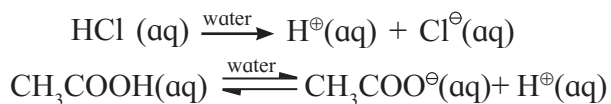### 3.3.1 Arrhenius theory of acids and bases

According to this theory acids and bases are defined as follows :

Acid : Acid is a substance which contains hydrogen and gives rise to $H^{\oplus}$ ions in aqueous solution. For example :

$$HCl\ (aq) \xrightarrow{water} H^{\oplus}(aq) + Cl^{\ominus}(aq)$$

$$CH_3COOH(aq) \xrightleftharpoons{water} CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

Arrhenius described $H^{\oplus}$ ions in water as bare ions; they hydrate in aqueous solutions and thus represented as hydronium ions $H_3O^{\oplus}$. We herewith conveniently represent them as $H^{\oplus}$.

Do you know ?

Hydrochloric acid, HCl present in the gastric juice is secreted by our stomach and is essential for digestion of food.

Base : Base is a substance that contains OH group and produces hydroxide ions ($OH^{\ominus}$) ions in aqueous solution. For example,

$$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$
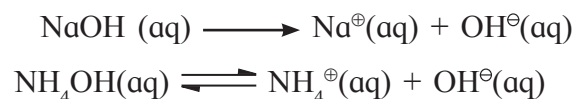
Arrhenius theory accounts for properties of different acids and bases and is applicable only to aqueous solutions. It does not account for the basicity of NH_3 and Na_2CO_3 which do not have OH group.

3.3.2 Bronsted - Lowry theory :

J. N. Bronsted and T. M. Lowry (1923) proposed a more general theory known as the Bronsted-Lowry proton transfer theory. According to this theory acids and bases are defined as follows.

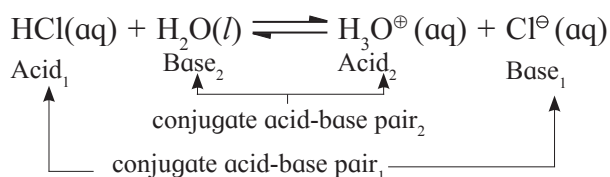**Acid :** Acid is a substance that donates a proton ($H^{\oplus}$) to another substance.

Base : Base is a substance that accepts a proton ($H^{\oplus}$) from another substance.

For example :

$$\underset{Acid_1}{HCl} + \underset{Base_2}{NH_3} \rightleftharpoons \underset{Acid_2}{NH_4^{\oplus}} + \underset{Base_1}{Cl^{\ominus}}$$

In the above reaction HCl and $NH_4^{\oplus}$ are proton donors and act as acids. The NH_3 and $Cl^{\ominus}$ are proton acceptors and act as bases. Further it follows that the products of the Bronsted-Lowry acid-base reactions are acids bases.

The base produced by releasing the proton from an acid is the conjugate base of that acid. Likewise the acid produced when a base accepts a proton is called the conjugate acid of that base. A pair of an acid and a base differing by a proton is said to be a **conjugate acid-base pair**.

$$\underset{Acid_1}{HCl(aq)} + \underset{Base_2}{H_2O(l)} \rightleftharpoons \underset{Acid_2}{H_3O^{\oplus}(aq)} + \underset{Base_1}{Cl^{\ominus}(aq)}$$

conjugate acid-base pair$_2$

conjugate acid-base pair$_1$

3.3.3 Lewis theory :
A more generalized acid-base concept was put forward by G.N. Lewis in 1923. According to this theory acids and bases are defined as follows.

Acid : Any species that accepts a share in an electron pair is called Lewis acid.

Base : Any species that donates a share in an electron pair is called Lewis base.

For example :
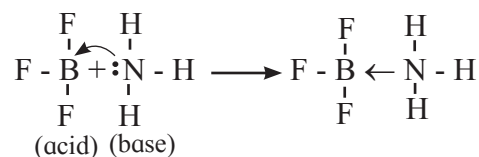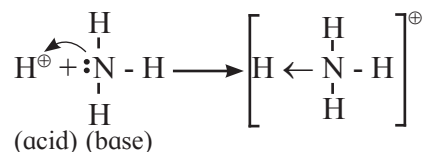
(acid) (base)

(acid) (base)

Amphoteric nature of water : Water has the ability to act as an acid as well as a base. Such behaviour is known as amphoteric nature of water. For example :

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^{\ominus}(aq) + NH_4^{\oplus}(aq)$$

Acid

$$H_2O(l) + HCl(aq) \rightleftharpoons H_3O^{\oplus}(aq) + Cl^{\ominus}(aq)$$

Base

H_2O acts as an acid towards NH_3 and as a base towards HCl. Therefore H_2O is amphoteric.

