28

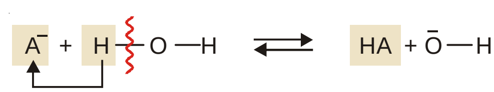
CHAPTER

Salt Hydrolysis

CONTENTS

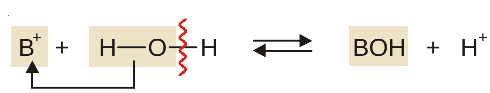
WHAT IS HYDROLYSIS?

The salt of a weak acid, HA and a strong base dissolves in water to form the anion A^-. The A^- anion tends to react with water by drawing a proton (H^+) from its molecule to form the unionised molecule.



...(1)

Similarly, the salt of a weak base, BOH, and a strong acid dissolves in water to form the cation B^+. The cation B^+ reacts with water by accepting OH^- ions from its molecule.



...(2)

The reaction of an anion or cation with water accompanied by cleavage of O–H bond is called Hydrolysis.

The term hydrolysis is derived from *hydro*, meaning water, and *lysis*, meaning breaking. It may be noted that in **anionic hydrolysis** shown in (1) the solution becomes slightly basic (pH > 7) due to the generation of excess OH^- ions. In **cationic hydrolysis** shown in (2), there is excess of H^+ ions which makes the solution slightly acidic (pH < 7).

BRONSTED–LOWRY CONCEPT OF HYDROLYSIS

HA and A^- are conjugate acid-base pair

$$\underset{\text{weak acid}}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{conjugate base}}{A^-}$$

Since HA is a weak acid (poor proton donor), its conjugate base, A^-, must be relatively strong (good proton acceptor). Owing to this fact, A^- ions tend to react with water by accepting proton from the latter to form HA molecule (anionic hydrolysis),

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

The presence of OH^- ions makes the solution basic.

Similarly, BOH and B^+ are a conjugate acid-base pair. Since BOH is a weak base, its conjugate acid, B^+, would be relatively strong. Thus B^+ would accept OH^- ions from water to form BOH molecules.

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

The presence of excess H^+ ions makes the solution acidic.

Why NaCl solution is neutral ?

NaCl dissociates in water to give the anion Cl^-. HCl and Cl^- constitute an acid-base conjugate pair.

$$HCl + H_2O \rightleftharpoons H_3O^+ + \underset{\text{conjugate base}}{Cl^-}$$

Since HCl is a strong acid, Cl^- is very weak base. Cl^- is unable to accept a proton (H^+) from an acid, particularly water. That is why Cl^- does not hydrolyse. It cannot generate OH^- ions as follows:

$$Cl^- + H_2O \not\longrightarrow HCl + OH^-$$

The pH of sodium chloride solution remains unaffected.

EXAMPLES OF HYDROLYSIS

The different salts may be classified into the following types according to their hydrolytic behaviour:

(1) Salts of Weak acids and Strong bases

(2) Salts of Weak bases and Strong acids

(3) Salts of Weak acids and Weak bases

We have already considered that a salt of strong acid and strong base *e.g.*, NaCl, does not show hydrolysis.

Salts of Weak acids and Strong bases

Sodium acetate, CH_3COONa, and sodium cyanide, NaCN, are examples of this type of salts.

Sodium acetate, CH_3COONa. This is a salt of the weak acid, CH_3COOH, and strong base, NaOH. It ionises in aqueous solution to form the anion CH_3COO^-. Being the conjugate base of a weak acid, CH_3COOH, it is a relatively strong base. Thus CH_3COO^- accepts H^+ ion from water and undergoes hydrolysis.

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

The resulting solution is slightly basic due to excess OH^- ions present.

Sodium Cyanide, NaCN. It is the salt of a weak acid, HCN, and a strong base, NaOH. It ionises to form CN^- anions. Being conjugate base of a weak acid, CN^- is relatively strong base. Thus the anion CN^- accepts a H^+ ion from water and undergoes hydrolysis.

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

The solution becomes basic due to the generation of OH^- ions.

Salts of Weak bases and Strong acids

Some salts of weak bases and strong acids undergo cationic hydrolysis and yield slightly acidic solutions.

Ammonium chloride is a typical example of this class of salts. It is the salt of a weak base. NH_4OH, and strong acid, HCl. It ionises in aqueous solution to form the cation, NH_4^+.

$$NH_4OH \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^+} + OH^-$$

NH_4^+ is a Bronsted conjugate acid of the weak base NH_4OH. Therefore, it is a relatively strong acid. It accepts OH^- ion from water (H_2O) and forms the unionised NH_4OH and H^+ ion.

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

The accumulation of H^+ ions in solution makes it acidic.

The other examples of this type of salts are ferric chloride, aluminium chloride, and copper sulphate.

Salts of Weak acids and Weak bases

The examples of this type of salts are ammonium acetate, ammonium cyanide and ammonium fluoride. Both the anion and the cation produced by ionisation of the salt undergo hydrolysis. The resulting solution is neutral, basic or acidic depending on the relative hydrolysis of the anions and the cations.

