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 :

$$H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq) \text{ with } [H^+] = [OH^-] \text{ (i.e neutral)}$$

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 H^+ and 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 ionises and fail to change the H^+ ion concentration of solution and hence the pH of the solution remains same. e.g. NaCl, $CaCl_2$, $BaCl_2$, KCl, $NaNO_3$, Na_2SO_4, $Ca(NO_3)_2$

$$NaCl(aq) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$
$$H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The final pH of the solution remains 7 at 25°C.
(*If NaOH and 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 : CH_3COONa, Na_2CO_3, K_2CO_3, KCN etc . For our discussion, we consider CH_3COONa (sodium acetate) in water. When CH_3COONa is put in water, it completely ionises to give CH_3COO^- (acetate) ions and Na^+ ions.

Now acetate ions (CH_3COO^-) absorb some H^+ ions from weakly dissociated H_2O molecules to form undissociated CH_3COOH. Na^+ remains in ionic state in water.

Now for K_w (ionic product) of water to remain constant, H_2O further ionises to produce more H^+ and OH^- ions. H^+ ions are taken up by CH_3COO^- ions leaving OH^- ions in excess and hence an alkaline solution.

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

$$BA(aq) + H_2O(aq) \rightleftharpoons BOH(aq) + HA(aq)$$

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

$$B^+ + A^- + H_2O \rightleftharpoons B^+(aq) + OH^-(aq) + HA(aq)$$

So, the net reaction is : $A^-(aq) + H_2O \rightleftharpoons OH^-(aq) + HA(aq)$ [Anionic Hydrolysis]

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

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

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.

$$\begin{array}{ccccccccc} A^- & + & H_2O & \rightleftharpoons & OH^- & + & HA & & \text{(Equation of hydrolysis)} \\ c & & & & & & & & \\ c - ch & & & & ch & & ch & & \end{array}$$

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

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

Now considering, dissociations of weak acid HA and H_2O.

$$HA \rightleftharpoons H^+ + A^- \quad ; \quad K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{....(i)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad ; \quad K_w = [H^+][OH^-] \quad \text{....(ii)}$$

$$\Rightarrow \quad K_h = \frac{K_w}{K_a}$$ (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*,

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

pH of solution :

pH of a basic solution is given as :

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

Substituting for K_h , we get :

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

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

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

Such salts give acidic solutions in water. Some of such salts are : NH_4Cl, $ZnCl_2$, $FeCl_3$ etc. For the purpose of discussion, we will consider hydrolysis of NH_4Cl.

When NH_4Cl is put in water, it completely ionises in water to give NH_4^+ and Cl^- ions. NH_4^+ ions combine with OH^- ions furnished by weakly dissociated water to form NH_4OH (weak base). Now for keeping K_w constant, water further ionises to give H^+ and OH^- ions, where OH^- ions are consumed by NH_4^+ ions leaving behind 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.

$$B^+ + A^- + H_2O \rightleftharpoons BOH(aq) + H^+(aq) + A^-(aq) \quad \text{[HA is strong acid]}$$

The net reaction of hydrolysis is :

$$\underset{c-ch}{B^+} + H_2O \rightleftharpoons \underset{ch}{BOH(aq)} + \underset{ch}{H^+(aq)} \qquad \text{[Cationic Hydrolysis]}$$

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

Considering ionisation of weak base BOH and H_2O.

$$BOH \rightleftharpoons B^+ + OH^- \quad ; \qquad K_b = \frac{[B^+][[OH^-]}{[BOH]}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad ; \qquad K_w = [H^+][OH^-]$$

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

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

pH of solution :

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

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

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

$$\Rightarrow \quad pH = \frac{1}{2}(pK_w - pK_b - \log_{10} c) \quad \text{or} \quad pH\,(\text{at } 25°C) = 7 - \frac{1}{2}(pK_b + \log_{10} c)$$

Try Your Self :

1. Calculate pH of M/100 solution of CH_3COONa at 25°C where K_a of CH_3COOH is 2.0×10^{-5}. [Ans : 8.35]

2. Calculate pH of M/100 solution of NH_4Cl at 25°C where K_b for NH_4OH is 2.0×10^{-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 (CH_3COONH_4) for our discussion. Both NH_4^+ ions and CH_3COO^- ions react respectively with OH^- and H^+ ions furnished by water to form NH_4OH (weak base) and CH_3COOH (acetic acid).