3.4 Ionisation of acids and bases

Acids and bases are classified as strong acids and strong bases, weak acids and weak bases on the basis of their **extent of dissociation**. Strong acids and bases are almost completely dissociated in water. For example :

$$HCl\ (aq) \longrightarrow H^{\oplus}(aq) + Cl^{\ominus}\ (aq)$$

$$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

Typical strong acids are HCl, HNO_3, H_2SO_4, HBr and HI while typical strong bases may include NaOH and KOH.

Weak acids and weak bases are partially dissociated in water. The solution of a weak acid or a weak base contains undissociated molecules along with a small number of ions at equilibrium. For example :

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$

Note that HCOOH, HF, H_2S are examples of weak acids while $Fe(OH)_3$, $Cu(OH)_2$ are examples of weak bases.

3.4.1 Dissociation constant of weak acids and weak bases :
The dissociation of a weak acid HA in water is expressed as

$$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$$

The equilibrium constant called acid-dissociation constant for this equilibrium is :

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} \qquad ....(3.3)$$

Similarly the dissociation of weak base BOH in water is represented as :

$$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

The equilibrium constant called base-dissociation constant for this equilibrium is,

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]} \qquad ....(3.4)$$

Thus, the dissociation constant of a weak acid or a weak base is defined as **the equilibrium constant for dissociation equilibrium of weak acid or weak base, respectively**.

3.4.2 Ostwald's dilution law :
Arrhenius concept of acids and bases was expressed quantitatively by F. W. Ostwald in the form of the dilution law in 1888.

a. Weak acids : Consider an equilibrium of weak acid HA that exists in solution partly as the undissociated species HA and partly $H^{\oplus}$ and $A^{\ominus}$ ions. Then

$$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$$

The acid dissociation constant is given by Eq. (3.3)

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

Suppose 1 mol of acid HA is initially present in volume V dm^3 of the solution. At equilibrium the fraction dissociated would be $\propto$, where $\propto$ is degree of dissociation of the acid. The fraction of an acid that remains undissociated would be $(1 - \propto)$.

HA(aq) $\rightleftharpoons$ H$^{\oplus}$(aq) + A$^{\ominus}$(aq)			
Amount present at equilibrium/ mol	$(1-\propto)$	$\propto$	$\propto$
concentration at equilibrium/ mol dm^{-3}	$\dfrac{1-\propto}{V}$	$\dfrac{\propto}{V}$	$\dfrac{\propto}{V}$

Thus, at equilibrium $[HA] = \dfrac{1-\propto}{V}$, mol dm^{-3},

$$[H^{\oplus}] = [A^{\ominus}] = \frac{\propto}{V} \text{ mol dm}^{-3}.$$

Substituting these in Eq. (3.3)

$$K_a = \frac{(\propto/V)(\propto/V)}{(1-\propto)/V} = \frac{\propto^2}{(1-\propto)V} \qquad \text{....... (3.5)}$$

If c is the initial concentration of an acid in mol dm^{-3} and V is the volume in dm^3 mol^{-1} then $c = 1/V$. Replacing $1/V$ in Eq. (3.5) by c we get

$$K_a = \frac{\propto^2 c}{1-\propto} \qquad \text{......(3.6)}$$

For the weak acid HA, $\propto$ is very small, or $(1-\propto) \cong 1$. With this Eq. (3.5) and (3.6) reduce.

$$K_a = \propto^2/V \text{ and } K_a = \propto^2 c \qquad \text{............ (3.7)}$$

$$\propto = \sqrt{\frac{K_a}{c}} \text{ or } \propto = \sqrt{K_a . V} \qquad \text{............ (3.8)}$$

The Eq. (3.8) implies that the degree of dissociation of a weak acid is inversely proportional to the square root of its concentration or directly proportional to the square root of volume of the solution containing 1 mol of the weak acid.

b. Weak base : Consider 1 mol of weak base BOH dissolved in V dm^3 of solution. The base dissociates partially as

$$\text{BOH (aq)} \rightleftharpoons \text{B}^{\oplus}\text{(aq)} + \text{OH}^{\ominus}\text{(aq)}$$

The base dissociation constant is

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}$$

Let the fraction dissociated at equilibrium is $\propto$ and that remains undissociated is $(1-\propto)$.

