(C) Hydrolysis of a salt of a weak acid and a weak base

(a) Expression for hydrolysis constant:
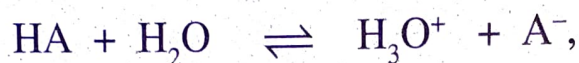
The hydrolysis of a salt BA (or B^+A^-) of a weak acid HA and a weak base BOH may be represented as:

$$B^+ + A^- + H_2O \rightleftharpoons HA + BOH$$

The hydrolysis constant K_h is given by:

$$K_h = \frac{[HA][BOH]}{[B^+][A^-]} \qquad \text{----} (1)$$

For the weak acid HA ionising as:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-,$$

the ionisation constant K_a is given by:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \text{----} (2)$$

For the weak base BOH ionising as:

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

the ionisation constant K_b is given by:

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

The ionic product of water K_w is given by:

$$K_w = [H_3O^+][OH^-] \qquad \text{----} (4)$$

$$\frac{(4)}{(2)\times(3)}: \qquad \frac{K_w}{K_a K_b} = \frac{[HA][BOH]}{[B^+][A^-]} \qquad \text{----} (5)$$

From eqns. (1) and (5), we can see that:

$$K_h = \frac{K_w}{K_a K_b} \qquad \text{----} (6)$$

(b) Expression for degree of hydrolysis:

Suppose 'c' is the initial molar concentration of the salt solution and 'x' the degree of hydrolysis of the salt BA (or B^+A^-). The hydrolytic equilibrium conditions may then be represented as follows:

Initial concn. :   c   c

$$B^+ \;+\; A^- \;+\; H_2O \rightleftharpoons HA \;+\; BOH$$

Eqbm. concn. : $c(1-x)$ $c(1-x)$ cx   cx

The expression for the hydrolysis constant K_h is:

$$K_h = \frac{[HA]\,[BOH]}{[B^+]\,[A^-]}$$

$$= \frac{cx \times cx}{c(1-x)\,c(1-x)} = \frac{x^2}{(1-x)^2}$$

When 'x' is small compared to unity, we can write:

$$K_h = x^2$$

Or

$$x = \sqrt{K_h} \qquad\qquad ---- (i)$$

Since $K_h = K_w/(K_a K_b)$, we may also write:

$$x = \sqrt{\frac{K_w}{K_a K_b}} \qquad\qquad ---- (ii)$$

The following points emerge from a consideration of eqn. (ii) applicable to a salt of a weak acid and a weak base:

(i) The smaller the values of K_a and K_b (*i.e.*, the weaker the acid and base), the greater is the degree of hydrolysis (x).

(ii) As eqn. (ii) does not contain the concentration term, the degree of hydrolysis (x) is independent of the concentration.

(iii) When temperature increases, as the increase in K_w is more dominant than that of K_a as well as K_b, the degree of hydrolysis (x) increases.

(c) *Expression for pH of the hydrolysed salt solution*

For the weak acid HA, ionising as:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-,$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Or

$$[H_3O^+] = K_a \cdot \frac{[HA]}{[A^-]} \qquad\qquad ---- (a)$$

Under hydrolytic equilibrium conditions for the salt (BA) of a weak acid (HA) and a weak base (BOH) in aqueous solution at 298 K,

$$[HA] = cx \text{ and } [A^-] = c(1-x)$$

where x is the degree of hydrolysis.

Substituting the above in eqn. (a), we get:

$$[H_3O^+] = K_a \cdot \frac{cx}{c(1-x)} = K_a \cdot \frac{x}{(1-x)} \quad \text{---- (b)}$$

But, we have seen that for the salt of a weak acid and a weak base, $K_h = \dfrac{x^2}{(1-x)^2}$.

