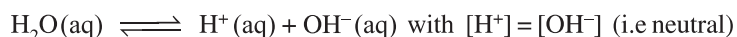


## HYDROLYSIS OF SALTS

## Section - 4

It involves the study of the reactions between a salt and water to yield an acid and a base. The salts are generally ionised in water. Here we will deal with salts which are almost fully soluble (not sparingly soluble salts).

Water in the presence of ionic impurities is visualized as follows :



Now, when a salt is put in the water, there is an interaction between ions of salt and ions of water. The phenomenon of interaction of cations and anions of the salts with  $\text{H}^+$  and  $\text{OH}^-$  ions furnished by water so that there is some net change in the pH of the resulting solution is known as *Hydrolysis of a salt*.

Four cases have been discussed here to understand the behavior of various type of salts.

### 1. Salts of strong acids and strong bases [SA-SB]

When such salts are dissolved in water, they do not undergo hydrolysis. They simply ionise and fail to change the  $\text{H}^+$  ion concentration of solution and hence the pH of the solution remains same. e.g.  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{KCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$



The final pH of the solution remains 7 at  $25^\circ\text{C}$ .

(If  $\text{NaOH}$  and  $\text{HCl}$  are formed, they neutralise each other to keep the pH same)

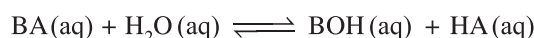
### 2. Salts of weak acids and strong bases [WA-SB]

Such salts give alkaline solutions in water. Some of such salts are :  $\text{CH}_3\text{COONa}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KCN}$  etc . For our discussion, we consider  $\text{CH}_3\text{COONa}$  (sodium acetate) in water. When  $\text{CH}_3\text{COONa}$  is put in water, it completely ionises to give  $\text{CH}_3\text{COO}^-$  (acetate) ions and  $\text{Na}^+$  ions.

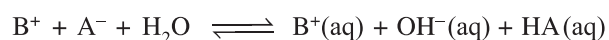
Now acetate ions ( $\text{CH}_3\text{COO}^-$ ) absorb some  $\text{H}^+$  ions from weakly dissociated  $\text{H}_2\text{O}$  molecules to form undissociated  $\text{CH}_3\text{COOH}$ .  $\text{Na}^+$  remains in ionic state in water.

Now for  $K_w$  (ionic product) of water to remain constant,  $\text{H}_2\text{O}$  further ionises to produce more  $\text{H}^+$  and  $\text{OH}^-$  ions.  $\text{H}^+$  ions are taken up by  $\text{CH}_3\text{COO}^-$  ions leaving  $\text{OH}^-$  ions in excess and hence an alkaline solution.

Let BA represents such a salt. As it is put in water ;



BA dissociates into ions and BOH being strong base also ionises.



So, the net reaction is :  $\text{A}^-(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{OH}^-(\text{aq}) + \text{HA}(\text{aq})$  [Anionic Hydrolysis]

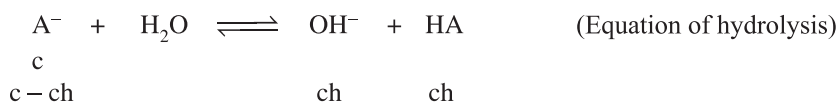
The above equation is known as *equation of hydrolysis* and equilibrium constant for such reactions is called as *Hydrolysis Constant* ( $K_h$ ).

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

### Degree of Hydrolysis :

It is defined as the fraction of total salt that has undergone hydrolysis on attainment of equilibrium. It is denoted by  $h$ .

Let  $c$  be the concentration of salt and  $h$  be its degree of hydrolysis.



$$K_h = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = \frac{(ch)(ch)}{c - ch} = \frac{ch^2}{1 - h}$$

$$\Rightarrow K_h = ch^2 \quad [\text{assuming } h \ll 1] \quad \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

Now considering, dissociations of weak acid HA and  $\text{H}_2\text{O}$ .



$$\Rightarrow K_h = \frac{K_w}{K_a} \quad (\text{Subtracting (i) from (ii), we get equation of hydrolysis})$$

- Note :** ➤ Weaker is the acid, greater is the hydrolysis constant.  
 ➤ Degree of hydrolysis increases when 'c' decreases i.e. with dilution.

