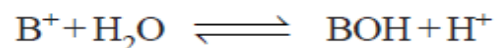


LECTURE 3

Salts of Weak bases and Strong acids

The hydrolysis of a salt of a weak base BOH (*e.g.*, NH_4OH) and a strong acid may be represented by the equation :



Hydrolysis Constant. Applying the Law of Mass Action to the above hydrolysis reaction, the hydrolysis constant, K_h , is given by

$$K_h = \frac{[\text{H}^+][\text{BOH}]}{[\text{B}^+][\text{H}_2\text{O}]}$$

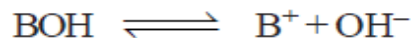
Since $[\text{H}_2\text{O}]$ is very large, it is taken to be constant and the hydrolysis constant expression is reduced to

$$K_h = \frac{[\text{H}^+][\text{BOH}]}{[\text{B}^+]} \quad \dots(1)$$

Relation between K_h , K_w and K_b . We know that the ionic product of water K_w is expressed as :

$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots(2)$$

For the dissociation of a weak base, BOH



The dissociation constant, K_b , can be expressed as :

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \quad \dots(3)$$

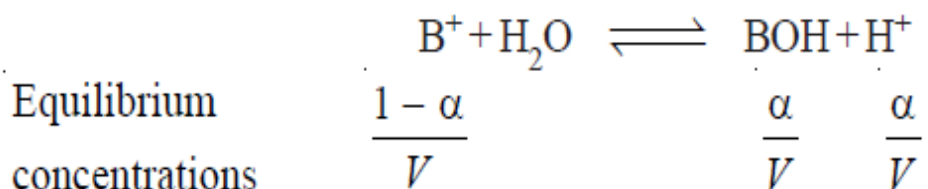
Dividing (2) by (3)

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

or
$$\frac{K_w}{K_b} = K_h \quad \dots(4)$$

Thus the hydrolysis constant, K_h , varies inversely as the dissociation constant, K_b , of the base. Therefore **weaker the base greater will be the hydrolysis constant of the salt.**

Relation between Hydrolysis constant and degree of hydrolysis. Suppose we start with one mole of the salt dissolved in V litres of solution. Then the concentrations when equilibrium is attained are :



Applying the Law of Mass Action, the hydrolysis constant, K_h is given by the expression

$$K_h = \frac{[H^+][BOH]}{[B^+]} = \frac{\alpha/V \times \alpha/V}{(1 - \alpha)/V} = \frac{\alpha^2}{(1 - \alpha)V}$$

When α is small, $(1 - \alpha)$ may be considered as equal to one. Then we have

$$K_h = \frac{\alpha^2}{V}$$

or

$$K_h \times V = \alpha^2$$

or

$$\alpha = \sqrt{K_h \times V}$$

From (4) we have

$$K_h = \frac{K_w}{K_b}$$

\therefore

$$\alpha = \sqrt{\frac{K_w}{K_b} \times V}$$

...(5)

$$= \sqrt{\frac{K_w}{K_b \times C}}$$

$$\left[\because C \propto \frac{1}{V} \right]$$

where C is the initial concentration of the salt.

Derivation of pH. From the above discussion it is clear that

$$[H^+] = \frac{\alpha}{V} = \alpha \times C$$

Substituting the value of α from equation (5), we have

$$[H^+] = \frac{1}{V} \sqrt{\frac{K_w \times V}{K_b}} = \sqrt{\frac{K_w}{K_b V}} = \sqrt{\frac{K_w \times C}{K_b}}$$

Taking logarithms and reversing the signs

$$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log C + \frac{1}{2}pK_b$$

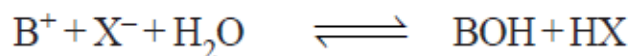
or

$$pH = 7 + \frac{1}{2}pK_b - \frac{1}{2}\log C$$

In this case it is evident that pH will always be less than 7. Thus, the solution of a salt of weak base and strong acid will always be acidic.

Salts of Weak acids and Weak bases

In this type of salt, both the anion of weak acid (X⁻) and the cation of weak base (B⁺) undergo hydrolysis simultaneously.



