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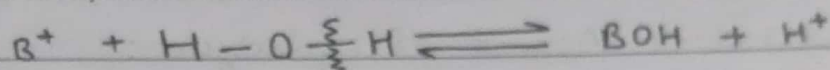
TDC PART - 2 CHEMISTRY HONOURS

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.



Similarly 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.



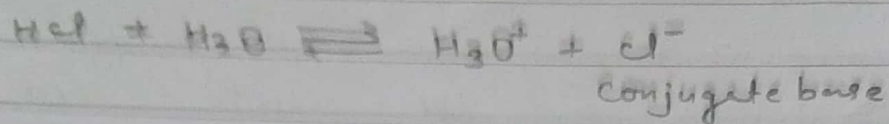
The term hydrolysis comes from two words hydro + lysis, "hydro" means "water" while "lysis" means breaking. The breaking of water molecule to form cation or anion, is called hydrolysis. Hydrolysis is also defined as; "the reaction between water and cation or anion accompanied by cleavage of OH bond is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



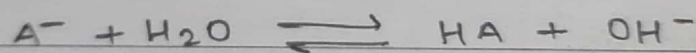
\therefore HCl is a strong acid, Cl^- is very weak base, which is unable to accept a proton (H^+) to form an acid, particularly in water. so Cl^- does not hydrolysis and can't generate OH^- and thus NaCl becomes neutral.

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 -



$$\text{Equilibrium Constant, } K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-][\text{H}_2\text{O}]}$$

Concentration of H_2O is very large (= constant) say

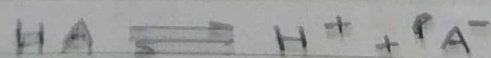
$$\text{Hydrolysis Constant, } K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \quad \text{--- (i)}$$

Relation between K_h , K_w , and K_a

we know that,

$$\text{Ionic product of water, } K_w = [\text{H}^+][\text{OH}^-] \quad \text{--- (ii)}$$

for weak acid, dissociation,



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

Divide (ii) by (iii), we get

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

But we know that from eqn (i)

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

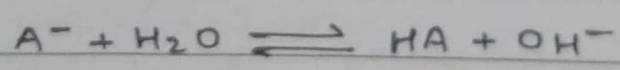
So, $\boxed{\frac{K_w}{K_a} = K_h}$

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:



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

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

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

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

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

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

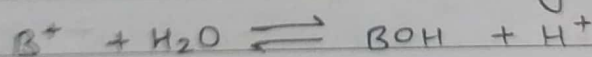
$$pH = \frac{1}{2} \log pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

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

pH of solution will always be greater than 7.

Solution will be always alkaline.

Similarly, salt of weak bases and strong acids



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

Relation between K_h , K_w and K_b

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

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.

Similarly, Salt of weak acids and weak bases

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

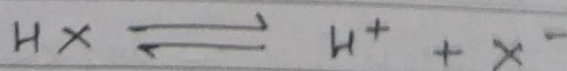


$$\text{So, } K_h = \frac{[BOH][HX]}{[B^+][X^-][H_2O]}, \text{ neglecting } [H_2O]$$

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

Relation between K_h , K_w , K_a , and K_b .

we have



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

Similarly $\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-$

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

Also, $K_w = [\text{H}^+][\text{OH}^-] \quad \text{--- (4)}$

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

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

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

$K_n = \frac{K_w}{K_b \times K_a} \quad \text{--- (5)}$

Relation between K_n and α ,

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

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

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

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

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

Taking both side logarithm and reversing sign,

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

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

$$\text{PH} = \frac{1}{2} pK_w = 7$$

Hence solution will neutral.