Let BA represents such a salt.

$$\begin{array}{lcccccc} & B^+ & + & A^- + H_2O & \rightleftharpoons & \underset{\text{(weak base)}}{BOH(aq)} & + \underset{\text{(weak acid)}}{HA(aq)} \\ \text{Initially} & c & & c & & 0 & \\ \text{At equilibrium} & c-ch & & c-ch & & ch & ch \end{array}$$

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

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

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

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.

$$HA \rightleftharpoons H^+ + A^- \quad ; \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$BOH \rightleftharpoons B^+ + OH^- \quad ; \qquad K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad ; \qquad K_w = [H^+][OH^-]$$

Combining K_h, K_b, K_a and K_w, we have

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

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

pH of Solution :

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

Since, base and acids are weaker, hence,

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

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

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

$$\Rightarrow \quad pH = \frac{1}{2}(pK_w + pK_a - pK_b) \quad \text{or} \quad \text{at } 25°C, \quad pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

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 :

$$\text{pH (at 25°C)} = 7 + \frac{1}{2}\,(\text{pK}_a + \log_{10} c)$$

Remember that for any acid and its conjugate base or vice-versa : $\text{pK}_a + \text{pK}_b = \text{pK}_w$

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 $= 14 - 4.7 = 9.3$

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

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* = 1.8×10^{-5} *and K_b (aniline)* = 4.5×10^{-10}. *Also calculate pH of the mixture.*

SOLUTION :

$$C_6H_5NH_2 + CH_3COOH \rightleftharpoons \underset{\text{(Acetanilide)}}{C_6H_5\overset{+}{N}H_3CH_3COO^-} + H_2O$$

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 :

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

Here, $K_h = \dfrac{K_w}{K_a . K_b} = \dfrac{10^{-14}}{1.8 \times 10^{-5} \times 4.5 \times 10^{-10}}$

$= 1.23$

$\Rightarrow \quad h = 0.52$

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

$$\text{pH} = 7 + \frac{1}{2}(\text{pK}_a - \text{pK}_b)$$

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

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

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 $\text{pH} = 7 + \frac{1}{2}(\text{pK}_a - \text{pK}_b)$ 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* $\left(K_b = 1 \times 10^{-12} \text{ at } 25^\circ C\right)$ *is titrated with* 2/15 *M HCl in water at* 25°C. *Find the concentration of H^+ ions at equivalence point.* $\left(K_w = 1 \times 10^{-14} \text{ at } 25^\circ C\right)$

SOLUTION :

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

meq of Base = meq of HCl

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

$$\Rightarrow \quad V_{HCl}=7.5\,mL$$

The net volume of the solution at the equivalent point $= V_{base} + V_{HCl} = 2.5+7.5=10\text{ mL}$

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

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

$$pH=7-\frac{1}{2}(pK_b+\log_{10}c)$$

$$=7-\frac{1}{2}(12+\log_{10}0.1)=1.5$$

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

Please note that the above solution is Incorrect. (Why?)

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

To check, calculate h using :

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

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

So we have to solve from basics as follows :

$$\begin{array}{ccccccc} B^+ & + & H_2O & \rightleftharpoons & BOH & + & H^+ \\ c-ch & & & & ch & & ch \end{array}$$

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

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

$$\Rightarrow \quad [H^+]=\frac{-10^{-2}+\sqrt{10^{-4}+4\times 10^{-3}}}{2}$$

$$=2.7\times 10^{-2}\ M$$

IN-CHAPTER EXERCISE - C

1. *Calculate the hydrolysis constant and degree of hydrolysis of NH_4Cl in 0.1 M solution.*
$K_b = 2.0\times 10^{-5}$. *Calculate the concentration of H^+ ions in the solution.*

2. *Calculate the amount of NH_4Cl required to dissolve in 500 mL of water to have a pH of 4.5.* $K_b = 2.0\times 10^{-5}$

3. *The ionisation constant K_b for hydrazine (N_2H_4) is 1.0×10^{-6}. What would be the % age hydrolysis of 0.001 M $\overset{+}{N}_2H_5Cl^-$, a salt containing acid ion conjugate to hydrazine base.*

4. *A 0.25 M solution of pyridinium chloride, $C_5H_5NH^+Cl^-$, was found to have a pH of 2.89. What is the pK_b for pyridine, C_5H_5N ?*

5. **Choose the correct alternative. Only one choice is correct.**

(i) *The hydrolysis constant of 0.1M aqueous solution of sodium acetate if K_a of $CH_3COOH = 1.8\times 10^{-5}$ is :*

(A) 5.5×10^{-10} **(B)** 4.5×10^{-8} **(C)** 5.5×10^{-12} **(D)** *None of these*

(ii) *The compound whose 0.1 M solution is basic is :*

(A) CH_3COONH_4 **(B)** NH_4Cl **(C)** $(NH_4)_2SO_4$ **(D)** CH_3COONa

(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 substances 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, $BaSO_4$, Ag_2S, 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^+ ions and Cl^- ions in aqueous solution remains constant. The following equilibrium exists. In this equilibrium, the equilibrium state is known as *Saturated state*.

$$AgCl\,(s) \rightleftharpoons Ag^+ + Cl^- \qquad [\text{insoluble} \rightleftharpoons \text{soluble (ions)}]$$

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 is 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_2SO_4, Ag_2CO_3, $PbCl_2$, $PbCrO_4$, PbS, ZnS, $Al(OH)_3$, $Ca_3(PO_4)_2$, $BaSO_4$, $CaSO_4$, MnS etc.