28

Salt Hydrolysis

CHAPTER

CONTENTS

WHAT IS HYDROLYSIS?

BRONSTED-LOWRY CONCEPT OF HYDROLYSIS

Why NaCl solution is neutral?

EXAMPLES OF HYDROLYSIS

Salts of Weak acids and Strong bases

Salts of Weak bases and Strong acids

Salts of Weak acids and Weak bases

QUANTITATIVE ASPECT OF **HYDROLYSIS**

Salt of a Weak acid and Strong base

RELATION BETWEEN $K_{h^{\prime}}$, K_{w} and K_{a}

RELATION BETWEEN HYDROLYSIS CONSTANT AND DEGREE OF HYDROLYSIS

Salts of Weak bases and Strong acids

Salts of Weak acids and Weak bases

DETERMINATION OF DEGREE OF HYDROLYSIS

DISSOCIATION CONSTANT METHOD

FROM CONDUCTANCE **MEASUREMENTS**

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.

$$
A + H \xrightarrow{\xi} 0 - H \xrightarrow{\xi} H A + \overline{0} - H
$$

...(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

SALT HYDROLYSIS 977

(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

$$
HA + H2O \xrightarrow{\longrightarrow} H3O+ + A-
$$

weak acid conjugate base

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.

$$
HCl + H_2O \xrightarrow{\longleftarrow} H_3O^+ + Cl^-
$$

conjugate base

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:

 $CI + H₂O$ \rightarrow \rightarrow 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, CH₃COONa, and sodium cyanide, NaCN, are examples of this type of salts.

Sodium acetate, CH₃COONa. This is a salt of the weak acid, CH₃COOH, and strong base, NaOH. It ionises in aqueous solution to form the anion CH₃COO[–]. Being the conjugate base of a weak acid, CH₃COOH, 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.

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

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. $NH₄OH$, and strong acid, HCl. It ionises in aqueous solution to form the cation, $NH₄⁺$.

$$
NH4OH \n\xrightarrow{\text{Coul}/\text{conjugate}} NH4+ + OH-
$$

conjugate
acid

 $NH₄⁺$ is a Bronsted conjugate acid of the weak base NH₄OH. Therefore, it is a relatively strong acid. It accepts OH⁻ ion from water (H₂O) and forms the unionised NH₄OH and H⁺ ion.

$$
NH_4^+ + H_2O \quad \Longrightarrow \quad NH_4OH + H^+
$$

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, $\text{CH}_3\text{COONH}_4$ **.** It is the salt of weak acid, CH_3COOH , and weak base, NH₄OH. 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 ($NH₄⁺$) are relatively strong. They accept H^+ and OH⁻ ions respectively from water and undergo considerable hydrolysis.

$$
CH_3COO^- + H_2O \implies CH_3COOH + OH^-
$$
...(1)

conjugate base

$$
NH_4^+ + H_2O \quad \Longleftrightarrow \quad NH_4OH + H^+ \qquad \qquad \dots (2)
$$

conjugate acid

The overall hydrolysis may be represented as

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

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 CH₃COONH₄), $[OH^-]= [H^+]$ 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

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

This leads to the equilibrium constant expression

$$
K_h = \frac{\text{[HA]} \, \text{[OH}^- \, \text{]} }{\text{[A}^- \, \text{]} \, \text{[H}_2 \text{O}]}
$$

The concentration of water, $[H_2O]$, is very large and is regarded as practically constant.

Thus the hydrolysis constant expression assumes the form

$$
K_h = \frac{\text{[HA]} \, \text{[OH}^- \, \text{]}}{\text{[A}^- \, \text{]}} \tag{1}
$$

Relation between K_h **,** K_w **and** K_a

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

$$
K_w = \text{[H}^+ \text{]} \text{[OH}^- \text{]} \tag{2}
$$

For the dissociation of a weak acid, HA,

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

the acid dissociation constant, K_a , is expressed as

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

Dividing (2) by (3)

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

$$
\frac{K_w}{K_a} = K_h
$$
...(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 :

Hence the hydrolysis constant K_h is given by

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

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

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

or

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

$$
\therefore \qquad \alpha = \sqrt{\frac{K_w V}{K_a}}
$$

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

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

and

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

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

$$
K
$$

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

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

But

$$
\therefore \qquad [\mathrm{H}^+] = \frac{K_w}{C} \sqrt{\frac{K_a C}{K_w}} = \sqrt{\frac{K_w K_a}{C}}
$$

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 CH₃COONa. 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

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

Calculation of pH

The hydrolysis equation is :

$$
CH_3COO^- + H_2O \xrightarrow{\longleftarrow} CH_3COOH + OH^-
$$

$$
K_h = \frac{[CH_3COOH][OH^-]}{[CUC]CCl^{-1}}
$$

Thus,

$$
X_h = \frac{[CH_3COOH][OH]}{[CH_3COO^-]}
$$

If *x* be the concentration of CH_3COOH and OH^- ions at equilibrium, the concentration of $CH₃COO⁻$ 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,