BOH(aq) $\rightleftharpoons$ B$^{\oplus}$(aq) +OH$^{\ominus}$(aq)			
Amount present at equilibrium	$(1-\propto)$	$\propto$	$\propto$
concentration at equilibrium	$\dfrac{1-\propto}{V}$	$\dfrac{\propto}{V}$	$\dfrac{\propto}{V}$

A equilibrium,

$$[BOH] = \frac{1-\propto}{V} \text{ mol dm}^{-3},$$

$$[B^{\oplus}] = [OH^{\ominus}] = \frac{\propto}{V} \text{ mol dm}^{-3}.$$

Substitution of these concentrations in Eq. (3.4), gives

$$K_b = \frac{(\propto/V)(\propto/V)}{(1-\propto)/V} = \frac{\propto^2}{(1-\propto)V} \qquad \text{.......... (3.9)}$$

Similar arguments in the case of weak acid, led to

$$K_b = \frac{\propto^2 c}{(1-\propto)} \qquad \text{............ (3.10)}$$

$$\propto = \sqrt{K_b . V} , \propto = \sqrt{\frac{K_b}{c}} \qquad \text{............ (3.11)}$$

The degree of dissociation of a weak base is inversely proportional to square root of its concentration and is directly proportional to square root of volume of the solution containing 1 mol of weak base.

Problem 3.1 : A weak monobasic acid is 0.05% dissociated in 0.02 M solution. Calculate dissociation constant of the acid.
Solution : The dissociation constant of acid is given by $K_a = \propto^2 c$. Here,

$$\propto = \frac{\text{percent dissociation}}{100}$$

$$= \frac{0.05}{100} = 5 \times 10^{-4}$$

$$c = 0.02 \text{ M} = 2 \times 10^{-2} \text{ M}$$

Hence $K_a = (5 \times 10^{-4})^2 \times 2 \times 10^{-2}$

$$= 25 \times 10^{-8} \times 2 \times 10^{-2}$$

$$= 50 \times 10^{-10} = 5 \times 10^{-9}$$

Problem 3.2 : The dissociation constant of NH_4OH is 1.8×10^{-5}. Calculate its degree of dissociation in 0.01 M solution.

Solution : The degree of dissociation is given by $\alpha = \sqrt{K_b/c}$. Here,

$K_b = 1.8 \times 10^{-5}$; $c = 0.01 = 1 \times 10^{-2}$ M

Hence, $\alpha = \sqrt{\dfrac{1.8 \times 10^{-5}}{1 \times 10^{-2}}} = \sqrt{1.8 \times 10^{-3}}$

$= \sqrt{18 \times 10^{-4}} = 4.242 \times 10^{-2} = 0.04242$

Problem 3.3 : A weak monobasic acid is 12% dissociated in 0.05 M solution. What is percent dissociation in 0.15 M solution.

Solution : If α_1 and α_2 are the values of degree of dissociation at two different concentrations c_1 and c_2 respectively, then

$K_a = \alpha_1^2 c_1 = \alpha_2^2 c_2$ Therefore $\alpha_1^2 c_1 = \alpha_2^2 c_2$

$\alpha_1 = \dfrac{12}{100}$ $c_1 = 0.05$ M, $c_2 = 0.15$ M,

$\alpha_2 = ?$

Substituting these values in the equation gives

$(0.12)^2 \times 0.05 = \alpha_2^2 \times 0.15$

$\alpha_2^2 = \dfrac{(12)^2 \times 0.05}{0.15} = 0.0048$

Hence $\alpha_2 = 0.0693\ \%$

$\therefore$ percent dissociation = 6.93 %

Problem 3.4 : Calculate $[H_3O^\oplus]$ in 0.1 mol dm³ solution of acetic acid.