Hence, $\dfrac{x}{(1-x)} = \sqrt{K_h}$. Putting this in eqn. (b), we get:

$$[H_3O^+] = K_a \cdot \sqrt{K_h} \quad \text{---- (c)}$$

$$= K_a \cdot \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

$$= \sqrt{\frac{K_w \cdot K_a}{K_b}} \quad \text{---- (d)}$$

Now, $\qquad\qquad$ pH $= -\log_{10}[H_3O^+] \quad \text{---- (e)}$

Putting eqn. (d) in eqn. (e), we get:

$$\text{pH} = -\log_{10}\sqrt{\frac{K_w \cdot K_a}{K_b}}$$

$$= \frac{1}{2}\left[-\log_{10}\frac{K_w \cdot K_a}{K_b}\right]$$

$$= \frac{1}{2}[-\log_{10} K_w - \log_{10} K_a + \log_{10} K_b]$$

i.e., $\qquad$ $\boxed{\text{pH} = \frac{1}{2}[pK_w + pK_a - pK_b]}$ $\qquad\qquad$ ---- (f)

$$= \frac{1}{2}[14 + pK_a - pK_b] \qquad [\because pK_w = 14, \text{ at } 298\,K]$$

Thus, $\qquad$ $\boxed{\text{pH} = 7 + \frac{1}{2}[pK_a - pK_b]}$ $\qquad\qquad$ ---- (g)

for an aqueous solution of the salt of a weak acid and a weak base at 298 K.

It is evident from the above equation that *the pH of a solution of a salt of a weak acid and a weak base is independent of the concentration of the solution.*

Table 3.4: Summary of important relationships regarding the hydrolysis of salts

Nature of salt	Hydrolysis constant, $K_h =$	Degree of hydrolysis, $x =$	pH of solution =
Salt of strong acid and strong base (e.g., NaCl, K_2SO_4, KNO_3, etc.)	(No hydrolysis)	(No hydrolysis)	7
Salt of weak acid and strong base (e.g., CH_3COONa, Na_2CO_3, K_2CO_3, etc.)	$\dfrac{K_w}{K_a}$	$\sqrt{\dfrac{K_h}{c}} = \sqrt{\dfrac{K_w}{K_a \cdot c}}$	$\frac{1}{2}[pK_w + pK_a + \log c]$ Or $7 + \frac{1}{2}[pK_a + \log c]$
Salt of strong acid and weak base(e.g., NH_4Cl, $CuSO_4$, $FeCl_3$, etc.)	$\dfrac{K_w}{K_b}$	$\sqrt{\dfrac{K_h}{c}} = \sqrt{\dfrac{K_w}{K_b \cdot c}}$	$\frac{1}{2}[pK_w - pK_b - \log c]$ Or $7 - \frac{1}{2}[pK_b + \log c]$
Salt of weak acid and weak base [e.g., CH_3COONH_4, $(NH_4)_2CO_3$, etc.]	$\dfrac{K_w}{K_a \cdot K_b}$	$\sqrt{K_h} = \sqrt{\dfrac{K_w}{K_a \cdot K_b}}$	$\frac{1}{2}[pK_w + pK_a + pK_b]$ Or $7 + \frac{1}{2}[pK_a - pK_b]$

SOLVED PROBLEMS

29. *Calculate the degree of hydrolysis of 0.2 M sodium acetate solution in water. (K_a of acetic acid = 1.8 × 10⁻⁵; K_w = 1 × 10⁻¹⁴). Also calculate the pH of the above solution.*

Solution:

Degree of hydrolysis 'x' is given by:

$$x = \sqrt{\frac{K_w}{K_a . c}}$$

Here, $c = 0.2$ M; $K_a = 1.8 \times 10^{-5}$; $K_w = 1 \times 10^{-14}$.