Now substituting the value of  $K_h$  in expression of  $h$ ,

$$\Rightarrow h = \sqrt{\frac{K_w}{K_a c}}$$

### pH of solution :

pH of a basic solution is given as :

$$\text{pH} = 14 + \log [\text{OH}^-] \quad \text{and} \quad [\text{OH}^-] = ch = \sqrt{K_h c}$$

Substituting for  $K_h$ , we get :

$$[\text{OH}^-] = \sqrt{\frac{K_w c}{K_a}} \quad \Rightarrow \quad \text{pH} = 14 + \log_{10} \sqrt{\frac{K_w c}{K_a}}$$

$$\Rightarrow \text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log_{10} c) \quad \text{or} \quad \text{pH (at } 25^\circ\text{C)} = 7 + \frac{1}{2} (\text{p}K_a + \log_{10} c)$$

### 3. Salts of strong acids and weak bases [SA-WB]

Such salts give acidic solutions in water. Some of such salts are :  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$  etc. For the purpose of discussion, we will consider hydrolysis of  $\text{NH}_4\text{Cl}$ .

When  $\text{NH}_4\text{Cl}$  is put in water, it completely ionises in water to give  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions.  $\text{NH}_4^+$  ions combine with  $\text{OH}^-$  ions furnished by weakly dissociated water to form  $\text{NH}_4\text{OH}$  (weak base). Now for keeping  $K_w$  constant, water further ionises to give  $\text{H}^+$  and  $\text{OH}^-$  ions, where  $\text{OH}^-$  ions are consumed by  $\text{NH}_4^+$  ions leaving behind  $\text{H}^+$  ions in solution to give an acidic solution.

Let BA be one of such salts. When it is put into water, the reaction is as follows.

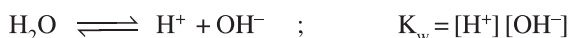


The net reaction of hydrolysis is :

$$\begin{array}{ccc} \text{B}^+ & + & \text{H}_2\text{O} \rightleftharpoons \text{BOH}(\text{aq}) + \text{H}^+(\text{aq}) \quad [\text{Cationic Hydrolysis}] \\ c - ch & & ch \quad ch \end{array}$$

$$\Rightarrow K_h = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]} = \frac{(ch)(ch)}{c - ch} = \frac{ch^2}{1 - h} \approx ch^2 \quad (h \ll 1) \quad \Rightarrow \quad h = \sqrt{\frac{K_h}{c}}$$

Considering ionisation of weak base BOH and  $\text{H}_2\text{O}$ .



From expressions for  $K_h$ ,  $K_b$  and  $K_w$ , we have : (As done in previous case)

$$K_h = \frac{K_w}{K_b} \quad \Rightarrow \quad h = \sqrt{\frac{K_w}{K_b c}}$$

#### pH of solution :

Now,  $\text{pH} = -\log [\text{H}^+]$

$$\text{and} \quad [\text{H}^+] = ch = c \sqrt{\frac{K_h}{c}} = \sqrt{K_h c} \quad \Rightarrow \quad [\text{H}^+] = \sqrt{\frac{K_w c}{K_b}}$$

$$\Rightarrow \quad \text{pH} = -\log_{10} \sqrt{\frac{K_w c}{K_b}}$$

$$\Rightarrow \quad \text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_b - \log_{10} c) \quad \text{or} \quad \text{pH (at } 25^\circ\text{C)} = 7 - \frac{1}{2}(\text{p}K_b + \log_{10} c)$$

#### Try Your Self :

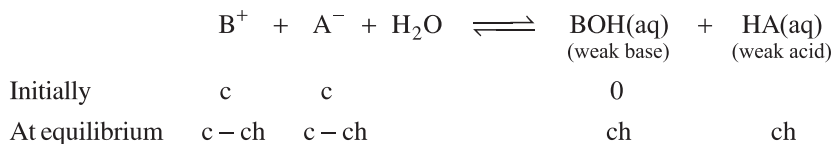
1. Calculate pH of M/100 solution of  $\text{CH}_3\text{COONa}$  at  $25^\circ\text{C}$  where  $K_a$  of  $\text{CH}_3\text{COOH}$  is  $2.0 \times 10^{-5}$ . [Ans : 8.35]
2. Calculate pH of M/100 solution of  $\text{NH}_4\text{Cl}$  at  $25^\circ\text{C}$  where  $K_b$  for  $\text{NH}_4\text{OH}$  is  $2.0 \times 10^{-5}$ . [Ans : 5.65]
3. In above two cases, find the degree of hydrolysis taking  $K_w = 10^{-14}$ .