Given : $K_a\ [CH_3COOH] = 1.8 \times 10^{-5}$

Solution : Let α_1 be the degree of dissociation. Concentrations of various species involved at equilibrium are as follows.

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^\ominus + H_3O^\oplus$
$\quad (1-\alpha)c \qquad\qquad\qquad \alpha c \qquad\quad \alpha c$

$\alpha = \sqrt{\dfrac{K_a}{c}} = \sqrt{\dfrac{1.8 \times 10^{-5}}{0.1}}$

$\qquad = 1.34 \times 10^{-2}$

$[H_3O^\oplus] = \alpha \times c = 1.34 \times 10^{-2} \times 0.1$

$\qquad\qquad = 1.34 \times 10^{-3}$ mol/L

3.5 Autoionization of water : Pure water ionizes to a very small extent. The ionization equilibrium of water is represented as,

$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^\oplus(aq) + OH^\ominus(aq)$

The equilibrium constant (K) for the ionization of water is given by

$$K = \dfrac{[H_3O^\oplus][OH^\ominus]}{[H_2O]^2} \qquad\ldots\ldots\ldots\ldots (3.12)$$

or $K[H_2O]^2 = [H_3O^\oplus][OH^\ominus]$ $\ldots\ldots\ldots\ldots(3.13)$

A majority of H_2O molecules are undissociated, consequently concentration of water $[H_2O]$ can be treated as constant. Then

$[H_2O]^2 = K'$. Substituting this in Eq. (3.13) we get,

$$K \times K' = [H_3O^\oplus][OH^\ominus] \qquad\ldots\ldots\ldots\ldots (3.14)$$

$$K_w = [H_3O^\oplus][OH^\ominus]$$

where $K_w = KK'$ is called ionic product of water. The product of molar concentrations of hydronium (or hydrogen) ions and hydroxyl ions at equilibrium in pure water at the given temperature is called ionic product of water.

In pure water $H_3O^\oplus$ ion concentration always equals the concentration of $OH^\ominus$ ion. Thus at 298 K this concentration is found to be 1.0×10^{-7} mol/L.

$$K_w = (1.0 \times 10^{-7})\ (1.0 \times 10^{-7})$$

$$K_w = 1.0 \times 10^{-14} \qquad\ldots\ldots\ldots\ldots (3.15)$$

Internet my friend

Find out the values of ionic product K_w of water at various temperatures.

273 K, 283K, 293K, 303K, 313K, 323 K

3.6 pH Scale : Instead of writing concentration of $H_3O^\oplus$ ions in mol dm⁻³, sometimes it is convenient to express it on the logarithmic scale. This is known as pH scale.

Sorensen in 1909 defined the pH of a solution as the negative logarithm to the base 10, of the concentration of $H^\oplus$ ions in solution in mol dm⁻³. Expressed mathematically as

$pH = -\log_{10}[H^{\oplus}]$

Similarly *pOH* of a solution can be defined as the negative logarithm to the base 10, of the molar concentration of $OH^{\ominus}$ ions in solution.

Thus, $pOH = -\log_{10}[OH^{\ominus}]$ .... (3.16)

3.6.1 Relationship between pH and pOH

The ionic product of water is

$K_w = [H_3O^{\oplus}][OH^{\ominus}]$

Now, $K_w = 1 \times 10^{-14}$ at 298 K and thus

$[H_3O^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14}$

Taking logarithm of both the sides, we write

$\log_{10}[H_3O^{\oplus}] + \log_{10}[OH^{\ominus}] = -14$

$-\log_{10}[H_3O^{\oplus}] + \{-\log_{10}[OH^{\ominus}]\} = 14$

From Eq. (3.16) and (3.17)

$pH + pOH = 14$ .... (3.18)

3.6.2 Acidity, basicity and neutrality of aqueous solutions

1. Neutral solution : For pure water or any aqueous neutral solution at 298 K

$[H_3O^{\oplus}] = [OH^{\ominus}] = 1.0 \times 10^{-7}$ M

Hence, $pH = -\log_{10}[H^{\oplus}] = -\log_{10}[1 \times 10^{-7}] = 7$

2. Acidic solution : In acidic solution, there is excess of $H_3O^{\oplus}$ ions, or $[H_3O^{\oplus}] > [OH^{\ominus}]$ Hence, $[H_3O^{\oplus}] > 1 \times 10^{-7}$ and $pH < 7$