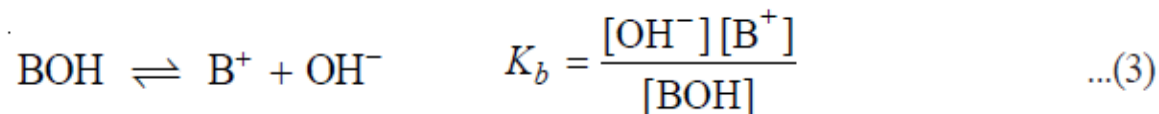
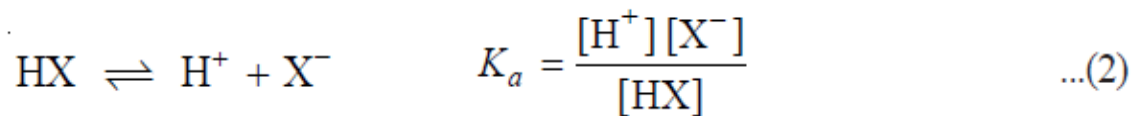
Hydrolysis constant. Applying Law of Mass Action to the above hydrolysis reaction we have the hydrolysis constant, K_h .

$$K_h = \frac{[BOH][HX]}{[B^+][X^-][H_2O]}$$

$[H_2O]$ is very large and is taken to be constant. The hydrolysis constant expression, therefore, becomes

$$K_h = \frac{[BOH][HX]}{[B^+][X^-]} \quad \dots(1)$$

Relation between K_h , K_w , K_a and K_b . Applying Law of Mass Action to the ionisation of weak acid, HX, weak base, BOH, and water, we can write



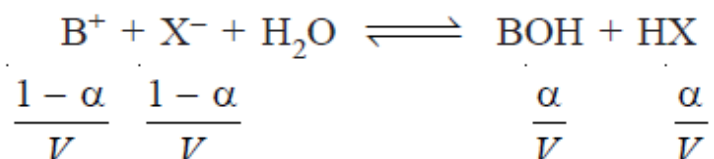
Dividing (4) by (3) and (2), we have

$$\frac{K_w}{K_a \times K_b} = \frac{[H^+][OH^-][HX][BOH]}{[X^-][H^+][B^+][OH^-]}$$

$$\therefore \quad = \frac{[\text{HX}][\text{BOH}]}{[\text{X}^-][\text{B}^+]}$$

$$\frac{K_w}{K_a \times K_b} = K_h \quad \dots(5)$$

Relation between Hydrolysis constant and Degree of Hydrolysis. Let us start with 1 mole of the salt of a weak acid and weak base. If α is the degree of hydrolysis (fraction hydrolysed), the equilibrium concentrations are :



Substituting these in the hydrolysis constant expression (1)

$$K_h = \frac{\alpha/V \times \alpha/V}{1 - \alpha/V \times 1 - \alpha/V}$$

or
$$K_h = \frac{\alpha^2}{(1 - \alpha)^2}$$

When α is small, $(1 - \alpha)$ may be taken as equal to one. Thus we have

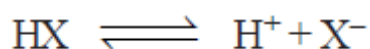
$$K_h = \alpha^2$$

or
$$\alpha = \sqrt{K_h}$$

From equation (5)
$$K_h = K_w / K_a \times K_b$$

$$\therefore \alpha = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \dots(6)$$

Derivation of pH. Hydrogen ion concentration of the solution of a salt of weak acid and weak base can be derived from the dissociation equilibrium of the weak acid, HX.



$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

$$\therefore [\text{H}^+] = \frac{K_a [\text{HX}]}{[\text{X}^-]}$$

From the hydrolysis reaction of the salt, we know that

$$[\text{HX}] = \frac{\alpha}{V} \quad \text{and} \quad [\text{X}^-] = \frac{1 - \alpha}{V}$$

Substituting these values we have

$$[\text{H}^+] = \frac{K_a \times \frac{\alpha}{V}}{\frac{1 - \alpha}{V}} = K_a \left(\frac{\alpha}{1 - \alpha} \right)$$

Ignoring α as compared to unity,

$$[\text{H}^+] = K_a \times \alpha$$

Substituting the value of α from equation (6),

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

Taking logarithms and reversing the sign throughout

$$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}K_a + \frac{1}{2}\log K_b$$

or

$$\text{pH} = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b$$

If

$$\text{p}K_a = \text{p}K_b$$

i.e., the dissociation constant of the acid is equal to that of the base,

$$\text{pH} = \frac{1}{2}\text{p}K_w = 7$$

Thus the solution will be neutral despite the fact that hydrolysis has taken place. Since the dissociation constant of acetic acid is almost the same as that of ammonium hydroxide, the solution of ammonium acetate is neutral *i.e.*, it has a pH of 7.