$$x = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.2}}$$

$$= 5.271 \times 10^{-5}$$

$$pH = 7 + \tfrac{1}{2}[pK_a + \log c]$$

$$= 7 + \tfrac{1}{2}[-\log(1.8 \times 10^{-5}) + \log 0.2]$$

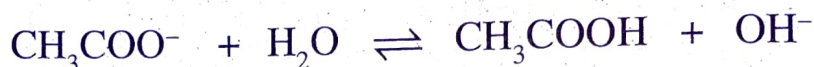$$= 7 + \tfrac{1}{2}[4.7447) - 0.6990]$$

$$= \quad 7 + 2.02285$$
$$= \quad 9.02285$$

30. *Potassium acetate in its 0.01M solution undergoes hydrolysis to the extent of 0.023%. Calculate its hydrolysis constant and the concentration of hydroxide ions.*

    Solution:

    Initial concn. : $\quad\quad c$

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

    Eqbm. concn.: $\quad c(1-x)$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad cx \quad\quad\quad cx$

    Here, $c = 0.01$ M; $x = 0.023/100 = 2.3 \times 10^{-4}$.

    Hydrolysis constant, $\quad\quad\quad\quad K_h \quad = \quad cx^2$
    $$= \quad 0.01 \times (2.3 \times 10^{-4})^2$$
    $$= \quad 5.29 \times 10^{-10}.$$

    $$[OH^-] \quad = \quad cx$$
    $$= \quad 0.01 \times 2.3 \times 10^{-4}$$
    $$= \quad 2.3 \times 10^{-6} \text{ mol L}^{-1}.$$

31. *Calculate the hydrolysis constant of ammonium chloride and its degree of hydrolysis in a 0.1 M solution at 298 K. K_b for $NH_4OH = 1.81 \times 10^{-5}$; $K_w = 1 \times 10^{-14}$. Also calculate the pH of the above solution.*

    Solution:

    The hydrolysis constant is given by:

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

    Here, $K_w = 1 \times 10^{-14}$; $K_b = 1.81 \times 10^{-5}$.

    $$K_h \quad = \quad \frac{1 \times 10^{-14}}{1.81 \times 10^{-5}}$$
    $$= \quad 5.525 \times 10^{-10}.$$

    Degree of hydrolysis 'x' is given by:

    $$x \quad = \quad \sqrt{\frac{K_h}{c}}$$

    Here, $K_h = 5.525 \times 10^{-10}$; $c = 0.1$ M.

$$x = \sqrt{\frac{5.525 \times 10^{-10}}{0.1}}$$

$$= 7.433 \times 10^{-5}$$

$$\begin{aligned} \text{pH} &= 7 + \tfrac{1}{2}[\,pK_b + \log c\,] \\ &= 7 + \tfrac{1}{2}[-\log(1.81 \times 10^{-5}) + \log 0.1] \\ &= 7 + \tfrac{1}{2}[4.7423 - 1] \\ &= 7 + 1.87115 \\ &= 8.87115 \end{aligned}$$

32. *Calculate the hydrolysis constant of ammonium acetate and its degree of hydrolysis in a 0.1 M solution at 298 K. K_b for $NH_4OH = 1.81 \times 10^{-5}$; $K_w = 1 \times 10^{-14}$; K_a for acetic acid $= 1.75 \times 10^{-5}$. Also calculate the pH of the above solution.*

Solution:

The hydrolysis constant is given by:

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

Here, $K_w = 1 \times 10^{-14}$; $K_a = 1.75 \times 10^{-5}$; $K_b = 1.81 \times 10^{-5}$

$$\begin{aligned} K_h &= \frac{1 \times 10^{-14}}{(1.75 \times 10^{-5}) \times (1.81 \times 10^{-5})} \\ &= 3.157 \times 10^{-5} \end{aligned}$$

Degree of hydrolysis 'x' is given by:

$$x = \sqrt{K_h}$$

Here, $K_h = 3.157 \times 10^{-5}$.

$$\begin{aligned} x &= \sqrt{3.157 \times 10^{-5}} \\ &= 5.619 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} \text{pH} &= 7 + \tfrac{1}{2}[\,pK_a - pK_b\,] \\ &= 7 + \tfrac{1}{2}[-\log(1.75 \times 10^{-5}) - \{-\log(1.81 \times 10^{-5})\}] \\ &= 7 + \tfrac{1}{2}[4.7570 - 4.7423] \\ &= 7 + \tfrac{1}{2}[0.0147] \\ &= 7 + 0.00735 \\ &= 7.00735 \end{aligned}$$

BUFFER SOLUTIONS

A) Buffer solution and its characteristics

A *buffer solution* is one which resists any change in its pH even upon the addition of small amounts of acids or bases.