Ammonium acetate, CH_3COONH_4. It is the salt of weak acid, CH_3COOH, and weak base, NH_4OH. In aqueous solution it ionises to form the anion CH_3COO^- and the cation NH_4^+. Since the acid and the base are both weak, their conjugate base (CH_3COO^-) and conjugate acid (NH_4^+) are relatively strong. They accept H^+ and OH^- ions respectively from water and undergo considerable hydrolysis.

$$\underset{\text{conjugate base}}{CH_3COO^-} + H_2O \rightleftharpoons CH_3COOH + OH^- \quad ...(1)$$

$$\underset{\text{conjugate acid}}{NH_4^+} + H_2O \rightleftharpoons NH_4OH + H^+ \quad ...(2)$$

The overall hydrolysis may be represented as

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

We have stated above that pH of the resulting solution will depend on the relative extent of anionic hydrolysis (1) and cationic hydrolysis (2). If both the ions react to the same extent (as shown for CH_3COONH_4), $[OH^-] = [H^+]$ and the solution is neutral. If the cation reacts to a greater extent, the solution is slightly acidic. If the anion is a little more reactive, the solution will be basic. Thus, a solution of CH_3COONH_4 is neutral, a solution of NH_4CN is slightly basic and a solution of NH_4F is slightly acidic.

QUANTITATIVE ASPECT OF HYDROLYSIS

Hydrolysis is a reversible reaction. The equilibrium constant derived by application of Law of Mass action to a hydrolysis (or hydrolytic) reaction is called the **Hydrolysis constant** or **Hydrolytic**

constant. The hydrolysis constant is represented by K_h.

Now, we proceed to discuss the mathematics of hydrolysis of the various types of salts.

Salt of a Weak acid and Strong base

The general hydrolysis reaction of a salt of weak acid (HA) and strong acid can be written as

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

This leads to the equilibrium constant expression

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

The concentration of water, $[H_2O]$, is very large and is regarded as practically constant. Thus the hydrolysis constant expression assumes the form

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

Relation between K_h, K_w and K_a

We know that the ionic product of water, K_w, is expressed as

$$K_w = [H^+]\,[OH^-] \qquad \text{...(2)}$$

For the dissociation of a weak acid, HA,

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

the acid dissociation constant, K_a, is expressed as

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

Dividing (2) by (3)

$$\frac{K_w}{K_a} = \frac{[OH^-]\,[HA]}{[A^-]} = K_h \qquad \text{[by equation (1)]}$$

or

$$\frac{K_w}{K_a} = K_h \qquad \text{...(4)}$$

It is clear from (4) that the hydrolysis constant (K_h) of the salt varies inversely as the dissociation constant K_a of the weak acid. Therefore, **weaker the acid greater is the hydrolysis constant of the salt.**

Relation between Hydrolysis constant and Degree of hydrolysis

The degree of hydrolysis is the fraction of the salt which has undergone hydrolysis when equilibrium is established. It is generally represented by α.

Suppose we start with one mole of the salt dissolved in V litres of solution. Then the equilibrium concentrations are :

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

	A^-	HA	OH^-
Equilibrium concentrations	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

Hence the hydrolysis constant K_h is given by

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]} = \frac{\alpha/V \times \alpha/V}{1-\alpha/V} = \frac{\alpha^2}{(1-\alpha)V}$$

If α is small, $(1-\alpha)$ may be taken as equal to one. Then,

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

or $$\alpha^2 = K_h V = \frac{K_w}{K_a} V$$

∴ $$\alpha = \sqrt{\frac{K_w V}{K_a}}$$

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

where C is the initial concentration of the salt. Knowing the values of K_w, K_a and C, the degree of hydrolysis can be calculated.

Derivation of pH. The pH of an aqueous solution of weak acid and strong base can be derived as follows :

From earlier discussion, we know that

$$[OH^-] = \frac{\alpha}{V} = \alpha C$$

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

∴ $$[H^+] = \frac{K_w}{\alpha C}$$

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

∴ $$[H^+] = \frac{K_w}{C}\sqrt{\frac{K_a C}{K_w}} = \sqrt{\frac{K_w K_a}{C}}$$

Taking logarithms and reversing the sign throughout

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

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

It is evident that pH of the solution will always be greater than 7. Thus **aqueous solution of salt of weak acid and strong base will be always alkaline.**

SOLVED PROBLEM 1. Calculate the hydrolysis constant and pH of 0.625 M solution of CH_3COONa. K_a 1.754×10^{-5}.

