B.SC(H) Botany & Zoology Sem II (GE-2)
Physical Chemistry

Ionic Equilibria

Hydrolysis or Salt hydrolysis:

It is the interaction of cations or anions of a salt with ions produced by water. It is the reverse process of acid-base neutralisation process.

Hydrolysis of salts produces only weakly acidic or alkaline solution because all hydrolytic reactions are reversible and increase in concentration of the product of hydrolysis tends to reverse the process of hydrolysis.

(1.) Salts of Strong Acids & Strong Bases:

e.g. KCl

If it is dissolved in water, it forms KOH & HCl, which are completely dissociated into respective ions. Hence, no change in the concentration of H_3O^+ or OH^- & the solution remains neutral.

Therefore, salts of strong acids & strong bases do not undergo hydrolysis.

(2.) Hydrolysis of salt formed from a weak acid & a strong base :

e.g. CH_3COONa

or NaA, where $A = CH_3COO^-$

$$A^- + H_2O \rightleftharpoons HA + OH^- \quad (1.)$$

Therefore, solution becomes basic.

A^- combines with H^+ of water, so concentration of H^+ decreases & hence to keep k_w constant, concentration of OH^- increases & hence solution becomes basic.

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad (2.)$$

From (1.)

k_h = Hydrolytic constant

$$= \frac{[HA][OH^-]}{[A^-]} \frac{[H_3O^+]}{[H_3O^+]} = \frac{k_w}{k_a} \quad (3.)$$

$\therefore k = \frac{[HA][OH^-]}{[A^-][H_2O]}$

$k[H_2O] = k_h = \frac{[HA][OH^-]}{[A^-]}$

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

$k_a = \frac{[A^-][H^+]}{[HA]}$ or $k_a = \frac{[A^-][H_3O^+]}{[HA]}$

Mass balance equation,

$[NaA]_0 = c =$ Initial concentration of salt.

$$c = \underbrace{[HA]}_{\text{hydrolyzed salt}} + \underbrace{[A^-]}_{\text{unhydrolyzed salt}} \quad (4.)$$

Charge balance equation,

$$[Na^+] + [H_3O^+] = [OH^-] + [A^-] \quad (5.)$$

$$[A^-] = [Na^+] + [H_3O^+] - [OH^-]$$

$$[A^-] = c + [H_3O^+] - \frac{kw}{[H_3O^+]} \quad \{\because [Na^+] = c\}$$

~~& $kw = [H_3O^+]$ for~~

— (6.) $\{kw = [H_3O^+][OH^-]\}$

Using eq. (6.) in (4)

$$[HA] = c - c - [H_3O^+] + \frac{kw}{[H_3O^+]}$$

$$[HA] = \frac{Kw}{[H_3O^+]} - [H_3O^+] \quad - (7.)$$

Using eq. (7.) in (3.)

$$\frac{Kw}{Ka} = Kh = \frac{\left\{\frac{Kw}{[H_3O^+]} - [H_3O^+]\right\}[OH^-]}{[A^-]}$$

Using eq. (6.) & using $Kw = [H_3O^+][OH^-]$, so $[OH^-] = \frac{kw}{[H_3O^+]}$

$$\frac{Kw}{Ka} = \frac{\left\{\frac{kw}{[H_3O^+]} - [H_3O^+]\right\}\frac{kw}{[H_3O^+]}}{\left\{c + [H_3O^+] - \frac{kw}{[H_3O^+]}\right\}} \quad — (8)$$

Approximations:

(1.) If $[H_3O^+] \leq 10^{-6}$ M, so $\frac{kw}{[H_3O^+]} \geq 10^{-8}$ M

(Solution is basic on hydrolysis, $[OH^-]$ increase & hence of $[H_3O^+]$ decreases).

Ignoring $[H_3O^+]$ in comparison to $\frac{kw}{[H_3O^+]}$ in eq. (8).

$$\frac{kw}{ka} = \frac{\frac{kw^2}{[H_3O^+]^2}}{c - \frac{kw}{[H_3O^+]}} \quad \text{(9)}$$

(2.) Amount of ions that actually react with water & converted to HA is negligible in comparison to total concentration of the ions dissolved.

Hence $[OH^-]$ released (or $\frac{kw}{[H_3O^+]}$) during hydrolysis can be ignored in comparison to 'c' as k_h is very small.

Equation (9) becomes

$$\frac{kw}{ka} = \frac{kw^2}{c[H_3O^+]^2}$$

$$\text{or } [H_3O^+] = \sqrt{\frac{kw\,ka}{c}}$$

taking log of both sides

$$\log [H_3O^+] = \frac{1}{2} \log \frac{kw\,ka}{c} \quad \left(\because \log x^a = a \log x\right)$$

$$= \frac{1}{2} \log kw + \frac{1}{2} \log ka - \frac{1}{2} \log c \quad \text{(10)}$$

$\left(\because \log \frac{a}{b} = \log a - \log b \text{ & } \log a.b = \log a + \log b\right)$

Multiplying eq. (10) by negative sign.

$$-\log [H_3O^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log c \quad \text{(11)}$$

$$\left.\begin{aligned} pH &= -\log [H_3O^+] \\ pK_a &= -\log K_a \\ pK_w &= -\log K_w \end{aligned}\right\} \text{(for very dilute solutions)} \quad \text{(12)}$$

Using equations (12) in (11)

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

pH of hydrolysis depends on pKa of the acid involved & also on the concentration of the salt solution.

Degree of hydrolysis:

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

At $t=0$	c	0	0
At t	$c(1-h)$	ch	ch

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

If $h \ll 1$, ignoring h in comparison to 1.

$$k_h = ch^2$$

$$\boxed{h = \sqrt{\frac{k_h}{c}} = \sqrt{\frac{k_w}{k_a c}}}$$

h = Degree of hydrolysis

It is the fraction of the total dissolved salt which exists in a solution as a weak base or a weak acid.

k_h = hydrolysis or hydrolytic constant.
= Equilibrium constant of the hydrolytic equilibrium.

Hydrolysis of a salt can be minimised or almost stopped by taking an excess of the corresponding acid or base.

Mass balance & charge balance equations are the approximations used to find the concentration of different species like $[A^-]$, $[HA]$, $[H_3O^+]$ etc.

$h \rightarrow$ increases with temperature as k_w increases with temperature & hence more hydrolysis.

→ More dilute is the solution, more is the hydrolysis.

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

Nature of A^-:

If A^- is a weaker base than OH^- like (CH_3COO^-, CN^-, NO_2^-, S^{2-} etc), more will be the hydrolysis.

Their conjugate acid (CH_3COOH, HCN, etc) are stronger than water but weaker than H_3O^+.

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

Low K_a value, weaker acid, more is K_h & more is hydrolysis.

Eg. $K_a(HCN) < K_a(CH_3COOH)$

$\therefore K_h(CN^-) > K_h(CH_3COO^-)$