Thus, a buffer solution is one which maintains its pH fairly constant even when a small quantity of an acid or a base is added to it.

An *acidic buffer* can be prepared by mixing solutions of a weak acid and its salt (from a strong base) in suitable proportions.

e.g., An equimolar mixture of *acetic acid and sodium acetate* solutions forms an acidic buffer. It maintains the pH around 4.74.

A *basic buffer* can be prepared by mixing solutions of a weak base and its salt (from a strong acid) in suitable proportions.

e.g., An equimolar mixture of *ammonium hydroxide and ammonium chloride* solutions forms a basic buffer. It maintains its pH around 9.25.

A buffer solution thus has the following characteristics:

(i) It has a definite pH value.

(ii) Its pH remains unaltered even on standing for a long time or on dilution.

(iii) Its pH remains almost unaltered upon the addition of a small amount of a strong acid or a strong base.

B) Mechanism of buffer action

The property by which a buffer solution resists any change in its pH even upon the addition of small quantities of acids or bases to it is called **buffer action**.

(i) Buffer mixture of a weak acid and its salt (Acidic buffer)

Let us consider the buffer action of acetic acid/sodium acetate buffer. Acetic acid is weakly ionised whereas sodium acetate is completely ionised in solution. Here, the addition of an acid (*i.e.,* H_3O^+) is countered by the CH_3COO^- ions to form feebly ionised acetic acid. On the other hand, the addition of a base (*i.e.,* OH^-) is countered by CH_3COOH.

$$CH_3COO^- + H_3O^+ \rightleftharpoons CH_3COOH + H_2O$$

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$
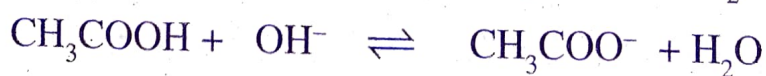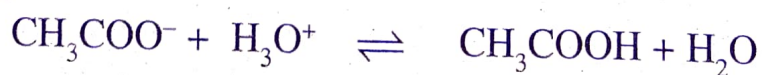
The pH is thereby maintained almost constant.

(ii) Buffer mixture of a weak base and its salt (Basic buffer)

Let us consider the buffer action of the NH_4OH/NH_4Cl buffer. NH_4OH is weakly

ionized while NH_4Cl is completely ionised in solution. The buffer action here can be explained by the fact that the addition of an acid (*i.e.*, H_3O^+) is countered by NH_4OH and the addition of a base (*i.e.*, OH^-) is countered by NH_4^+.

$$NH_4OH + H_3O^+ \rightleftharpoons NH_4^+ + 2H_2O$$

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH.$$

The pH is thus maintained fairly constant.

(iii) *Buffer action of the salt of a weak acid and a weak base*

Ammonium acetate solution (pH ≈ 7) can act as a buffer. On adding an acid, the acetate ions furnished by the salt combine with the H_3O^+ added to form feebly ionized CH_3COOH. On adding a base, the ammonium ions furnished by the salt combine with the OH^- ions added to form weakly ionized NH_4OH.

$$CH_3COO^- + H_3O^+ \rightleftharpoons CH_3COOH + H_2O$$

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH.$$

The pH is thus kept constant.

C) Buffer index

The **buffer index** (β) of a buffer solution can be defined as the differential ratio of the *increment of the added strong base or strong acid* to *the variation in pH*.

i.e.,
$$\beta = \frac{dB}{d(pH)}$$

where dB is the small increment of the strong base or strong acid, expressed in moles per kg of the solvent, added to the buffer and $d(pH)$ is the consequent small variation in the pH of the solution.