**Note :** The results of above two cases of hydrolysis of salts can be used directly.

#### 4. Salts of weak acids and weak bases [WA-WB]

Let us consider ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ) for our discussion. Both  $\text{NH}_4^+$  ions and  $\text{CH}_3\text{COO}^-$  ions react respectively with  $\text{OH}^-$  and  $\text{H}^+$  ions furnished by water to form  $\text{NH}_4\text{OH}$  (weak base) and  $\text{CH}_3\text{COOH}$  (acetic acid).

Let BA represents such a salt.



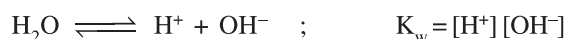
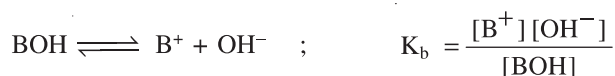
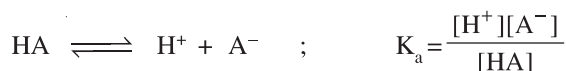
$$\Rightarrow K_h = \frac{[\text{BOH}][\text{HA}]}{[\text{B}^+][\text{A}^-]} = \frac{(ch)(ch)}{(c - ch)^2}$$

$$\Rightarrow K_h = \frac{h^2}{(1 - h)^2} \quad ; \quad \text{Taking square root on both sides to get :}$$

$$h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}} \quad (\text{Here, } 1 - h \neq 1; \text{ Think why ?})$$

Hence the degree of hydrolysis of such salts is independent of concentration of salt solution.

Now considering the dissociation of both weak base and acid.



Combining  $K_h$ ,  $K_b$ ,  $K_a$  and  $K_w$ , we have

$$K_h = \frac{K_w}{K_a K_b} \quad \text{and} \quad h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}} \quad [\text{Cation - Anionic Hydrolysis}]$$

(Observe that  $1 - h \neq 1$ )

#### pH of Solution :

$$\text{Consider,} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \Rightarrow \quad [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

Since, base and acids are weaker, hence,

$$[\text{BOH}] = [\text{HA}] \quad \Rightarrow \quad [\text{B}^+] = [\text{A}^-]$$

$$\Rightarrow K_h = \frac{[\text{BOH}][\text{HA}]}{[\text{B}^+][\text{A}^-]} = \frac{[\text{HA}]^2}{[\text{A}^-]^2} \quad \Rightarrow \quad [\text{H}^+] = K_a \sqrt{K_h} = \sqrt{\frac{K_w K_a}{K_b}}$$

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

$$\Rightarrow \text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a - \text{p}K_b) \quad \text{or} \quad \text{at } 25^\circ\text{C,} \quad \text{pH} = 7 + \frac{1}{2}(\text{p}K_a - \text{p}K_b)$$

**Illustrating the concept :**

What is the pH of a 0.50 M aqueous NaCN solution ?  $pK_b$  of  $CN^-$  is 4.70.

**SOLUTION :**

NaCN is a salt of weak acid and strong base. The pH of its aqueous solution is given by :

$$pH \text{ (at } 25^\circ\text{C)} = 7 + \frac{1}{2} (pK_a + \log_{10} c)$$

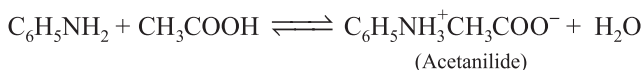
Remember that for any acid and its conjugate base or vice-versa :  $pK_a + pK_b = pK_w$

e.g. For acid (say HA),  $pK_a$  corresponds to HA and  $pK_b$  corresponds to its conjugate base :  $A^-$

Thus,  $pK_a$  of HCN =  $14 - 4.7 = 9.3$

$$\text{So, } pH \text{ (at } 25^\circ\text{C)} = 7 + \frac{1}{2} (pK_a + \log_{10} c) = 7 + \frac{1}{2} (9.3 + \log_{10} 0.5) = 11.5$$

**Illustration - 11** Calculate the degree of hydrolysis of a mixture of aniline and acetic acid each of them being 0.01 M.  $K_a$  of acetic acid =  $1.8 \times 10^{-5}$  and  $K_b$  (aniline) =  $4.5 \times 10^{-10}$ . Also calculate pH of the mixture.