3. Basic solution : In basic solution, the excess of $OH^{\ominus}$ ions are present that is $[H_3O^{\oplus}] < [OH^{\ominus}]$ or $[H_3O^{\oplus}] < 1.0 \times 10^{-7}$ with $pH > 7$.
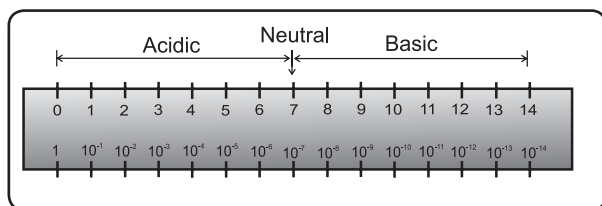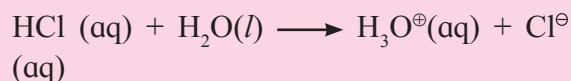

Fig. 3.1 : *pH* scale

Problem 3.5 : Calculate *pH* and *pOH* of 0.01 M HCl solution.

Solution : HCl is a strong acid. It dissociates almost completely in water as

$HCl\ (aq) + H_2O(l) \longrightarrow H_3O^{\oplus}(aq) + Cl^{\ominus}$ (aq)

Hence, $[H_3O^{\oplus}] = c = 0.01M = 1 \times 10^{-2}$ M

$pH = -\log_{10}[H_3O^+] = -\log_{10}[1 \times 10^{-2}] = 2$

We know that $pH + pOH = 14$

$\therefore pOH = 14 - pH = 14 - 2 = 12$

Problem 3.6 : *pH* of a solution is 3.12. Calculate the concentration of $H_3O^{\oplus}$ ion.

Solution : *pH* is given by

$$pH = -\log_{10}[H_3O^{\oplus}]$$

$\log_{10}[H_3O^{\oplus}] = -pH$

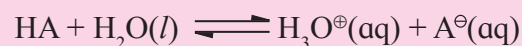$= -3.12$

$= -3 - 0.12 + 1 - 1$

$= (-3 - 1) + 1 - 0.12$

$= -4 + 0.88 = \overline{4}.88$

Thus $[H_3O^{\oplus}] = $ antilog $[\overline{4}.88]$

$= 7.586 \times 10^{-4}$ M

Problem 3.7 : A weak monobasic acid is 0.04 % dissociated in 0.025M solution. What is *pH* of the solution ?

Solution : A weak monobasic acid HA dissociates as :

$HA + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq) + A^{\ominus}(aq)$

Percent dissociation $= \propto \times 100$

or $\propto = \dfrac{\text{percent dissociation}}{100}$

$= \dfrac{0.04}{100} = 4 \times 10^{-4}$

Now $[H_3O^{\oplus}] = \propto \times c$

$= 4 \times 10^{-4} \times 0.025$ M $= 10^{-5}$ M

$\therefore pH = -\log_{10}[H_3O^{\oplus}] = -\log_{10}[10^{-5}] = 5$

Problem 3.8 : The *pH* of monoacidic weak base is 11.2. Calculate its percent dissociation in 0.02 M solution.

Solution : *pOH* of the solution is given as :

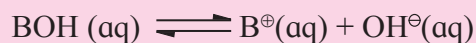$$pOH = 14 - pH = 14 - 11.2 = 2.8$$

$$pOH = -\log_{10}[OH^\ominus]$$

$$\log_{10}[OH^\ominus] = -pOH$$

$$= -2.8 = -2 - 0.8 - 1 + 1$$

$$= -3 + 0.2 = \overline{3}.2$$

$$[OH^\ominus] = \text{antilog } \overline{3}.2 = 1.585 \times 10^{-3} \text{ mol/dm}^3$$

For monoacidic base,

$$BOH \text{ (aq)} \rightleftharpoons B^\oplus\text{(aq)} + OH^\ominus\text{(aq)}$$

$$[OH^\ominus] = \propto c$$

$$\propto = \frac{[OH^\ominus]}{c} = \frac{1.585 \times 10^{-3}}{0.02} = 0.07925$$