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

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

Hence

$$
\begin{aligned}\n\lambda &= \sqrt{3.50 \times 10^{-5} \, \text{M}} \\
\text{[OH^-]} &= 1.89 \times 10^{-5} \, \text{M} \\
\text{pOH} &= -\log \left[\text{OH}^- \right] = -\log \left(1.89 \times 10^{-5} \right) = 4.72 \\
\text{pH} &= 14.00 - \text{pOH} = 14.00 - 4.72 \\
&= 9.28\n\end{aligned}
$$

SOLVED PROBLEM 2. What is the pH of a 0.2 M solution of NaCN ? K_a for HCN = 4.0 \times 10⁻¹⁰. **SOLUTION**

Calculation of Hydrolysis Constant

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

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

Calculation of pH

From the hydrolysis reaction,

$$
CN^{-} + H_2O \xrightarrow{\longleftarrow} HCN + OH^{-}
$$

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

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 because *x* is negligible

Substituting these values in the expression above,

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

Hence,
\n
$$
x = \sqrt{2.5 \times 0.2 \times 10^{-5}}
$$
\n
$$
[OH^{-}] = x = 2.24 \times 10^{-3}
$$
\n
$$
pOH = -\log(2.24 \times 10^{-3}) = 2.65
$$
\n
$$
pH = 14 - pOH = 11.35
$$

Salts of Weak bases and Strong acids

The hydrolysis of a salt of a weak base BOH (*e.g*, NH4OH) and a strong acid may be represented by the equation :

$$
B^+ + H_2O \xrightarrow{\longrightarrow} BOH + H^+
$$

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

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

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

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

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

$$
K_{w} = \text{[H}^{+}\text{]} \text{[OH}^{-}\text{]}
$$
...(2)

For the dissociation of a weak base, BOH

$$
BOH \xrightarrow{\longrightarrow} B^+ + OH^-
$$

The dissociation constant, K_b , can be expressed as :

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

Dividing (2) by (3)

$$
\frac{K_w}{K_b} = \frac{\text{[H+][BOH]}}{\text{[B+]}} = K_h
$$
\nor\n
$$
\frac{K_w}{K_b} = K_h \qquad \qquad ...(4)
$$

Thus the hydrolysis constant, K_h , varies inversely as the dissociation constant, K_h , 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

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

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

SALT HYDROLYSIS 983

2 $K_h = \frac{\alpha^2}{V}$ or $K_h \times V = \alpha^2$ or $\alpha = \sqrt{K_h} \times V$

From (4) we have

From (4) we have
\n
$$
K_h = \frac{K_w}{K_b}
$$
\n
$$
\alpha = \sqrt{\frac{K_w}{K_b} \times V} \qquad ...(5)
$$
\n
$$
= \sqrt{\frac{K_w}{K_b \times C}} \qquad \qquad [\because C \propto \frac{1}{V}]
$$

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

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

Taking logarithms and reversing the signs

$$
-\log[H^{+}] = -\frac{1}{2}\log K_{w} - \frac{1}{2}\log C + \frac{1}{2}pK_{b}
$$

$$
pH = 7 + \frac{1}{2}pK_{b} = \frac{1}{2}\log C
$$

or

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

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

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

Calculation of pH

The hydrolysis of $NH₄Cl$ can be represented as

$$
NH_4^+ + H_2O \xrightarrow{\longrightarrow} NH_4OH + H^+
$$

0.20-x

Let *x* be the concentration of NH₄OH and H⁺ at equilibrium. The concentration of NH_4^+ will be $(0.20 - x)$.

Thus,

$$
K_h = \frac{\text{[NH}_4\text{OH}]\,\text{[H}^+]}{\text{[NH}_4^+]}
$$

or
\n
$$
x^2 = K_h \times 0.20 = (5.56 \times 10^{-10}) \times 0.20
$$
\n
$$
x^2 = K_h \times 0.20 = (5.56 \times 10^{-10}) \times 0.20
$$
\n
$$
x = \sqrt{1.11 \times 10^{-10}} = [H^+] = 1.053 \times 10^{-5} \text{ mol}^{-1}
$$
\nand
\n
$$
pH = -\log [H^+] = -\log (1.053 \times 10^{-5}) = 4.9775
$$
\n(

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

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.

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

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

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

[H₂O] is very large and is taken to be constant. The hydrolysis constant expression, therefore, becomes

$$
K_h = \frac{[\text{BOH}] [\text{HX}]}{[\text{B}^+] [\text{X}^-]} \tag{1}
$$

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

$$
HX \implies H^{+} + X^{-} \qquad K_{a} = \frac{[H^{+}][X^{-}]}{[HX]}
$$
...(2)

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

$$
K_w = \left[\mathrm{H}^+\right] \left[\mathrm{OH}^-\right] \tag{4}
$$

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

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

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

$$
\frac{K_w}{K_a \times K_b} = K_h \tag{5}
$$

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 :

$$
B^{+} + X^{-} + H_{2}O \implies BOH + HX
$$

$$
\frac{1 - \alpha}{V} \quad \frac{1 - \alpha}{V} \qquad \frac{\alpha}{V} \qquad \frac{\alpha}{V}
$$

