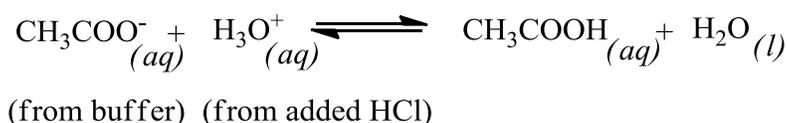
Produced acetic acid do not dissociate much in presence of sodium acetate due to common ion effect.

Hence the effect produced by H_3O^+ ions is neutralized and practically there is no change in pH.

➢ **Adding an alkali to this buffer solution,**

Added NaOH increases the concentration of OH^- ions in the solution, which will increase the pH of the solution. The OH^- ions present in solution will combine with the H_3O^+ ions present in the buffer to form unionized water molecule.

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons 2H_2O_{(l)}$$

from buffer   from NaOH
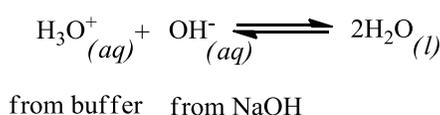
This removal of H_3O^+ ions from the solution increase the ionization of CH_3COOH, till the concentration of H_3O^+ ions is retained to its original value (acc. to Le Châtelier's principle), so practically there is no change in pH observed.

[2] Basic buffer solutions

Suppose we take solution containing ammonium hydroxide (weak base) and ammonium chloride (salt of ammonium hydroxide with strong acid HCl)

Ammonium hydroxide is weak electrolyte, it will not ionize completely.

Ammonium chloride is a strong electrolyte, it will ionize completely.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
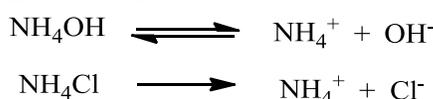
The dissociation of ammonium hydroxide further decreases in presence of ammonium chloride due to common ion effect.

This solution contains large number of NH_4^+ ions due to dissociation of ammonium chloride.

➢ **Adding an alkali to this buffer solution**,

Added NaOH increases the concentration of OH^- ions in the solution, which will increase the pH of the solution. The excess OH^- ions present will combine with the NH_4^+ ions present in the buffer to form weakly ionized NH_4OH molecule.

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightleftharpoons NH_4OH_{(aq)}$$

from buffer   from NaOH
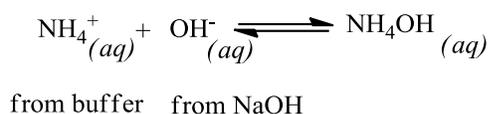
Produced ammonium hydroxide does not dissociate much in presence of ammonium chloride due to common ion effect.

Hence the effect produced by OH^- ions is neutralized and practically there is no change in pH.

➢ **Adding an acid to this buffer solution**,

Added HCl increases the concentration of H_3O^+ ions concentration in the solution, which will decrease the pH of the solution. The OH^- ions present in solution will combine with the H_3O^+ ions to form unionized water molecule..

$$OH^-{}_{(aq)} + H_3O^+{}_{(aq)} \rightleftharpoons 2H_2O_{(l)}$$

from buffer   from HCl
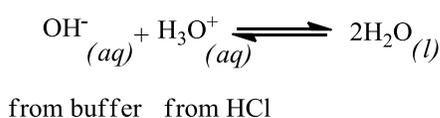
This removal of H_3O^+ ions from the solution increase the ionization of NH_4OH, till the loss of OH^- ions is compensated (acc. to Le Châtelier's principle) , so practically there is no change in pH observed.

✓ **pH of buffer solution**

• **pH of acidic buffer solution**

To understand the pH of buffer solution considers the example of acetic acid (weak acid) and sodium acetate (salt of acetic acid with strong base NaOH).

Acetic acid is weak electrolyte, it will not ionize completely.

Sodium acetate is a strong electrolyte, it will ionize completely.

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

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$
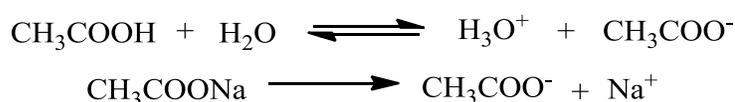
pH is observed only due to dissociation of acetic acid as it gives formation of H_3O^+ ions.