Percent dissociation $= \propto \times 100$

$$= 0.07925 \times 100$$

$$= 7.925 \%$$

3.7 Hydrolysis of salts

3.7.1 Types of salts

These are of four types

I. Salts derived from **strong acid and strong base**. For example : $NaCl$, Na_2SO_4, $NaNO_3$, KCl, KNO_3.

II. Salts derived from **strong acids and weak bases**. For example : NH_4Cl, $CuSO_4$, NH_4NO_3, $CuCl_2$.

III. Salts derived from **weak acids and strong bases**. For example : CH_3COONa, KCN, Na_2CO_3.

IV. Salts derived from **weak acids and weak bases**. For example : CH_3COONH_4, NH_4CN.

3.7.2 Concept of hydrolysis :

When a salt is dissociated in water, it dissociates completely into its constituent ions. The solvent water dissociates slightly as,

$$H_2O \text{ (}l\text{)} + H_2O \text{ (}l\text{)} \rightleftharpoons H_3O^\oplus\text{(aq)} + OH^\ominus\text{(aq)}$$

Pure water is neutral and $[H_3O^\oplus] = [OH^\ominus]$. If the ions of the salt do not interact with water, the hydronium and hydroxyl ion concentrations remain equal and the solution is neutral. When one or more of the salt ions react with water, the equality of concentrations of $H_3O^\oplus$ and $OH^\ominus$ ions is disturbed. The solution, does not remain neutral and becomes acidic or basic depending on the type of the salt. Such a reaction between the ions of salt and the ions of water is called hydrolysis of salt. **Hydrolysis of salt is defined as the reaction in which cations or anions or both ions of a salt react with ions of water to produce acidity or alkalinity (or sometimes even neutrality).**

3.7.3 Salts of strong acids and strong bases

$NaCl$ is a salt of strong acid HCl and a strong base $NaOH$. When it is dissolved in water, it dissociates completely into its ions.

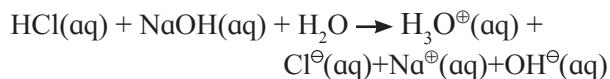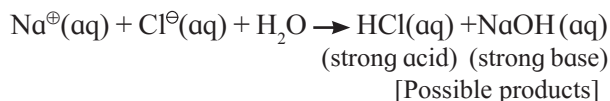$$NaCl \text{ (aq)} \longrightarrow Na^\oplus\text{(aq)} + Cl^\ominus\text{(aq)}$$

The ions $Na^\oplus$ and $Cl^\ominus$ have no tendency to react with water. This is because the possible products, $NaOH$ and HCl of such reactions are

strong electrolytes and dissociate completely in aqueous solutions.

In other words,

$$Na^{\oplus}(aq) + Cl^{\ominus}(aq) + H_2O \longrightarrow HCl(aq) + NaOH(aq)$$
$$\text{(strong acid)} \quad \text{(strong base)}$$
$$\text{[Possible products]}$$

$$HCl(aq) + NaOH(aq) + H_2O \longrightarrow H_3O^{\oplus}(aq) +$$
$$Cl^{\ominus}(aq) + Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

Thus the reactants and the products are the same. This implies that neither the cation nor anion of the salt reacts with water or there is no hydrolysis. Equality $H_3O^{\oplus} = OH^{\ominus}$ produced by ionization of water is not disturbed and solution is neutral. It may be concluded that salt of strong acid and strong base does not undergo hydrolysis.

3.7.4 Salts of strong acids and weak bases :

$CuSO_4$ is salt of strong acid H_2SO_4 and weak base $Cu(OH)_2$. When $CuSO_4$ is dissolved in water, it dissociates completely as,

$$CuSO_4(aq) \longrightarrow Cu^{2\oplus}(aq) + SO_4^{2\ominus}(aq)$$

$SO_4^{2\ominus}$ ions of salt have no tendency to react with water because the possible product H_2SO_4 is strong electrolyte. The reaction of $Cu^{2\oplus}$ ions with $OH^{\ominus}$ ions form unionized $Cu(OH)_2$. The hydrolytic equilibrium for $CuSO_4$ is then written as,

$$Cu^{2\oplus}(aq) + 4H_2O(l) \rightleftharpoons Cu(OH)_2(aq) + 2H_3O^{\oplus}(aq)$$

Due to the presence of excess of $H_3O^{\oplus}$ ions, the resulting solution of $CuSO_4$ becomes acidic and turns blue litmus red.

