3. Hydrolysis of salt formed from strong acid & weak base :

e.g. NH_4Cl, anilinium chloride

$B^+ = NH_4^+$,

$$B^+ + 2H_2O \rightleftharpoons BOH + H_3O^+ \quad -(1.)$$

(Solution will be acidic)

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

From (1.), $$K_h = \frac{[BOH][H_3O^+]}{[B^+]} \quad -(3.)$$

Multiply & divide, eq. (3) by $[OH^-]$

$$k_h = \frac{k_w}{k_b} = \frac{[BOH][H_3O^+][OH^-]}{[B^+]\,[OH^-]}$$

k_w

k_b

$$\left\{ \because k_w = [H_3O^+][OH^-] \right.$$

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

$$\left. k_b = \frac{[B^+][OH^-]}{[BOH]} \right\}$$

$$k_h = \frac{k_w}{k_b} = \frac{[BOH][H_3O^+]}{[B^+]} \quad -(4)$$

Mass Balance equation

$$[BCl]_0 = c = [B^+] + [BOH] \quad -(5)$$

Charge Balance equation

$$[B^+] + [H_3O^+] = [Cl^-] + [OH^-]$$

~~$[Cl = B^+$~~

$$[B^+] = [Cl^-] + [OH^-] - [H_3O^+]$$

$$[B^+] = c + [OH^-] - \frac{k_w}{[OH^-]} \quad -(6)$$

$\Big\{ \because [Cl^-] = c =$ Initial concentration of salt

& $k_w = [H_3O^+][OH^-]$

or $[H_3O^+] = \dfrac{k_w}{[OH^-]} \Big\}$

Using (6) in (5)

$$[BOH] = c - c - [OH^-] + \frac{k_w}{[OH^-]}$$

$$[BOH] = \frac{k_w}{[OH^-]} - [OH^-] \quad -(7)$$

Using (6) in (7) in (4)

$$k_h = \frac{k_w}{k_b} = \frac{\left\{ \frac{k_w}{[OH^-]} - [OH^-] \right\} [H_3O^+]}{\left\{ c + [OH^-] - \frac{k_w}{[OH^-]} \right\}}$$

$$\frac{k_w}{k_b} = \frac{\left\{\frac{k_w}{[OH^-]} - [OH^-]\right\}\frac{k_w}{[OH^-]}}{\left\{c + [OH^-] - \frac{k_w}{[OH^-]}\right\}} \quad (8.) \quad \left\{\because k_w = [H_3O^+][OH^-]\right\}$$

Approximations:

(1) Solution becomes acidic on hydrolysis, $[H_3O^+]$ increases.

$\therefore$ $[H_3O^+]$ of resultant solution $\geq 10^{-6}$ M

& hence $\frac{k_w}{[H_3O^+]} \leq 10^{-8}$ M

~~Also [OH⁻]~~ i.e. $[OH^-] \leq 10^{-8}$ M, so $[OH^-]$ can be ignored in comparison to $\frac{k_w}{[OH^-]}$

So equation (8.) becomes,

$$\frac{K_w}{k_b} = \frac{\frac{k_w^2}{[OH^-]^2}}{c - \frac{k_w}{[OH^-]}} = \frac{[H_3O^+]^2}{c - [H_3O^+]} \quad (9.)$$

(2) k_h is very small, so value of $[H_3O^+]$ generated by hydrolysis can be ignored in comparison to initial concentration of salt (c), now equation (9.) becomes

$$\frac{k_w}{k_b} = \frac{[H_3O^+]^2}{c}$$

$$[H_3O^+] = \sqrt{\frac{c k_w}{k_b}} = \sqrt{c k_h}$$

$$[H_3O^+] = \sqrt{\frac{c\,k_w}{k_b}}$$

$$\log[H_3O^+] = \frac{1}{2}\log k_w - \frac{1}{2}\log k_b + \frac{1}{2}\log c$$

$$-\log[H_3O^+] = -\frac{1}{2}\log k_w - \left(-\frac{1}{2}\log k_b\right) - \frac{1}{2}\log c$$

$$\boxed{pH = \frac{1}{2}pk_w - \frac{1}{2}pk_b - \frac{1}{2}\log c}$$

$$B^+ + 2H_2O \rightleftharpoons H_3O^+ + BOH$$

	B^+	H_3O^+	BOH
At $t=0$	c	0	0
At t	$c(1-h)$	ch	ch

$$k_h = \frac{[H_3O^+][BOH]}{[B^+]} = \frac{ch\,ch}{c(1-h)} = \frac{ch^2}{1-h}$$

If $h << 1$

$$k_h = ch^2$$

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

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

Both the cation & anion of such a salt undergo hydrolysis to different extents. An aqueous solution of such a salt may be neutral, acidic or alkaline depending upon the relative strengths of the conjugate acid & base e.g. CH_3COONH_4, NH_4CN etc.

$$B^+ + 2H_2O \rightleftharpoons BOH + H_3O^+, \quad \frac{k_w}{k_b} = k_{hc} = \frac{[BOH][H_3O^+]}{[B^+]} \quad (1)$$

$$A^- + H_2O \rightleftharpoons AH + OH^-, \quad \frac{k_w}{k_a} = k_{ha} = \frac{[HA][OH^-]}{[A^-]} \quad (2)$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-, \quad k_w = [H_3O^+][OH^-] \quad (3)$$