β is always taken a positive quantity. For the addition of the strong base, both dB and $d(pH)$ are positive. However, for the addition of a strong acid, since $d(pH)$ would be negative (corresponding to a decrease in pH), dB also is considered a negative quantity so that β would be positive. In short, buffer index is the numerical value of the ratio $dB/d(pH)$.

D) pH of buffer mixtures: Henderson's equations

a) pH of acidic buffer

Consider a buffer solution containing a weak acid (HA) and its highly dissociated salt (BA). The ionisation of the acid may be represented as

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The ionisation constant, $\quad K_a \quad = \quad \dfrac{[H_3O^+][A^-]}{[HA]}$

$$[H_3O^+] \quad = \quad K_a \cdot \dfrac{[HA]}{[A^-]} \qquad \text{---- (i)}$$

Since the ionisation of the weak acid, being further suppressed by the added *common ion A⁻*, is very slight, [HA] may be regarded as the total concentration of the *acid* initially taken. Further, since the salt BA added is completely ionised into B⁺ and A⁻, [A⁻] may be regarded as the concentration of the *salt* added, Thus, equation (i) may be written as

$$[H_3O^+] \quad = \quad K_a \cdot \dfrac{[Acid]}{[Salt]} \qquad \text{---- (ii)}$$

Taking logarithms of equation (ii),

$$\log [H_3O^+] \quad = \quad \log K_a + \log \dfrac{[Acid]}{[Salt]}$$

Or $\qquad\qquad -\log [H_3O^+] \quad = \quad -\log K_a + \log \dfrac{[Salt]}{[Acid]}$

Thus, since $-\log [H_3O^+] = pH$ and $-\log K_a = pK_a$, we get

$$pH \quad = \quad pK_a + \log \dfrac{[Salt]}{[Acid]} \qquad \text{---- (iii)}$$

Equation (iii) is called *Henderson's equation* (or *Henderson-Hasselbalch equation*) for an acidic buffer.

b) pH of basic buffer

Consider a buffer solution containing a weak base (BOH) and its highly dissociated salt (BA). The ionisation of the base may be represented as:

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

The ionisation constant, $\quad K_b \quad = \quad \dfrac{[B^+][OH^-]}{[BOH]}$

or $\qquad\qquad [OH^-] \quad = \quad K_b \cdot \dfrac{[BOH]}{[B^+]} \qquad \text{---- (a)}$

Since the ionisation of the weak base BOH, being further suppressed by the added common ion B⁺, is very slight and since the salt BA added is completely ionised into

B^+ and A^-, [BOH] and [B^+] may be regarded as the respective concentrations of the *base* and *salt* taken. Thus, equation (*a*) may be written as

$$[OH^-] = K_b \cdot \frac{[Base]}{[Salt]} \qquad \text{----} (b)$$

Taking logarithms of equation (*b*),

$$\log [OH^-] = \log K_b + \log \frac{[Base]}{[Salt]}$$

Or

$$-\log [OH^-] = -\log K_b + \log \frac{[Salt]}{[Base]}$$

Thus, since $-\log [OH^-] = pOH$ and $-\log K_b = pK_b$, we get

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} \qquad \text{----} (c)$$

Eqn. (*c*) is the *Henderson's equation* (or *Henderson-Hasselbalch equation*) for the pOH of a basic buffer. Then,

$$pH = 14 - pOH.$$

Utility of the Henderson's equations

The *Henderson's equations* enable (i) the calculation of the pH of buffer solutions prepared by mixing known quantities of a weak acid and its salt or a weak base and its salt, and (ii) the calculation of the quantities of the components that need be mixed in order to get a buffer solution of a definite pH.