According to the law of equilibrium

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$[H_3O^+] = K_a \cdot \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Acetic acid being weak electrolyte, it will not ionize completely moreover ionization decreases due to common ion effect hence

Value of $[CH_3COOH]$ is taken as initial concentration of acid, while

Value of $[CH_3COO^-]$ is taken as initial concentration of salt, then we have

$$[H_3O^+] = K_a \cdot \frac{[Acid]}{[Salt]}$$

Applying –log to above equation

$$-\log[H_3O^+] = -\log_{10}[K_a \cdot \frac{[Acid]}{[Salt]}]$$

$$-\log[H_3O^+] = -\log_{10}K_a - \log_{10}[Acid] - (-\log_{10}[Salt])$$

$$pH = pK_a + \log_{10}\frac{[Salt]}{[Acid]}$$

This is the required equation for the pH of the acidic buffer. This equation is known as Henderson-Hasselbatch equation.

- **pH of basic buffer solution**

Suppose we take solution containing ammonium hydroxide (weak base) and ammonium chloride (salt of ammonium hydroxide with strong acid HCl)

Ammonium hydroxide is weak electrolyte, it will not ionize completely.

Ammonium chloride is a strong electrolyte, it will ionize completely.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

pH is observed only due to dissociation of ammonium hydroxide as it gives formation of OH^- ions.

According to the law of equilibrium

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$[OH^-] = K_b \cdot \frac{[NH_4OH]}{[NH_4^+]}$$

Ammonium hydroxide being weak electrolyte, it will not ionize completely, moreover ionization decreases due to common ion effect hence

Value of $[NH_4OH]$ is taken as initial concentration of base, while

Value of $[NH_4^+]$ is taken as initial concentration of salt, then we have

$$[OH^-] = K_b \cdot \frac{[Base]}{[Salt]}$$

Applying –log to above equation

$$-\log[OH^-] = -\log_{10}[K_b \cdot \frac{[Base]}{[Salt]}]$$

$$-\log[OH^-] = -\log_{10}K_b - \log_{10}[Base] - (-\log_{10}[salt])$$

$$pOH = pK_b + \log_{10}\frac{[Salt]}{[Base]}$$

We know that, $pH = pK_w - pOH$ applying this value in above equation.

$$pH = pK_w - pK_b - \log_{10}\frac{[Salt]}{[Base]}$$

This is the required equation for the pH of the basic buffer.

✓ **Buffer capacity**

The capacity of a buffer solution to resist the pH is termed as the buffer capacity.

$$\beta = \frac{dB}{d(pH)}$$

dB = no. of moles of acid or base added to 1 lit buffer solution.

dpH = resulting change in pH, If dpH = 1, then

β = dB = no. of moles of acid or base added to 1 lit buffer solution.

Buffer capacity is defined as number of moles of acid or base added to 1 lit buffer solution to change its pH by unity.

It has been found that the buffer solution having the ratio $\frac{[Salt]}{[Base]}$ or $\frac{[Salt]}{[Acid]}$ nearly equal to 1 are most effective and do nto undergo an appreciable change in pH on addition of acid or base.

✓ **Importance of Buffer Solution**

A buffer is a mixture of molecules that release or bind H^+ in order to maintain a relatively stable pH. Note that the function of a buffer is NOT to keep a solution neutral (at pH 7); its function is to minimize the change in pH when base or acid is added to the solution. Also note that there are many different buffers, and each one will stabilize the pH of a solution only within a specific pH range. One buffer may be effective within a range of pH 2 to pH 6, while another may be effective within a range of pH 10 to pH 12. Beyond its buffering range, a buffer no longer acts to stabilize the pH of the solution.

Buffer **standards solutions** (pH = 4.0, 7.0, 9.2) are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. pH buffers standards are essential for routine pH meter calibration in order to obtain accurate readings. Inorganic Ventures carries a full line of colored and colorless pH buffer options for any test.

Buffers are extremely important to living organisms because most biochemical processes proceed normally only when the pH remains within a fairly narrow range. An excess of H^+ or OH^- can interfere with the structure and activity of many biomolecules, especially proteins. Therefore, buffers are commonly used in living organisms to help maintain a relatively stable pH. In humans, for example, buffers act to maintain blood pH between 7.35 and 7.45 even though acids and bases are continually being added to and removed from the blood as it travels through the body. The 3 main buffer systems in our bodies are the bicarbonate buffer system, the phosphate buffer system, and the protein buffer system.

In the laboratory, molecular and cellular biologists make extensive use of buffers to stabilize the pH of aqueous solutions. When studying biomolecules in a test tube, the biomolecules may be altered or may behave in ways that are uncharacteristic of their natural behavior if they are in a solution with a pH that is significantly different from the pH of their natural environment.

Strong Concepts + Smart Practice = Success

Best of Luck