Total reaction,

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

$$k_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{[BOH][HA][H_3O^+][OH^-]}{[B^+][A^-][H_3O^+][OH^-]}$$

$$= \frac{[BOH]}{[B^+][OH^-]} \frac{[HA]}{[A^-][H_3O^+]} [H_3O^+][OH^-]$$

$$k_h = \frac{k_w}{k_a k_b}$$

$$\therefore \frac{k_w}{k_a k_b} = \frac{[BOH][HA]}{[B^+][A^-]} \quad (4)$$

Mass Balance Equation.

$$\left.\begin{aligned} c = [B^+]_0 &= [B^+] + [BOH] \\ c = [A^-]_0 &= [A^-] + [HA] \\ [B^+] &= c - [BOH] \\ [A^-] &= c - [HA] \end{aligned}\right\} \quad (5)$$

Charge balance equation

$$[B^+] + [H_3O^+] = [A^-] + [OH^-] \quad (6)$$

from (1)

$$[BOH] = \frac{k_w}{k_b}\frac{[B^+]}{[H_3O^+]}$$

from (2)

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

$\Big\}$ — (7)

using (7) in (5)

$$[B^+] = C - \frac{k_w[B^+]}{k_b[H_3O^+]}$$

$$[A^-] = C - \frac{k_w[A^-]}{k_a[OH^-]}$$

$$\therefore [B^+] = \frac{Ck_b[H_3O^+] - k_w[B^+]}{k_b[H_3O^+]}$$

$$[B^+]k_b[H_3O^+] + k_w[B^+] = Ck_b[H_3O^+]$$

$$[B^+] = \frac{Ck_b[H_3O^+]}{k_w + k_b[H_3O^+]} = \frac{C}{1 + \frac{k_w}{k_b[H_3O^+]}} \quad \text{— (8)}$$

$$\therefore [A^-] = \frac{Ck_a[OH^-] - k_w[A^-]}{k_a[OH^-]}$$

$$[A^-]k_a[OH^-] + k_w[A^-] = Ck_a[OH^-]$$

$$[A^-] = \frac{C\,k_a[OH^-]}{k_a[OH^-] + k_w} = \frac{C}{1 + \frac{k_w}{k_a[OH^-]}}$$

$$[A^-] = \frac{C}{1 + \frac{[H_3O^+][OH^-]}{k_a[OH^-]}} \quad \text{— (9)}$$

Using (8) & (9) in equation (6)

~~A~~ c

$$\frac{c}{1+\frac{k_w}{k_b[H_3O^+]}} + [H_3O^+] = \frac{c}{1+\frac{[H_3O^+]}{k_a}} + [OH^-]$$

Amount of $[H_3O^+]$ on left hand side & $[OH^-]$ on right side can be ignored as amount of H_3O^+ & OH^- formed on hydrolysis is very less as k_{h} & k_{ha} are very small.

$$\frac{\cancel{c}}{1+\frac{k_w}{k_b[H_3O^+]}} = \frac{\cancel{c}}{1+\frac{[H_3O^+]}{k_a}}$$

$$\cancel{1}+\frac{[H_3O^+]}{k_a} = \cancel{1}+\frac{k_w}{k_b[H_3O^+]}$$

$$[H_3O^+]^2 = \frac{k_w k_a}{k_b}$$

$$[H_3O^+] = \sqrt{\frac{k_w k_a}{k_b}}$$

$$\log[H_3O^+] = \frac{1}{2}\log k_w + \frac{1}{2}\log k_a - \frac{1}{2}\log k_b$$

$$-\log[H_3O^+] = -\frac{1}{2}\log k_w - \frac{1}{2}\log k_a - \left(-\frac{1}{2}\log k_b\right)$$

$$\boxed{pH = \frac{1}{2}pk_w + \frac{1}{2}pk_a - \frac{1}{2}pk_b}$$

If $k_a = k_b$, then $[H_3O^+] = 10^{-7}M$, solution is neutral.
If $k_a > k_b$, then $[H_3O^+] > 10^{-7}M$, solution is acidic.
If $k_a < k_b$, then $[H_3O^+] < 10^{-7}M$, solution is alkaline.

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

	B^+	A^-		BOH	HA
At t_0	c	c		0	0
~~At~~	~~$c(1-h)$~~	~~$c(1-h)$~~			
At t	$c(1-h)$	$c(1-h)$		ch	ch

$$K_h = \frac{k_w}{k_a k_b} = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{ch\, ch}{c(1-h)\, c(1-h)} \quad (10)$$

$$K_h = \frac{h^2}{(1-h)^2}$$

$$\frac{h}{1-h} = \sqrt{k_h}$$

If $h \ll 1$, $\boxed{h = \sqrt{k_h} = \sqrt{\frac{k_w}{k_a k_b}}}$

Since $[B^+] = [A^-]$ or $[HA] = [BOH]$

So equation (10) becomes.

$$K_h = \frac{[HA]^2}{[A^-]^2} = \frac{[H_3O^+]^2}{K_a^2}$$

$$\left(k_a = \frac{[A^-][H_3O^+]}{[HA]} \right)$$

$$\left\{ \frac{[HA]}{[A^-]} = \frac{[H_3O^+]}{k_a} \right\}$$

$$[H_3O^+] = \sqrt{K_h}\, K_a$$

$$[H_3O^+] = \sqrt{\frac{k_w}{k_a k_b}}\, k_a = \sqrt{\frac{k_w k_a^2}{k_a k_b}} = \sqrt{\frac{k_w k_a}{k_b}}$$

$$-\log[H_3O^+] = -\frac{1}{2}\log k_w - \frac{1}{2}\log k_a - \left(-\frac{1}{2}\log k_b\right)$$

$$pH = \frac{1}{2}pk_w + \frac{1}{2}pk_a - \frac{1}{2}pk_b$$