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Salt Hydrolysis

The salt of a weak acid, HA and a strong base dissolve 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 molecules.

$$A^- + H^+ \!\!\wr\, O^- - H \rightleftharpoons HA + O^- - H$$

Similarily 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.

$$B^+ + H - O \wr H \rightleftharpoons BOH + H^+$$

The term hydrolysis comes from two words hydro + lysis, "hydro" means "water" while "lysis" means breaking. The breaking of water molecule to form cation or anion, is called hydrolysis. Hydrolysis is also defined as; "the reaction between water and cation or anion accompanied by cleavage of OH bond is called Hydrolysis."

- Reaction 1st shows anionic hydrolysis, the solution becomes slightly basic due to generation of excess of OH^- ion and pH becomes greater than 7.
- Reaction 2nd shows cationic hydrolysis, the solution becomes slightly acidic due to generation of excess of H^+ ion and pH becomes lesser than 7.

Examples of Hydrolysis : The different salts may be classified into the following types according to their hydrolysis behaviour.

1. Salts of weak acids and strong bases (CH_3COONa), ($NaCN$) etc.
2. Salts of weak bases and strong acid ($FeCl_3$, NH_4Cl) etc
3. Salts of weak acids and weak bases (CH_3COONH_4, NH_4CN, NH_4F)

NOTE: The salts of strong acid and strong base, e.g. NaCl does not show hydrolysis, thats why it is neutral.

$NaCl(aq) \rightarrow Na^+ + Cl^-$

$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$
conjugate base

∵ HCl is a strong acid, Cl^- is very weak base, which is unable to accept a proton (H^+) to form an acid, particularily in water. So Cl^- doesnot hydrolysis and cann't generate OH^- and thus NaCl becomes neutral.

Quantitative Aspect of Hydrolysis :

we know that hydrolysis is a reversible reaction. The equilibrium constant derived by the application of law of Mass action to hydrolytic reaction is called Hydrolysis constant or Hydrolytic Constant. It is represented by K_h.

salt of weak acid and strong base

Reaction is represented in such way –

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

Equilibrium Constant, $K_h = \dfrac{[HA][OH^-]}{[A^-][H_2O]}$

Concentration of H_2O is very large (= constant) say

Hydrolysis Constant, $K_h = \dfrac{[HA][OH^-]}{[A^-]}$ —— (i)

Relation between K_h, K_w, and K_a

we know that,

Ionic product of water, $K_w = [H^+][OH^-]$ —— (ii)

for weak acid, dissociation,

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

and, dissociation constant $K_a = \dfrac{[H^+][A^-]}{[HA]}$ —— (iii)

Divide (ii) by (iii), we get

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

But we know that from eqn (i)

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

so,

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

we say that the hydrolysis constant is the ratio of ionic product of water to dissociation constant.

Thus $K_h \propto \frac{1}{K_a}$

we say that "Hydrolysis constant of salt is inversely proportional to the dissociation constant of weak acid".

Derivation of pH : The pH of an aqueous solution of weak acid and strong base, derived below:

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

Equilibrium Concentration $\frac{1-\alpha}{V}$ $\frac{\alpha}{V}$ $\frac{\alpha}{V}$, where α is degree of hydrolysis

$$\boxed{\frac{1}{V} = C}$$

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

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

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But, $\alpha = \sqrt{\frac{K_W}{K_a C}}$

Thus,

$$[H^+] = \frac{K_w}{C} \times \frac{1}{\alpha} = \frac{K_w}{C}\sqrt{\frac{K_a C}{K_w}} = \sqrt{\frac{K_w K_a}{C}}$$

Taking logarithms and reversing the sign throughout

$$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

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

$$= 7 + \frac{1}{2} pK_a + \frac{1}{2}\log C.$$

pH of solution will always be greater than 7.
Solution will be always alkaline.

Similarily, salt of weak bases and strong acids

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

Hydrolysis Constant $K_h = \frac{[H^+][BOH]}{[B^+]}$

Relation between K_h, K_w and K_b

$$\frac{K_w}{K_b} = K_h \quad (=) \quad K_h \propto \frac{1}{K_b}$$

Hence, The hydrolysis constant K_h is inversely proportional to the dissociation constant, K_b of the base.

Derivation of pH.

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

$$\text{But } \alpha = \sqrt{\frac{K_w}{K_b C}}$$

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

Taking logarithms and reversing signs,

$$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log C + \frac{1}{2} pK_b$$

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

So, pH will be always less than 7.

Similarily, Salt of weak acids and weak bases

Both the anion of weak acid (X^-) and the cation of weak base (B^+) undergo hydrolysis together,

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

$$\text{So, } K_h = \frac{[BOH][HX]}{[B^+][X^-][H_2O]} \text{, neglecting } [H_2O]$$

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

Relation between K_h, K_w, K_a, and K_b.

we have

$$HX \rightleftharpoons H^+ + X^-$$

$$\text{And, } K_a = \frac{[H^+][X^-]}{[HX]} \quad \text{--- (2)}$$

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

And, $K_b = \frac{[B^+][OH^-]}{[BOH]}$ — (3)

Also, $K_w = [H^+][OH^-]$ — (4)

On dividing eqn (4) by (3) and (2), we have

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

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

$$\boxed{K_h = \frac{K_w}{K_b \times K_a}} \quad — (5)$$

Relation between K_h and α,

$$\alpha = \sqrt{\frac{K_w}{K_b \times K_a}} \quad — (6)$$

Derivation of pH; $HX \rightleftharpoons H^+ + X^-$, $K_a = \frac{[H^+][X^-]}{[HX]}$

$[H^+] = K_a \times \frac{[HX]}{[X^-]}$ But $[HX] = \frac{\alpha}{V}$ and $[X^-] = \frac{1-\alpha}{V}$ (say)

$[H^+] = \frac{K_a \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = K_a \left(\frac{\alpha}{1-\alpha}\right)$, neglecting $(1-\alpha)$

$[H^+] = K_a \times \alpha = K_a \sqrt{\frac{K_w}{K_b \times K_a}}$

Taking both side logarithm and reversing sign,

$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2} K_a + \frac{1}{2}\log K_b$

~~log~~ $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$ $(= pK_a)$

$pH = \frac{1}{2} K_w = 7$

Hence solution will neutral.