SOLUTION

Calculation of K_h

We know that for salt of a weak acid and strong base

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

Substituting the values of K_w and K_a

$$K_h = \frac{10^{-14}}{1.754 \times 10^{-5}} = \mathbf{5.701 \times 10^{-10}}$$

Calculation of pH

The hydrolysis equation is :

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

Thus, $$K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]}$$

If x be the concentration of CH_3COOH and OH^- ions at equilibrium, the concentration of CH_3COO^- ions is $0.625 - x$. Substituting these values in the hydrolysis constant expression

$$K_h = \frac{x \times x}{0.625 - x} = 5.701 \times 10^{-10}$$

Assuming that x is negligible as compared to 0.625,

$$x^2 = 0.625 \times (5.701 \times 10^{-10}) = 3.56 \times 10^{-10}$$

$$x = \sqrt{3.56 \times 10^{-10}} = 1.89 \times 10^{-5}\ \text{M}$$

Hence $$[OH^-] = 1.89 \times 10^{-5}\ \text{M}$$

$$pOH = -\log [OH^-] = -\log (1.89 \times 10^{-5}) = 4.72$$

$$pH = 14.00 - pOH = 14.00 - 4.72$$

$$= \mathbf{9.28}$$

SOLVED PROBLEM 2. What is the pH of a 0.2 M solution of NaCN ? K_a for HCN = 4.0×10^{-10}.

SOLUTION

Calculation of Hydrolysis Constant

NaCN is the salt of weak acid HCN and strong base. Therefore,

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{4 \times 10^{-10}} = \mathbf{2.5 \times 10^{-5}}$$

Calculation of pH

From the hydrolysis reaction,

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$K_h = \frac{[HCN]\,[OH^-]}{[CN^-]} = 2.5 \times 10^{-5}$$

Let x be the concentration of OH^- ions produced by hydrolysis. Therefore at equilibrium, we have

$$[HCN] = x$$

$$[OH^-] = x$$

$$[CN^-] = 0.2 - x = 0.2 \text{ because } x \text{ is negligible}$$

Substituting these values in the expression above,

$$K_h = \frac{x \times x}{0.2} = 2.5 \times 10^{-5}$$

$$x = \sqrt{2.5 \times 0.2 \times 10^{-5}}$$

Hence, $[OH^-] = x = 2.24 \times 10^{-3}$

$$pOH = -\log(2.24 \times 10^{-3}) = 2.65$$

$$pH = 14 - pOH = \mathbf{11.35}$$

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 :

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

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

$$K_h = \frac{[H^+][BOH]}{[B^+][H_2O]}$$

Since $[H_2O]$ is very large, it is taken to be constant and the hydrolysis constant expression is reduced to

$$K_h = \frac{[H^+][BOH]}{[B^+]} \qquad ...(1)$$

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

$$K_w = [H^+][OH^-] \qquad ...(2)$$

For the dissociation of a weak base, BOH

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

The dissociation constant, K_b, can be expressed as :

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

Dividing (2) by (3)

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

or

$$\frac{K_w}{K_b} = K_h \qquad ...(4)$$

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 :

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

Equilibrium concentrations $\qquad \frac{1-\alpha}{V} \qquad\qquad \frac{\alpha}{V} \qquad \frac{\alpha}{V}$

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

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

∴ $$\alpha = \sqrt{\frac{K_w}{K_b} \times V} \qquad ...(5)$$

$$= \sqrt{\frac{K_w}{K_b \times C}} \qquad \left[\because C \propto \frac{1}{V}\right]$$

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.**

SOLVED PROBLEM 1. Calculate the pH of a 0.20 M solution of ammonium chloride, $K_b = 1.8 \times 10^{-5}$.

SOLUTION

Calculation of K_h

NH_4Cl is salt of a weak base NH_4OH and strong acid HCl. Therefore,

$$K_h = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \mathbf{5.56 \times 10^{-10}}$$

Calculation of pH

The hydrolysis of NH_4Cl can be represented as

$$\underset{0.20-x}{NH_4^+} + H_2O \rightleftharpoons \underset{x}{NH_4OH} + \underset{x}{H^+}$$

Let x be the concentration of NH_4OH and H^+ at equilibrium. The concentration of NH_4^+ will be $(0.20 - x)$.

Thus,

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$$= \frac{x \times x}{0.20} \qquad (\because x \text{ is small})$$

or $$x^2 = K_h \times 0.20 = (5.56 \times 10^{-10}) \times 0.20$$

∴ $$x = \sqrt{1.11 \times 10^{-10}} = [H^+] = 1.053 \times 10^{-5} \text{ mol l}^{-1}$$

and $$\text{pH} = -\log [H^+] = -\log (1.053 \times 10^{-5}) = \mathbf{4.9775}$$

SOLVED PROBLEM 2. Calculate the pH value of 0.15 M solution of ammonium chloride if the dissociation constant for ammonia is 1.80×10^{-5}.

SOLUTION

This is an alternative solution to that given for Example 1.