If $\text{p}K_a > \text{p}K_b$ *i.e.*, the acid is relatively weaker than the base, the solution will be alkaline as pH is more than 7. If $\text{p}K_a < \text{p}K_b$ *i.e.*, the acid is relatively stronger, the solution will be acidic as pH will be less than 7.

DETERMINATION OF DEGREE OF HYDROLYSIS

The degree of hydrolysis of a salt can be determined by a number of methods. The more important ones are described below.

Dissociation Constant Method

The degree of hydrolysis, α , is related to the ionic product of water, K_w , and the dissociation constant of the weak acid, K_a , or of the base, K_b , from which the salt is obtained. The various relationships are listed below :

(i) For salt of a Weak acid and Strong base :

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

(ii) For salt of a Weak base and Strong acid :

$$\alpha = \sqrt{\frac{K_w}{K_b \times C}}$$

(iii) For salt of a Weak acid and Weak base :

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Substituting the values of K_w , K_a , K_b and C , the initial concentration of the salt, in the appropriate expression, α can be calculated.

It may be noted that the degree of hydrolysis for the salt of a weak acid and weak base is independent of the concentration. However in this case, the value of α is not small and $(1 - \alpha)$ cannot be taken as equal to one. Therefore the relationship for calculating the degree of hydrolysis is considered in the form

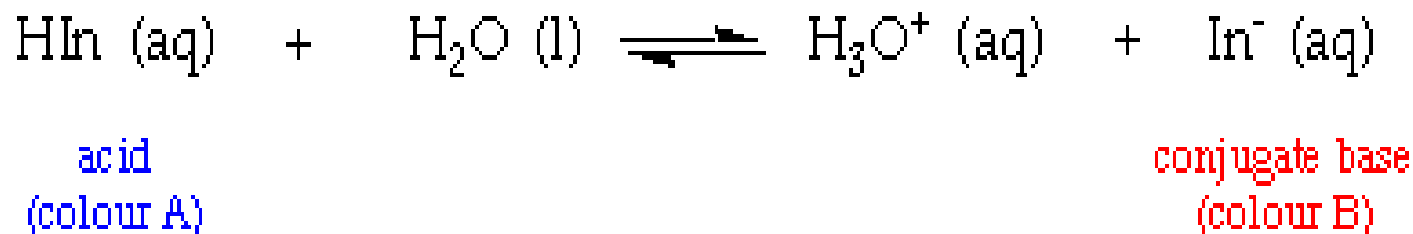
$$\frac{\alpha^2}{(1 - \alpha)^2} = \sqrt{\frac{K_w}{K_a \times K_b}}$$

This is by far the most accurate method for determining the degree hydrolysis of a salt and is used in all modern work.