E) Importance/Applications of buffers

1. Buffer solutions are of great importance in analytical chemistry because many of the reactions in qualitative analysis and quantitative analysis require maintenance of constant pH. *e.g.*, Acetic acid/sodium acetate buffer is used in the elimination of *phosphate* radical in qualitative analysis. NH_4OH/NH_4Cl buffer is used in complexometric titrations using EDTA.

2. Buffer solutions are used for maintaining constant pH in alcoholic fermentation, tanning of leather, etc.

3. Buffer systems such as citric acid/sodium citrate are used for sterilizing pencillin preparations, milk of magnesia, etc.

4. Most of the biological reactions in animal systems require constant pH conditions and these are made possible by various buffer systems such as carbonic acid/bicarbonate.

SOLVED PROBLEMS

33. *A buffer solution contains 0.40 mole of acetic acid and 0.20 mole of sodium acetate per litre. Calculate the pH of the solution. K_a of acetic acid = 1.75 × 10^{-5} mol L^{-1}.*

   Solution :

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Or

$$pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$$

Here, K_a = 1.75 × 10^{-5} mol L^{-1}; [Salt] = 0.20 mol L^{-1} ; [Acid] = 0.40 mol L^{-1}.

$$\therefore \quad pH = -\log (1.75 \times 10^{-5}) + \log \left(\frac{0.20}{0.40} \right)$$

$$= -\log 1.75 - \log 10^{-5} + \log 0.20 - \log 0.40$$

$$= -0.2430 + 5.0000 - 0.6990 + 0.3979$$

$$= 4.4559$$

34. *A buffer solution contains 0.2 mole of NH_4OH and 0.5 mole of NH_4Cl per litre. Calculate the pH of the solution. The dissociation constant of NH_4OH is 1.8 × 10^{-5} mol L^{-1}.*

   Solution:

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

or

$$pOH = -\log K_b + \log \frac{[Salt]}{[Base]}$$

Here, K_b = 1.8 × 10^{-5} mol L^{-1}; [Salt] = 0.5 mol L^{-1}; [Base] = 0.2 mol L^{-1}.

$$\therefore \quad pOH = -\log (1.8 \times 10^{-5}) + \log \left(\frac{0.5}{0.2} \right)$$

$$= -\log 1.8 - \log 10^{-5} + \log 0.5 - \log 0.2$$

$$= -0.2553 + 5.0000 - 0.3010 - 0.6990$$

$$= 5.1427$$

$$\therefore \quad pH = 14 - pOH = 14 - 5.1427 = 8.8573.$$

35. *A buffer solution containing 0.2 mole of acetic acid and 0.25 mole of potassium acetate per litre has a pH 4.8416 at 298 K. Calculate the ionisation constant of acetic acid at 298 K.*

Solution:

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

Or

$$pH = -\log K_a + \log\frac{[Salt]}{[Acid]}$$

Or

$$\log K_a = -pH + \log\frac{[Salt]}{[Acid]}$$

Here, pH = 4.8416; [Salt] = 0.25 mol L^{-1}; [Acid] = 0.2 mol L^{-1}

$$\therefore \quad \log K_a = -4.8416 + \log\left(\frac{0.25}{0.2}\right)$$

$$= -4.8416 + \log 0.25 - \log 0.2$$

$$= -4.8416 + (-0.6021) - (-0.6990)$$

$$= -4.7447$$

$$\therefore \quad K_a = \text{Antilog} (-4.7447)$$

$$= 1.8 \times 10^{-5}.$$

QUESTIONS

Section A

Fill in the blanks

1. The solubility of a sparingly soluble salt AB_3 is 'x' mol dm^{-3}. Its solubility product, K_{sp} = ...

2. The expression relating the hydrolysis constant K_h of a salt of a weak acid and a strong base to the ionization constant K_a of the acid and the ionic product of water K_w is ....

3. The pH of a solution of potassium acetate in water will be .... 7.

4. The fraction of the total number of moles of an electrolyte dissociated is known as its .... under the specified conditions.

5. The solubility products of the IV group metal sulphides are .... than those of the II group metal sulphides.