Here we use the expression

$$\text{pH} = \frac{1}{2}\text{p}K_w - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log C$$

Now $$\text{p}K_w = -\log K_w = -\log 1 \times 10^{-14} = 14$$

$$\text{p}K_b = -\log K_b = -\log (1.8 \times 10^{-5}) = 4.7444$$

and $$\log C = \log (0.15) = -0.8239$$

∴ $$\text{pH} = 7 - 2.3722 - (-0.4119)$$

$$= \mathbf{5.0397}$$

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.

$$B^+ + X^- + H_2O \rightleftharpoons BOH + HX$$

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

$$K_h = \frac{[BOH]\,[HX]}{[B^+]\,[X^-]} \qquad ...(1)$$

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

$$HX \rightleftharpoons H^+ + X^- \qquad K_a = \frac{[H^+]\,[X^-]}{[HX]} \qquad ...(2)$$

$$BOH \rightleftharpoons B^+ + OH^- \qquad K_b = \frac{[OH^-]\,[B^+]}{[BOH]} \qquad ...(3)$$

$$K_w = [H^+]\,[OH^-] \qquad ...(4)$$

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

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

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

$$\frac{K_w}{K_a \times K_b} = K_h \qquad ...(5)$$

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 :

$$\begin{array}{cccccc} B^+ & + \; X^- & + \; H_2O & \rightleftharpoons & BOH & + \; HX \\ \frac{1-\alpha}{V} & \frac{1-\alpha}{V} & & & \frac{\alpha}{V} & \frac{\alpha}{V} \end{array}$$

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)

$$K_h = K_w/K_a \times K_b$$

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

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.

$$HX \rightleftharpoons H^+ + X^-$$

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

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

From the hydrolysis reaction of the salt, we know that

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

Substituting these values we have

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

Ignoring α as compared to unity,

$$[H^+] = K_a \times \alpha$$

Substituting the value of α from equation (6),

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

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.

SOLVED PROBLEM. Calculate the pH of a solution of ammonium acetate. Given that : $K_a = 1.75 \times 10^{-5}$, $K_b = 1.8 \times 10^{-5}$ and $K_w = 1.0 \times 10^{-14}$.

SOLUTION

We know that

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

Now,
$$\frac{1}{2}\text{p}K_w = -\frac{1}{2}\log(1.0 \times 10^{-14}) = 7$$

$$\frac{1}{2}\text{p}K_a = -\frac{1}{2}\log K_a = -\frac{1}{2}\log(1.75 \times 10^{-5})$$

$$= \frac{1}{2} \times 4.7570 = 2.3785$$

and
$$\frac{1}{2}\log K_b = -\frac{1}{2}\log(1.8 \times 10^{-5})$$

$$= \frac{1}{2} \times 4.7447 = 2.3723$$

$\therefore$
$$\text{pH} = 7 + 2.3785 - 2.3723$$
$$= \mathbf{7.006}$$

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 relationship 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.

SOLVED PROBLEM 1. What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for NaCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$.

SOLUTION

Since NaCN is the salt of a weak acid (HCN) and strong base (NaOH), the degree of hydrolysis, α is given by the expression

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

$$= \frac{1.0 \times 10^{-14} \times 80}{1.3 \times 10^{-9}}$$

$$= \sqrt{6.16 \times 10^{-4}}$$

$$= 2.48 \times 10^{-2}$$

$\therefore$ Percentage hydrolysis of NaCN in N/80 solution is **2.48.**

SOLVED PROBLEM 2. Calculate the hydrolysis constant and degree of hydrolysis of NH_4Cl in 0.001 M solution. $K_b = 1.8 \times 10^{-5}$, $K_w = 1.0 \times 10^{-14}$.

SOLUTION

Since NH_4Cl is the salt of a weak base and a strong acid, the degree of hydrolysis, α, is given by the expression

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

$$= \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.001}}$$

$$= \sqrt{5.5 \times 10^{-7}}$$
$$= 7.4 \times 10^{-4} = 0.00074$$

For the salt of a weak base and strong acid,

$$K_h = \frac{K_w}{K_b}$$
$$= \frac{10^{-14}}{1.8 \times 10^{-5}} = \mathbf{5.55 \times 10^{-10}}$$

SOLVED PROBLEM 3. Calculate the degree of hydrolysis of ammonium acetate, if the dissociation constant of ammonium hydroxide is 1.8×10^{-5}, that for acetic acid is 1.8×10^{-5} and the ionic product of water is 1.0×10^{-14}

SOLUTION

Ammonium acetate is the salt of a weak acid (CH_3COOH) and weak base (NH_4OH).

$$\therefore \quad K_h = \frac{K_w}{K_a \times K_b}$$

We know that

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

Thus,
$$\frac{\alpha^2}{(1-\alpha)^2} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}$$

or
$$\frac{\alpha}{1-\alpha} = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}}$$
$$= \frac{1.0 \times 10^{-2}}{1.8} = \frac{1}{180}$$

Hence
$$\alpha = 0.0055 = \mathbf{0.55 \times 10^{-2}}$$

From Conductance measurements

The degree of hydrolysis, α, of a salt can be determined by conductance measurements. Let us consider a solution containing the salt of a weak base and a strong acid. The hydrolysis reaction can be written as

$$\underset{(1-\alpha)}{B^+} + H_2O \rightleftharpoons \underset{\alpha}{BOH} + \underset{\alpha}{H^+}$$

If it be assumed that the base is so weak that it is not dissociated at all, it will contribute nothing to conductance of the solution. The equivalent conductance of the salt, therefore, consists of :

(*a*) that due to $(1 - \alpha)$ equivalents of the salt.