Acid-Base Indicators

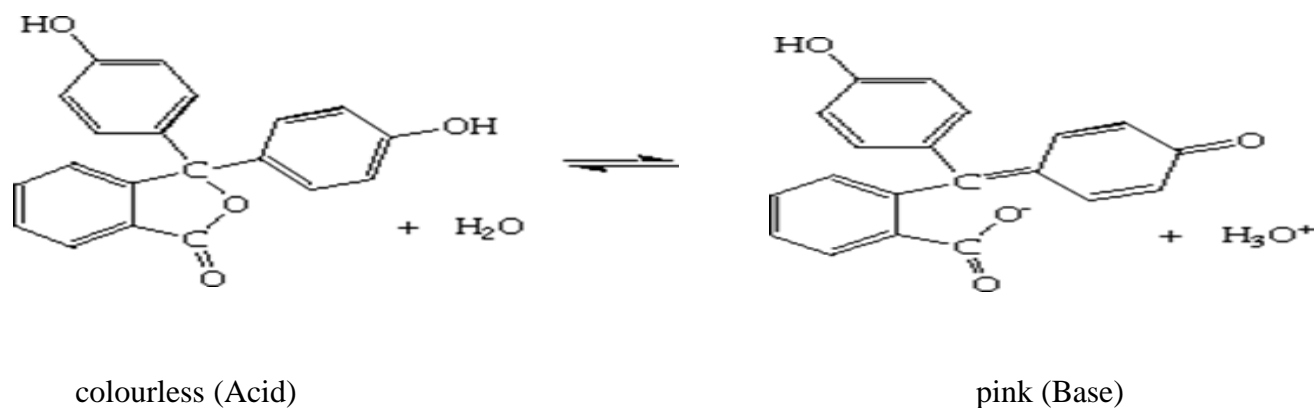
Acid - Base indicators (also known as pH indicators) are substances which change colour with pH. They are usually weak acids or bases, which when dissolved in water dissociate slightly and form ions.

Consider an indicator which is a weak acid, with the formula HIn. At equilibrium, the following equilibrium equation is established with its conjugate base



The acid and its conjugate base have different colours. At low pH values the concentration of H_3O^+ is high and so the equilibrium position lies to the left. The equilibrium solution has the colour A. At high pH values, the concentration of H_3O^+ is low - the equilibrium position thus lies to the right and the equilibrium solution has colour B.

Phenolphthalein is an example of an indicator which establishes this type of equilibrium in aqueous solution:



Phenolphthalein is a colourless, weak acid which dissociates in water forming pink anions. Under acidic conditions, the equilibrium is to the left, and the concentration of the anions is too low for the pink colour to be observed. However, under alkaline conditions, the equilibrium is to the right, and the concentration of the anion becomes sufficient for the pink colour to be observed.

We can apply equilibrium law to indicator equilibria - in general for a weak acid indicator:

$$K_{\text{In}} = \left(\frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \right)_{\text{eq}}$$

K_{In} is known as the indicator dissociation constant. The colour of the indicator turns from colour A to colour B or vice versa at its turning point. At this point:

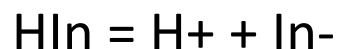
$$[\text{HIn}] = [\text{In}^-]$$

So from equation:

$$K_{\text{In}} = [\text{H}_3\text{O}^+]$$

The pH of the solution at its turning point is called the $\text{p}K_{\text{In}}$ and is the pH at which half of the indicator is in its acid form and the other half in the form of its conjugate base.

we represent a general indicator by the formula HIn , and its ionization in a solution by the equilibrium,



and define the equilibrium constant as K_{In} ,

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

Which can be rearranged to give

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}^+]}$$

When $[\text{H}^+]$ is greater than $10 K_{\text{In}}$, In^- color dominates, whereas color due to HIn dominates if $[\text{H}^+] < K_{\text{In}} / 10$. The above equation indicates that the color change is the most sensitive when $[\text{H}^+] = K_{\text{In}}$ in numerical value.

We define $pK_{In} = -\log(K_{In})$, and the pK_{In} value is also the pH value at which the color of the indicator is most sensitive to pH changes.

Taking the negative log of K_{In} gives,

$$-\log K_{In} = -\log[H^+] - \log \frac{[In^-]}{[HIn]}$$

or

$$pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$$

This is a very important formula, and its derivation is very simple. Start from the definition of the equilibrium constant K , you can easily derive it. Note that $pH = pK_{In}$ when $[In^-] = [HIn]$. In other words, when the pH is the same as pK_{In} , there are equal amounts of acid and base forms. When the two forms have equal concentration, the color change is most noticeable.

Colors of substances make the world a wonderful place. Because of the colors and structures, flowers, plants, animals, and minerals show their unique characters.

Many indicators are extracted from plants. For example, red cabbage juice and tea pigments show different colors when the pH is different. The color of tea darkens in a basic solution, but the color becomes lighter when lemon juice is put into a tea. Red cabbage juice turns blue in a basic solution, but it shows a distinct red color in an acidic solution