Formation of sparingly soluble $Cu(OH)_2$ by hydrolysis makes the aqueous solution of $CuSO_4$ turbid. If H_2SO_4, that is $H_3O^{\oplus}$ ions are added, the hydrolytic equilibrium shifts to the left. A turbidity of $Cu(OH)_2$ dissolves to give a clear solution. To get clear solution of $CuSO_4$, the addition of H_2SO_4 would be required.

3.7.5 Salts of weak acids and strong bases

CH_3COONa is a salt of weak acid CH_3COOH and strong base NaOH, when dissolved in water, it dissociates completely.

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus}(aq) + Na^{\oplus}(aq)$$

Water dissociates slightly as,

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

Solution of CH_3COONa contains $Na^{\oplus}$, $H_3O^{\oplus}$, $CH_3COO^{\ominus}$, $OH^{\ominus}$. The $Na^{\oplus}$ ions of salt have no tendency to react with $OH^{\ominus}$ ions of water since the possible product of the reaction is NaOH, a strong electrolyte.

On the other hand the reaction of $CH_3COO^{\ominus}$ ions of salt with the $H_3O^{\oplus}$ ions from water produces unionized CH_3COOH.

$$CH_3COO^{\ominus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^{\ominus}(aq)$$
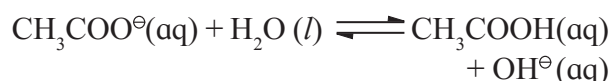
Thus, the hydrolytic equilibrium for CH_3COONa is,

$$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + Na^{\oplus}(aq) + OH^{\ominus}(aq)$$
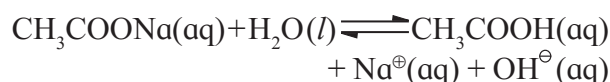
As a result of excess $OH^{\ominus}$ ions produced the solution becomes basic. The solution of CH_3COONa is therefore basic.

Can you tell ?
Why an aqueous solution of NH_4Cl is acidic while that of HCOOK basic ?

Remember...
As a general rule the solutions of salts of strong acids and strong bases are neutral, the solutions of salts of strong acids and weak bases are acidic and the solutions of salts of strong bases and weak acids are basic.
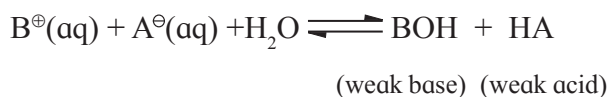
3.7.6 Salts of weak acids and weak bases:

When salt BA of weak acid HA and weak base BOH is dissolved in water, it dissociates completely as

$$BA(aq) \longrightarrow B^{\oplus}(aq) + A^{\ominus}(aq)$$

The hydrolysis reaction involves the interaction of both the ions of the salt with water,

$B^{\oplus}(aq) + A^{\ominus}(aq) + H_2O \rightleftharpoons BOH + HA$

(weak base) (weak acid)

The solution may turn out acidic, basic or neutral depending on the relative strength of weak base and weak acid formed in the hydrolysis.
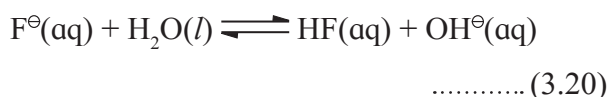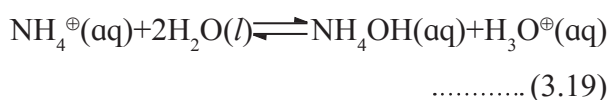
   i. if, $K_a > K_b$, the solution will be acidic.

   ii. if, $K_a < K_b$, the solution will be basic.

   iii. if, $K_a = K_b$, the solution will be neutral.

i. Salt of weak acid and weak base for which $K_a > K_b$.