(*b*) that due to α equivalents of the acid produced by hydrolysis.

Thus, we can say that :

$$\wedge = (1-\alpha)\wedge_{salt} + \alpha \wedge_{acid}$$
$$\wedge - \wedge_{salt} = \alpha(\wedge_{acid} - \wedge_{salt})$$

or
$$\alpha = \frac{\wedge - \wedge_{salt}}{(\wedge_{acid} - \wedge_{salt})}$$

$\wedge$ is found by conductance measurements. $\wedge_{acid}$ is taken as the value for strong acid at infinite dilution. $\wedge_{acid}$ is determined by adding excess of weak base to the solution to suppress hydrolysis so that the resulting experimentally determined value of $\wedge$ can be taken as that of the unhydrolysed salt.

SOLVED PROBLEM. The equivalent conductance of a solution of aniline hydrochloride, $C_6H_5NH_3Cl$, was found to be 144 ohm^{-1} cm^2 eqvt^{-1} at a certain dilution and at 25°C. In the presence of excess of aniline, the value of conductance is 103.6 ohm^{-1} cm^2 eqvt^{-1}. If $\wedge$ for HCl at this temperature is 383, calculate the degree of hydrolysis.

SOLUTION

$$\alpha = \frac{\wedge - \wedge_{salt}}{\wedge_{HCl} - \wedge_{salt}}$$

Substituting the values

$$\alpha = \frac{144 - 103.6}{383 - 103.6} = \mathbf{0.1445}$$

EXAMINATION QUESTIONS

1. Define or explain the following terms :
   (*a*) Anionic Hydrolysis (*b*) Cationic Hydrolysis
   (*c*) Hydrolysis constant (*d*) Degree of Hydrolysis
2. Sodium phenate is hydrolysed to the extent of 0.03% in 0.1 M aqueous solution at 25°C. Calculate
   (*i*) The hydrolysis constant of the salt; and (*ii*) the ionic product of water at 25°C. The dissociation constant of phenol is 1.3×10^{-10} at 25°C.
   Answer. (*i*) 9×10^{-5}; (*ii*) 1.17×10^{-14}
3. A 0.02 M solution of sodium acetate in water at 25°C has a hydrogen ion concentration of 3×10^{-9} M. What is the hydrolysis constant of the salt?
   Answer. 5.5×10^{-10}
4. (*a*) What is hydrolysis constant of salt? Why aqueous solution of sodium carbonate is alkaline? Derive an expression for the hydrolysis constant and pH of this solution.
   (*b*) Calculate the pH of a decinormal solution of ammonium chloride. (pK_a = 5.7 and pK_w = 14)
   Answer. 10.35
5. The dissociation constant of acetic acid is 1.8×10^{-5} at 18°C. The ionic product of water is 10^{-14} at 18°C. What would be the degree of hydrolysis in a 0.012 N solution of sodium acetate?
   Answer. 2.150×10^{-6}
6. What is meant by the terms 'Degree of Hydrolysis' and 'Hydrolysis constant'? Deduce the relation between hydrolysis constant and the dissociation constant of the base in the case of the hydrolysis of a salt of a strong acid and a weak base.
7. (*a*) What is hydrolysis? Derive an expression for the hydrolysis constant of a salt of a weak acid and a strong base in terms of dissociation constant of a weak acid and ionic product of water.
   (*b*) Calculate the degree of hydrolysis of sodium acetate. Dissociation constant of acetic acid is 1.80×10^{-5}. Ionic product of water is 1×10^{-14}.
   Answer. (*b*) 7.452×10^{-5}
8. Derive the relation between hydrolysis constant ionic product of water and dissociation constant of a strong acid and a weak base.

9. Ammonium hydroxide undergoes hydrolysis in aqueous solution. Give the equation for the hydrolysis constant and show that it is related to dissociation constant of ammonium hydroxide.

10. Calculate the hydrolysis constant, degree of hydrolysis and pH value of 10^{-2} M NH_4Cl solution at 298 K. ($K_b = 1.8 \times 10^{-5}$ and $K_w = 1.0 \times 10^{-14}$)

Answer. 5.555×10^{-10}; 2.357×10^{-9}; 3.372

11. Deduce an expression for the degree of hydrolysis of a salt of a weak acid and a strong base.

12. What is hydrolysis? For a salt of weak acid and weak base, derive

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

13. The hydrogen ion concentration of 0.02 M sodium acetate solution is found to be 3.0×10^{-9} M at 25°C. Calculate the hydrolysis constant of this salt. $K_w = 1.0 \times 10^{-14}$.