**SOLUTION :**

Now when we mix equal concentrations of aniline and acetic acid, they will neutralise each other to form anilinium acetate (salt). The salt is of weak base and weak acid, so hydrolysis takes place. The degree of hydrolysis of the salt of weak acid and weak base is given by :

$$h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}}$$

$$\text{Here, } K_h = \frac{K_w}{K_a \cdot K_b} = \frac{10^{-14}}{1.8 \times 10^{-5} \times 4.5 \times 10^{-10}} = 1.23$$

$$\Rightarrow h = 0.52$$

However the pH of solution can be calculated by using the standard result :

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

$$\Rightarrow pH = 7 + \frac{1}{2} \left[ -\log_{10} 1.8 \times 10^{-5} - (-\log_{10} 4.5 \times 10^{-10}) \right]$$

$$\Rightarrow pH = 7 + \frac{1}{2} \log_{10} \frac{4.5 \times 10^{-10}}{1.8 \times 10^{-5}} = 4.7$$

**Note :** ➤ Solution in this case is acidic. In such salts, pH depends upon which of two i.e. weak acid or weak base is stronger than the other, i.e. by comparing  $K_a$  and  $K_b$ ; one can theoretically get an idea about the pH of solution.

➤ The formula  $pH = 7 + \frac{1}{2} (pK_a - pK_b)$  is applicable even when 'h' is large as no approximation of 'h' comparison with unity, has been taken in the derivation (see derivation yourself).

**Illustration - 12** 2.5 mL of 0.4 M weak mono-acidic base ( $K_b = 1 \times 10^{-12}$  at  $25^\circ\text{C}$ ) is titrated with 2/15 M HCl in water at  $25^\circ\text{C}$ . Find the concentration of  $H^+$  ions at equivalence point. ( $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ )

**SOLUTION :**

First find the volume of HCl required to reach the equivalence point.

meq of Base = meq of HCl

$$\Rightarrow 2.5 \times (0.4 \times 1) = \left( \frac{2}{15} \times 1 \right) V_{\text{HCl}}$$

$$\Rightarrow V_{\text{HCl}} = 7.5 \text{ mL}$$

The net volume of the solution at the equivalent

$$\text{point} = V_{\text{base}} + V_{\text{HCl}} = 2.5 + 7.5 = 10 \text{ mL}$$

$$\Rightarrow [\text{salt}] = c = \frac{0.4 \times 2.5}{10} = 0.1 \text{ M}$$

pH of an aqueous solution of such a salt is given by :

$$\begin{aligned} \text{pH} &= 7 - \frac{1}{2}(\text{p}K_b + \log_{10} c) \\ &= 7 - \frac{1}{2}(12 + \log_{10} 0.1) = 1.5 \end{aligned}$$

$$\Rightarrow [\text{H}^+] = 10^{-1.5} = \frac{1}{10\sqrt{10}} \approx 3.2 \times 10^{-2} \text{ M}$$

Please note that the above solution is Incorrect.

(Why?)

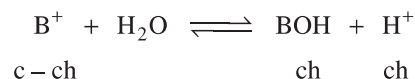
Actually,  $\text{pH} = 7 - \frac{1}{2}(\text{p}K_b + \log_{10} c)$  is valid only when  $1 - h \approx 1$

To check, calculate  $h$  using :

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_b c}} = \sqrt{\frac{10^{-14}}{10^{-12} \times 0.1}} = \sqrt{0.1}$$

$$\Rightarrow 1 - \sqrt{0.1} \neq 1$$

So we have to solve from basics as follows :



$$\Rightarrow K_h = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]} = \frac{(ch)(ch)}{c - ch}$$

$$\Rightarrow K_h = \frac{K_w}{K_b} = 10^{-2} = \frac{[\text{H}^+]^2}{c - [\text{H}^+]} \quad (ch = [\text{H}^+])$$

$$\begin{aligned} \Rightarrow [\text{H}^+] &= \frac{-10^{-2} + \sqrt{10^{-4} + 4 \times 10^{-3}}}{2} \\ &= 2.7 \times 10^{-2} \text{ M} \end{aligned}$$

