

SALT HYDROLYSIS

Pure water is a weak electrolyte and neutral in nature, i.e., H^+ ion concentration is exactly equal to OH^- ion concentration



When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as **salt hydrolysis**. It is defined as **a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity**.

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.



Weak base

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.



Weak acid

The process of **salt hydrolysis** is actually the reverse of neutralization.



If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.

Examples: $FeCl_3$, $CuCl_2$, $AlCl_3$, NH_4Cl , $CuSO_4$, etc.

(ii) Salt of a strong base and a weak acid.

Examples: CH_3COONa , $NaCN$, $NaHCO_3$, Na_2CO_3 , etc.

(iii) Salt of a weak acid and a weak base.

Examples: $\text{CH}_3\text{COONH}_4$, $(\text{NH}_4)_2\text{CO}_3$, NH_4HCO_3 , etc.

(iv) Salt of a strong acid and a strong base.

Examples: NaCl , K_2SO_4 , NaNO_3 , NaBr , etc.

Salt of a strong acid and a weak base:

The solution of such a salt is acidic in nature. The cation of the salt which has come from **weak base** is reactive. It reacts with water to form a **weak base** and H^+ ions.



Weak base

Consider, for example, NH_4Cl . It ionises in water completely into NH_4^+ and Cl^- ions. NH_4^+ ions react with water to form a **weak base** (NH_4OH) and H^+ ions.



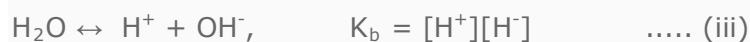
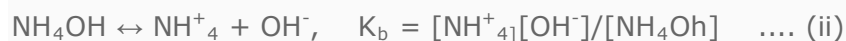
Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

$$K_h = \frac{[\text{H}^+][\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \frac{\text{Cx} \cdot \text{Cx}}{\text{C}(1-x)} = \frac{x^2 \text{C}}{(1-x)} \quad \dots \dots (i)$$

where C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are



From eqs. (ii) and (iii)

$$K_w/K_b = \frac{[\text{H}^+][\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = K_h \quad \dots (iv)$$

$$[\text{H}^+] = \frac{K_h[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = \frac{K_w}{K_b} \times \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$\log [\text{H}^+] = \log K_w - \log K_b + \log [\text{salt}]/[\text{base}]$$

$$-\text{pH} = -\text{p}K_w + \text{p}K_b + \log [\text{salt}]/[\text{base}]$$

$$\text{p}K_w - \text{pH} = \text{p}K_b + \log [\text{salt}]/[\text{base}]$$

$$\text{pOH} = \text{p}K_b + \log [\text{salt}]/[\text{base}]$$

Relation between Hydrolysis constant and Degree of hydrolysis

The extent to which **hydrolysis** proceeds is expressed as the degree of **hydrolysis** and is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as h or x .

$$h = (\text{Amount of salt hydrolysed})/(\text{Total salt taken})$$

Considering again eq. (i),

$$K_h = x^2C/(1-x) \quad \text{or} \quad K_h = h^2C/(1-h)$$

When h is very small $(1-h) \rightarrow 1$,

$$K_h = h^2 \times C$$

$$\text{or } h = \sqrt{(K_h/C)}$$

$$= \sqrt{(K_w/K_b * C)}$$

$$[H^+] = h \times C = \sqrt{(C * K_h)}/K_b$$

$$\log [H^+] = 1/2 \log K_w + 1/2 \log C - 1/2 \log K_b$$

$$\text{pH} = 1/2 \text{p}K_w - 1/2 \log C - 1/2 \text{p}K_b$$

$$= 7 - 1/2 \text{p}K_b - 1/2 \log C$$

Source : <http://ciseche10.files.wordpress.com/2013/12/ionic-equilibrium.pdf>