Answer. 5.555×10^{-10}

14. Explain degree of hydrolysis and hydrolysis constant. (*Guru Nanak Dev BSc, 2000*)

15. Obtain expression for the hydrolysis constant and degree of hydrolysis for the salt of a strong acid and weak base. (*Panjab BSc, 2000*)

16. Derive $K_h = \dfrac{K_w}{K_a}$ or $K_h = \dfrac{K_w}{K_b}$

and write the equation for pH of this solution using K_w, K_a, K_b and c. (*Jiwaji BSc,2002*)

17. What is meant by the terms 'Degree of hydrolysis' and 'Hydrolysis constant'?

(*MD Rohtak BSc, 2002*)

18. Find out the expression for hydrolysis constant of a salt of strong acid and weak base in terms of K_w and K_h. (*Purvanchal BSc, 2002*)

19. Show that the degree of hydrolysis of ammonium acetate is independent of concentration.

(*Kalyani BSc, 2003*)

20. (*a*) Define salt hydrolysis and degree of hydrolysis. Establish a relation between hydrolysis constant and dissociation constant of a salt of weak acid and weak base.

(*b*) Calculate the hydrolysis constant and degree of hydrolysis of 0.1 M sodium acetate solution.

Given : $K_w = 1.0 \times 10^{-14}$, $K_a = 1.75 \times 10^{-6}$

Answer. 7.5×10^{-5} (*Delhi BSc, 2004*)

21. (*a*) Explain why an aqueous solution of $CuSO_4$ is acidic and that of NaCl is neutral.

(*b*) Calculate the percentage of hydrolysis of sodium acetate in 0.1 N solution at 25°C using the following data. It is to be assumed that the salt is completely dissociated. $K_a = 1.8 \times 10^{-5}$; $K_w = 1.02 \times 10^{-14}$.

Answer. (*b*) 7.452×10^{-5} (*Mysore BSc, 2004*)

22. 20 ml of 0.2 M NaOH solution be treated with 40 ml of 0.2 M acetic acid solution to give 70 ml. Calculate the *pH* of the solution.

Answer. 4.5684 (*Madras BSc, 2005*)

23. Calculate the *pH* at the equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH. K_a for acetic acid is 1.9×10^{-5}.

Answer. 8.71 (*Baroda BSc, 2005*)

24. Calculate the percentage hydrolysis of sodium acetate in 0.1 N solution at 298 K, assuming the salt to be completely dissociated. (K_a for Acetic acid = 1.8×10^{-5})

Answer. 0.0075% (*Nagpur BSc, 2006*)

25. What happens to the *pH* of 500 ml of solution that is 0.1 molar in sodium acetate and 0.1 molar in acetic acid when 10 ml of 0.1 M NaOH is added ?

Answer. *pH* will increase (*Agra BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. The reaction of an anion or cation with water accompanied by cleavage of O–H bond is called
(*a*) neutralization (*b*) hydrolysis
(*c*) acidification (*d*) ionisation
Answer. (*b*)

2. In anionic hydrolysis the pH of solution is
(*a*) greater than 7 (*b*) equal to 7
(*c*) less than 7 (*d*) less than zero
Answer. (*c*)

3. In cationic hydrolysis, the resulting solution is
(*a*) acidic (*b*) basic
(*c*) neutral (*d*) sometimes acidic, sometimes basic
Answer. (*b*)

4. A salt of weak acid and strong base on hydrolysis yields a solution which is
(*a*) slightly acidic (*b*) slightly basic
(*c*) neutral (*d*) highly acidic
Answer. (*b*)

5. NaCN on hydrolysis produces a solution which has
(*a*) pH > 7 (*b*) pH = 7
(*c*) pH < 7 (*d*) pH = 0
Answer. (*b*)

6. A salt of weak base and strong acid on hydrolysis gives a solution which has
(*a*) more H^+ ions than OH^- (*b*) more OH^- ions than H^+
(*c*) equal H^+ and OH^- ions (*d*) no H^+ ions
Answer. (*a*)

7. A salt of weak acid and weak base on hydrolysis gives a solution which is
(*a*) acidic (*b*) basic
(*c*) neutral (*d*) sometimes acidic, sometimes basic
Answer. (*d*)

8. The hydrolysis constant of a salt of weak acid and strong base is given by the expression
(*a*) $K_h = \frac{[HA][OH^-]}{[A^-]}$ (*b*) $K_h = \frac{[HA][H^+]}{[A^-]}$
(*c*) $K_h = \frac{[HA][A^-]}{[OH^-]}$ (*d*) $K_h = \frac{[HA][A^-]}{[OH^-]}$
Answer. (*a*)

9. The dissociation constant of weak acid, K_a and that of a base K_b are related to hydrolysis constant of the salt by the relation
(*a*) $K_w = K_a \times K_b$ (*b*) $K_a = K_w \times K_b$
(*c*) $K_b = K_w \times K_a$ (*d*) $K_w = K_a / K_b$
Answer. (*a*)

10. Weaker the acid, greater is the
(*a*) ionic product (*b*) dissociation constant
(*c*) hydrolysis constant (*d*) degree of ionisation
Answer. (*c*)