Substituting these in the hydrolysis constant expression (1)

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

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

or

∴

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)

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

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

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

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,

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

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

$$
pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b
$$

If

$$
pK_a = pK_b
$$

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

$$
\mathrm{pH}=\frac{1}{2}\mathrm{p}K_{w}=7
$$

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 $pK_a > pK_b$ *i.e.*, the acid is relatively weaker than the base, the solution will be alkaline as pH is more than 7. If $pK_a < pK_b$ *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

or

We know that

$$
pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b
$$

Now,
\n
$$
\frac{1}{2}pK_w = -\frac{1}{2}\log(1.0 \times 10^{-14}) = 7
$$
\n
$$
\frac{1}{2}pK_a = -\frac{1}{2}\log K_a = -\frac{1}{2}\log(1.75 \times 10^{-5})
$$
\n
$$
= \frac{1}{2} \times 4.7570 = 2.3785
$$
\nand
\n
$$
\frac{1}{2}\log K_b = -\frac{1}{2}\log(1.8 \times 10^{-5})
$$
\n
$$
= \frac{1}{2} \times 4.7447 = 2.3723
$$
\n
$$
\therefore \text{ pH } = 7 + 2.3785 - 2.3723
$$
\n
$$
= 7.006
$$

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 × 10⁻²

∴ Percentage hydrolysis of NaCN in N/80 solution is **2.48.**

SOLVED PROBLEM 2. Calculate the hydrolysis constant and degree of hydrolysis of NH₄Cl in 0.001 M solution. $K_b = 1.8 \times 10^{-5}$, $K_w = 1.0 \times 10^{-14}$.

SOLUTION

Since NH₄Cl 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 × 10⁻⁴ = 0.00074

For the salt of a weak base and strong acid,

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

= $\frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$

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 (CH₃COOH) and weak base (NH₄OH).

∴ $K_h = \frac{K_w}{K_a \times K_b}$ $K_h = \frac{K_w}{K_a \times K}$

We know that

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

Thus,

or

Thus,
\n
$$
\frac{\alpha^2}{(1-\alpha)^2} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}
$$
\nor
\n
$$
\frac{\alpha}{1-\alpha} = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}}
$$
\n
$$
= \frac{1.0 \times 10^{-2}}{1.8} = \frac{1}{180}
$$
\nHence
\n
$$
\alpha = 0.0055 = 0.55 \times 10^{-2}
$$

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

$$
B^+ + H_2O \xrightarrow{\qquad} BOH + H^+ \qquad (1-\alpha) \qquad \alpha \qquad \alpha
$$

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 :

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

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

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

or

 \land is found by conductance measurements. \land_{acid} is taken as the value for strong acid at infinite dilution. λ_{acid} is determined by adding excess of weak base to the solution to suppress hydrolysis so that the resulting experimentally determined value of ∧ 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 cm² 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 cm² eqvt⁻¹. If \land for HCl at this temperature is 383, calculate the degree of hydrolysis.

SOLUTION

$$
\alpha = \frac{\lambda - \lambda_{\text{salt}}}{\lambda_{\text{HCl}} - \lambda_{\text{salt}}}
$$

Substituting the values
144 - 103.6

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

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 NH₄Cl 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

$$
K_{\rm h} = \frac{K_{\rm w}}{K_{\rm a} K_{\rm b}}
$$

- **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
$$
K_h = \frac{K_w}{K_a}
$$
 or $K_h = \frac{K_w}{K_b}$

and write the equation for pH of this solution using K_{ω} , K_{ω} , K_{μ} and c. , *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 : $K_{\text{w}} = 1.0 \times 10^{-14}$, $K_{\text{a}} = 1.75 \times 10^{-6}$

Answer. 7.5 × 10–5 (*Delhi BSc, 2004*)

- **21.** (*a*) Explain why an aqueous solution of $CuSO₄$ 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*)

- -
	- (*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

$$
Answer. (a)
$$

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

Answer. (*a*)

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

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)
$$
\alpha = \sqrt{\frac{K_b}{K_h \times C}}
$$

\n(b) $\alpha = \frac{K_b}{K_h \times C}$
\n(c) $\alpha = \frac{K_b}{K_h \times C^2}$
\n(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*) $pH = 7 + \frac{1}{2} pK_b + \frac{1}{2} \log C$

	(*b*) $pH = 7 + \frac{1}{2} pK_b \frac{1}{2} \log C$

	(*d*) $pH = 7 \frac{1}{2} pK_b \frac{1}{2} \log C$
	- (*d*) $pH = 7 \frac{1}{2} pK_b \frac{1}{2} \log C$ **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

42. An aqueous solution of $CuSO₄$.5H₂O 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*) NH4Cl gives alkaline solution (*b*) sodium acetate given acidic solution in water (*c*) ZnCl₂ gives basic solution in water (*d*) KNO₃ gives neutral solution in water **Answer.** (*d*) **47.** Which one of the following will not be hydrolysed? (*a*) KNO₃ (*b*) K₂CO₃ (*c*) KCN (*d*) CH3COOK **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

SALT HYDROLYSIS 995