**IN-CHAPTER EXERCISE - C**

- Calculate the hydrolysis constant and degree of hydrolysis of  $\text{NH}_4\text{Cl}$  in 0.1 M solution.  
 $K_b = 2.0 \times 10^{-5}$ . Calculate the concentration of  $\text{H}^+$  ions in the solution.
- Calculate the amount of  $\text{NH}_4\text{Cl}$  required to dissolve in 500 mL of water to have a pH of 4.5.  $K_b = 2.0 \times 10^{-5}$
- The ionisation constant  $K_b$  for hydrazine ( $\text{N}_2\text{H}_4$ ) is  $1.0 \times 10^{-6}$ . What would be the % age hydrolysis of  $0.001 \text{ M } \text{N}_2\text{H}_5\text{Cl}^+$ , a salt containing acid ion conjugate to hydrazine base.
- A 0.25 M solution of pyridinium chloride,  $\text{C}_5\text{H}_5\text{NH}^+\text{Cl}^-$ , was found to have a pH of 2.89. What is the  $\text{p}K_b$  for pyridine,  $\text{C}_5\text{H}_5\text{N}$ ?
- Choose the correct alternative. Only one choice is correct.**
  - The hydrolysis constant of 0.1M aqueous solution of sodium acetate if  $K_a$  of  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$  is :  
 (A)  $5.5 \times 10^{-10}$  (B)  $4.5 \times 10^{-8}$  (C)  $5.5 \times 10^{-12}$  (D) None of these
  - The compound whose 0.1 M solution is basic is :  
 (A)  $\text{CH}_3\text{COONH}_4$  (B)  $\text{NH}_4\text{Cl}$  (C)  $(\text{NH}_4)_2\text{SO}_4$  (D)  $\text{CH}_3\text{COONa}$

(iii) The expression to compute pH of sodium acetate solution at 25°C is :

(A)  $pH = 7 + \frac{1}{2} pK_b (CH_3COOH) - \frac{1}{2} \log [salt]$

(B)  $pH = 7 + \frac{1}{2} pK_a (CH_3COOH) - \frac{1}{2} \log [salt]$

(C)  $pH = 7 + \frac{1}{2} pK_b (CH_3COOH) + \frac{1}{2} \log [salt]$

(D)  $pH = 7 + \frac{1}{2} pK_a (CH_3COOH) + \frac{1}{2} \log [salt]$

(iv) The correct order of increasing  $[H_3O^+]$  in the following aqueous solution is :

(A)  $0.01 M H_2S < 0.01 M H_2SO_4 < 0.01 M NaCl < 0.01 M NaNO_3$

(B)  $0.01 M NaCl = 0.01 M NaNO_3 < 0.01 M H_2S < 0.01 M H_2SO_4$

(C)  $0.01 M H_2S < 0.01 M NaNO_3 = 0.01 M NaCl < 0.01 M H_2SO_4$

(D)  $0.01 M H_2S < 0.01 M NaNO_3 < 0.01 M NaCl < 0.01 M H_2SO_4$

(v) pH of water is 7. When a substance Y is dissolved in water, the pH becomes 11. The substance Y is a salt of :

(A) weak acid and weak base

(B) strong acid and strong base

(C) strong acid and weak base

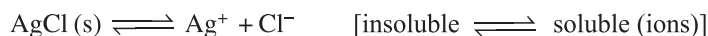
(D) weak acid and strong base

## SOLUBILITY PRODUCT ( $K_{sp}$ ) AND PRECIPITATION OF SALTS

## Section - 5

Here, we will study those salts which are generally considered as insoluble in water. (e.g. AgCl, BaSO<sub>4</sub>, Ag<sub>2</sub>S, PbS etc) Actually no insoluble salt is actually completely insoluble, they have a very small solubility. Consider a vessel containing water with a sufficient amount of AgCl being put into it. A very small amount of it dissolves in water (*because generally salts are composed of ions or contain polarised atoms*). The small amount which is soluble is almost 100% ionised.

The situation achieved at this stage is *Dynamic* in nature; with some of ions (soluble) being solidifying and some solid always dissolving. Thus a state of equilibrium exists (like in earlier cases). This means at a given temperature, the concentration of Ag<sup>+</sup> ions and Cl<sup>-</sup> ions in aqueous solution remains constant. The following equilibrium exists. In this equilibrium, the equilibrium state is known as *Saturated state*.



The equilibrium constant for this reaction is known as *solubility product* ( $K_{sp}$ ) and is written as :

$$K_{sp} = [Ag^+] [Cl^-]$$

$K_{sp}$  is expressed in concentration units. The reaction coefficient, Q in such system is known as ionic product (I.P)

- Note :** ➤ The solubility of a salt in water depends upon other substances (ions) present in water (at that time) and the solubility product is a constant value (at a given temperature) and is independent of presence of any other ion present. Like other equilibrium constants such as :  $K_p$ ,  $K_c$ ,  $K_a$  and  $K_b$ , it is also constant at a certain temperature and can change only when temperature changes.
- The salts like AgCl are regarded as sparingly soluble salts. Some of them are : Ag<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>CO<sub>3</sub>, PbCl<sub>2</sub>, PbCrO<sub>4</sub>, PbS, ZnS, Al(OH)<sub>3</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, BaSO<sub>4</sub>, CaSO<sub>4</sub>, MnS etc.