11. The degree of hydrolysis of a salt is that fraction of it which undergoes _______ when equilibrium is established.

(*a*) dissociation (*b*) racemisation

(*c*) saponification (*d*) hydrolysis

Answer. (*d*)

12. The aqueous solution of salt of a weak acid and strong base will always be

(*a*) acidic (*b*) alkaline

(*c*) neutral (*d*) none of these

Answer. (*b*)

13. The pH of an aqueous solution of weak acid and strong base is given by the relation

(*a*) pH = 7 + ½ pK_a + ½ log C (*b*) pH = 7 + ½ pK_a – ½ log C

(*c*) pH = 7 – ½ pK_a + ½ log C (*d*) pH = 7 – ½ pK_a – ½ log C

Answer. (*a*)

14. The hydrolysis constant of a salt of weak base and strong acid is given by

(*a*) $K_h = \frac{[H^+][BOH]}{[B^+]}$ (*b*) $K_h = \frac{[H^+][B^+]}{[BOH]}$

(*c*) $K_h = \frac{[H^+][OH^-]}{[B^+]}$ (*d*) $K_h = \frac{[H^+][B^+]}{[BOH]^2}$

Answer. (*a*)

15. The dissociation constant K_b, the hydrolysis constant K_h and ionic product K_w are related to each other by the relation

(*a*) $K_w / K_b = K_h$ (*b*) $K_w / K_h = K_b$

(*c*) $K_w = K_h \times K_b$ (*d*) all of these

Answer. (*d*)

16. The hydrolysis constant K_h of a weak base and a strong acid is _______ to the dissociation constant K_b, of the base

(*a*) directly proportional (*b*) inversely proportional

(*c*) equal (*d*) not equal

Answer. (*b*)

17. The degree of hydrolysis of a weak base and strong acid is given by the relation

(*a*) $\alpha = \sqrt{\frac{K_b}{K_h \times C}}$ (*b*) $\alpha = \frac{K_b}{K_h \times C}$

(*c*) $\alpha = \frac{K_b}{K_h \times C^2}$ (*d*) $\alpha = \frac{K_b}{K_h \times \sqrt{C}}$

Answer. (*a*)

18. The pH of a solution of a salt of weak base and strong acid is

(*a*) greater than 7 (*b*) less than 7

(*c*) equal to 7 (*d*) equal to zero

Answer. (*b*)

19. The pH of a solution of a salt of weak base and strong acid is given by the expression

(*a*) pH = 7 + ½ pK_b + ½ log C (*b*) pH = 7 + ½ pK_b – ½ log C

(*c*) pH = 7 – ½ pK_b + ½ log C (*d*) pH = 7 – ½ pK_b – ½ log C

Answer. (*b*)

20. Which is the correct relation for a salt of weak acid and a weak base?

(*a*) $K_h = \frac{K_w}{K_a \times K_b}$ (*b*) $K_h = \frac{K_w \times K_a}{K_b}$

(c) $K_h = \frac{K_w \times K_b}{K_a}$ (d) $K_h = K_w \times K_a \times K_b$

Answer. (*a*)

21. The degree of hydrolysis of a salt of weak acid and weak base is given by the expression

(*a*) $\alpha = \sqrt{\frac{K_w \times K_b}{K_a}}$ (*b*) $\alpha = \sqrt{\frac{K_w \times K_a}{K_b}}$

(*c*) $\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$ (*d*) $\alpha = \sqrt{K_w \times K_a \times K_b}$

Answer. (*c*)

22. The aqueous solution of a salt of weak acid and weak bases is

(*a*) always acidic (*b*) always basic

(*c*) always neutral (*d*) sometimes acidic, sometimes basic

Answer. (*d*)

23. Sodium acetate and sodium cyanide are the salts of weak acids and strong bases. Their aqueous solution will be

(*a*) acidic (*b*) basic

(*c*) neutral (*d*) sometimes acidic, sometimes basic

Answer. (*b*)

24. NH_4Cl, $AlCl_3$ and $FeCl_3$ are the salts of _______ acids and _______ bases.

(*a*) weak, weak (*b*) weak, strong

(*c*) strong, weak (*d*) strong, strong

Answer. (*b*)

25. NH_4F, NH_4CN and CH_3COONH_4 are the salts of _______ acid and _______ bases.

(*a*) strong, strong (*b*) strong, weak

(*c*) weak, strong (*d*) weak, weak

Answer. (*d*)

26. When a salt of strong acid and weak base is dissolved in water _______ occurs to give _______ solution

(*a*) ionisation, basic (*b*) ionisation, acidic

(*c*) hydrolysis, acidic (*d*) hydrolysis, basic

Answer. (*c*)

27. Hydrolysis is reverse of _______.

(*a*) ionisation (*b*) neutralisation

(*c*) acidification (*d*) saponification

Answer. (*b*)