NH$_4$F is a salt of weak acid HF ($K_a = 7.2 \times 10^{-4}$) and weak base NH$_4$OH (K$_b$ = 1.8 × 10^{-5}). Here, K_a is greater than K_b. The salt hydrolyses as

$NH_4^{\oplus}(aq) + F^{\ominus}(aq) + H_2O \rightleftharpoons NH_4OH(aq) + HF(aq)$

(weak base) (weak acid)
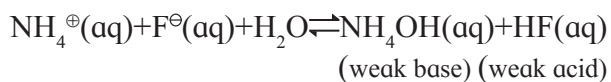
The acid HF is slightly stronger than base NH$_4$OH. The two ions react with water as

$NH_4^{\oplus}(aq) + 2H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$

.... (3.19)

$F^{\ominus}(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^{\ominus}(aq)$
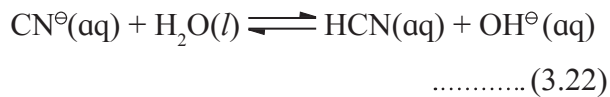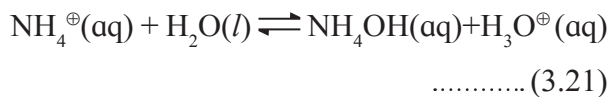
.... (3.20)

The NH$_4^{\oplus}$ ions hydrolyse to a slightly greater extent than the F$^{\ominus}$ ions. That means the reaction produces more H$_3$O$^{\oplus}$ ions than the OH$^{\ominus}$ ions produced in reaction (3.20). In other words, NH$_4^{\oplus}$ ions are slightly stronger as acid than F$^{\ominus}$ ions as base. The solution of NH$_4$F is thus only slightly acidic and turns blue litmus red.

ii. Salt of weak acid and weak base for which $K_a < K_b$: NH$_4$CN is the salt of weak acid HCN ($K_a = 4.0 \times 10^{-10}$) and weak base NH$_4$OH ($K_b = 1.8 \times 10^{-5}$) showing that $K_a < K_b$. When NH$_4$CN is dissolved in water, it hydrolyses as

$NH_4^{\oplus}(aq) + CN^{\ominus}(aq) + H_2O(l)$

$\rightleftharpoons NH_4OH(aq) + HCN(aq)$

(weak base) (weak acid)
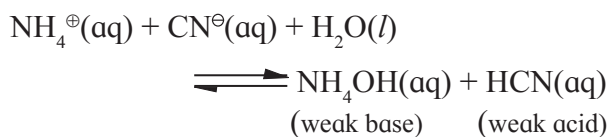
The base NH$_4$OH is stronger than the acid HCN. The ions of the salt react with water as,

$NH_4^{\oplus}(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$

.... (3.21)

$CN^{\ominus}(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^{\ominus}(aq)$

.... (3.22)

The CN$^{\ominus}$ ions hydrolyse to a greater extent than NH$_4^{\oplus}$ ions, The reaction (3.22) produces more OH$^{\ominus}$ ions than the H$_3$O$^{\oplus}$ ions produced in reaction (3.21). The solution of NH$_4$CN is, basic and turns red litmus blue.

iii. Salt of weak acid and weak base for which $K_a = K_b$.

CH$_3$COONH$_4$ is a salt of weak acid, CH$_3$COOH ($K_a = 1.8 \times 10^{-5}$) and weak base, NH$_4$OH ($K_b = 1.8 \times 10^{-5}$).

When the salt CH$_3$COONH$_4$ is dissolved in water, it undergoes hydrolysis :

$CH_3COO^{\ominus}(aq) + NH_4^{\oplus}(aq) + H_2O(l)$

$\rightleftharpoons CH_3COOH(aq) + NH_4OH(aq)$

(weak acid) (weak base)
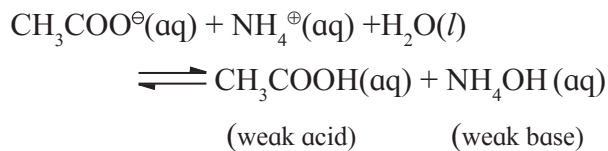
The ions of the salt react with water as

i. $CH_3COO^{\ominus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^{\ominus}(aq)$

ii. $NH_4^{\oplus}(aq) + 2H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$

As $K_a = K_b$, the relative strength of acid and base produced in hydrolysis is the same. Therefore, the solution is neutral. Hydrolysis of NH$_4^{\oplus}$ produces as many H$_3$O$^{\oplus}$ ions as that of CH$_3$COO$^{\ominus}$ produces OH$^{\ominus}$ ions.

3.8 Buffer solutions : Buffer solution is defined as a solution which resists drastic changes in pH when a small amount of strong acid or strong base or water is added to it.