28. Sodium sulphide (Na_2S) on hydrolysis give a solution which is

(*a*) neutral (*b*) acidic

(*c*) basic (*d*) may be acidic or basic

Answer. (*c*)

29. The heat of neutralisation of all strong acids and strong bases is

(*a*) equal to zero (*b*) nearly the same

(*c*) not fixed (*d*) varies from acid to acid

Answer. (*b*)

30. Which salt out of the following will be hydrolysed to give basic solution.

NaCN, NaCl, $NaNO_3$, NH_4Cl

(*a*) NaCN (*b*) NaCl

(*c*) $NaNO_3$ (*d*) NH_4Cl

Answer. (*a*)

31. Borax ($Na_2B_4O_7$) on hydrolysis produces a solution which is
(*a*) acidic
(*b*) basic
(*c*) neutral
(*d*) sometimes acidic, sometimes basic
Answer. (*b*)

32. The solution of Na_2CO_3 is alkaline due to
(*a*) hydrolysis of CO_3^{2-} ions
(*b*) hydrolysis of Na^+ ions
(*c*) neutralisation of CO_3^{2-} ions
(*d*) neutralisation of Na^+ ions
Answer. (*a*)

33. A weak base becomes weaker in the presence of its salt. This statement is
(*a*) false
(*b*) true
(*c*) cannot be predicted
(*d*) none of these
Answer. (*b*)

34. NH_4OH becomes weaker in the presence of NH_4Cl due to
(*a*) ionisation
(*b*) hydrolysis
(*c*) neutralisation
(*d*) common ion effect
Answer. (*d*)

35. The pH value of an aqueous solution is
(*a*) equal to 7
(*b*) equal to 0
(*c*) less than 7
(*d*) more than 7
Answer. (*d*)

36. The pH value of $AlCl_3$ solution is
(*a*) less than 7
(*b*) greater than 7
(*c*) equal to 7
(*d*) equal to 0
Answer. (*a*)

37. The aqueous solutions of KNO_3, $ZnCl_2$, and K_2CO_3 separately are
(*a*) neutral, acidic and basic respectively
(*b*) acidic, neutral and basic respectively
(*c*) basic, neutral and acidic respectively
(*d*) neutral, basic and acidic respectively
Answer. (*a*)

38. The aqueous solution of $ZnCl_2$ is acidic due to
(*a*) cation hydrolysis
(*b*) anion hydrolysis
(*c*) hydrolysis of both cation & anion
(*d*) ionisation
Answer. (*a*)

39. A salt 's' is dissolved in pure water of pH = 7. The resulting solution is having pH > 7. The salt is made up of
(*a*) a strong acid and a weak base
(*b*) a weak acid and a strong base
(*c*) a weak acid and a weak base
(*d*) a strong acid and a weak base
Answer. (*b*)

40. An aqueous solution of ammonium carbonate is
(*a*) weakly acidic
(*b*) weakly basic
(*c*) strongly acidic
(*d*) neutral
Answer. (*d*)

41. Which one of the following aqueous solutions will have highest pH value?
(*a*) NaCl
(*b*) KNO_3
(*c*) $ZnCl_2$
(*d*) Na_2CO_3
Answer. (*d*)

42. An aqueous solution of $CuSO_4.5H_2O$ turns blue litmus red. It is due to the
(*a*) presence of Cu^{2+} ions
(*b*) presence of SO_4^{2-} ions
(*c*) hydrolysis of Cu^{2+} ions
(*d*) hydrolysis of SO_4^{2-} ions
Answer. (*c*)

43. One or both the ions of a salt react with water to produce acidic, basic or neutral solution. This process is called
(*a*) neutralisation
(*b*) ionisation
(*c*) saponification
(*d*) hydrolysis
Answer. (*d*)

44. When a pinch of NaCN is added to pure water, the pH
(*a*) increases
(*b*) decreases
(*c*) remains the same
(*d*) none of these
Answer. (*a*)

45. A salt undergoes cationic hydrolysis in water. The pH of the resulting solution would be
(*a*) less than 7
(*b*) greater than 7
(*c*) equal to 7
(*d*) equal to 0
Answer. (*a*)

46. Which statement is correct?
(*a*) NH_4Cl gives alkaline solution
(*b*) sodium acetate given acidic solution in water
(*c*) $ZnCl_2$ gives basic solution in water
(*d*) KNO_3 gives neutral solution in water
Answer. (*d*)

47. Which one of the following will not be hydrolysed?
(*a*) KNO_3
(*b*) K_2CO_3
(*c*) KCN
(*d*) CH_3COOK
Answer. (*a*)

48. The degree of hydrolysis of ammonium acetate
(*a*) depends upon its concentration
(*b*) does not depend upon its concentration
(*c*) directly proportional to the square of its concentration
(*d*) does not depend upon temperature
Answer. (*b*)

49. A solution of ammonium acetate is _______ and its pH value is _______.
(*a*) acidic, less than 7
(*b*) basic, more than 7
(*c*) neutral, less than 7
(*d*) basic, more than 14
Answer. (*c*).

Top