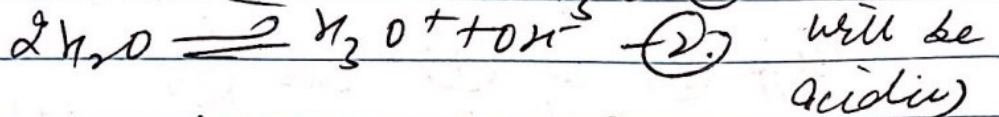
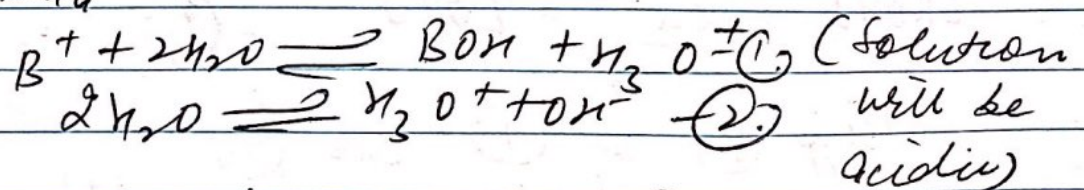
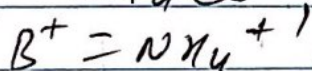


(3) Hydrolysis of salt formed from strong acid & weak base:

e.g.  $\text{NH}_4\text{Cl}$ , ammonium chloride



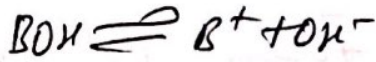
(Solution will be acidic)

$$\text{From (1), } K_h = \frac{[\text{BOH}][\text{H}_3\text{O}^+]}{[\text{B}^+]} \quad (3)$$

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

$$k_h = \frac{k_w}{k_b} = \frac{[BOH][CH_3O^+][OH^-]}{[B^+][OH^-]}$$

$$\therefore k_w = [CH_3O^+][OH^-]$$



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

$$k_h = \frac{k_w}{k_b} = \frac{[BOH][CH_3O^+]}{[B^+]} \quad (4)$$

Mass Balance equation

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

Charge Balance equation

$$[B^+] + [CH_3O^+] = [Cl^-] + [OH^-]$$

$$[B^+] = [Cl^-] + [OH^-] - [CH_3O^+]$$

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

Using (6) in (5)

$$[BOH] = c - \left( c + [OH^-] - \frac{k_w}{[OH^-]} \right) + \frac{k_w}{[OH^-]}$$

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

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

$$k_h = \frac{k_w}{k_b} = \frac{\left( \frac{k_w}{[OH^-]} - [OH^-] \right) [CH_3O^+]}{\left\{ c + [OH^-] - \frac{k_w}{[OH^-]} \right\}}$$

$$\{c = [B^+]\}$$

$\therefore [Cl^-] = c = \text{Initial concentration of salt}$   
 &  $k_w = [CH_3O^+][OH^-]$   
 or  $[CH_3O^+] = \frac{k_w}{[OH^-]}$



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

$$\left\{ c + [OH^-] - \frac{k_w}{[OH^-]} \right\}$$

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

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

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

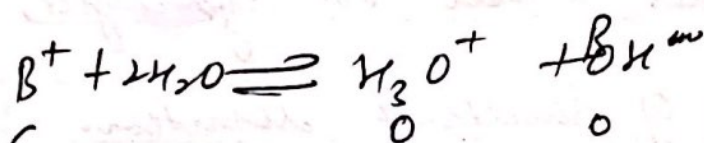
$$[H_3O^+] = \sqrt{\frac{c k_w}{k_b}}$$

(10)

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

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

$$\boxed{pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c}$$



At  $t=0$

C

0

0

At  $t$

$C(1-h)$

$Ch$

$Ch$

$$K_h = \frac{[H_3O^+][BOH]}{[B^+]} = \frac{Ch \cdot Ch}{C(1-h)} = \frac{Ch^2}{1-h}$$

If  $h \ll 1$   
 $K_h = Ch^2$

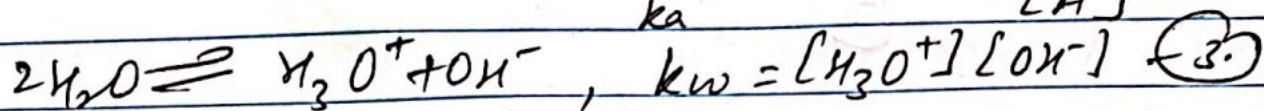
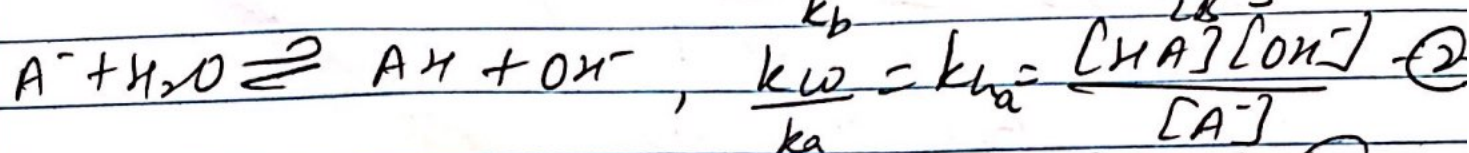
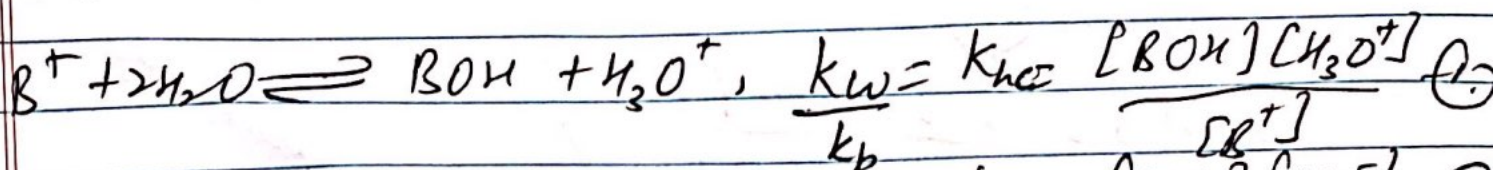
$$\boxed{h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{k_w}{k_b C}}}$$

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

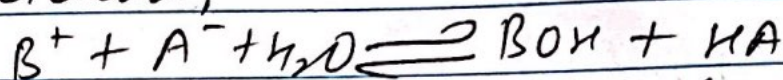
Both the cation & anion of such a salt undergo hydrolysis to different extents. An aqueous solution of such a salt may be neutral, acidic or alkaline depending upon the relative strengths of the conjugate acid & base.



e.g.  $\text{CH}_3\text{COONH}_4$ ,  $\text{NH}_4\text{CN}$  etc.



Total reaction,



$$K_h = \frac{[\text{BOH}][\text{HA}]}{[\text{B}^+][\text{A}^-]} = \frac{[\text{BOH}][\text{HA}][\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{B}^+][\text{A}^-][\text{H}_3\text{O}^+][\text{OH}^-]} \\ = \frac{[\text{BOH}]}{[\text{B}^+][\text{OH}^-]} \cdot \frac{[\text{HA}]}{[\text{A}^-][\text{H}_3\text{O}^+]}$$

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

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

Mass Balance Equations.

$$c = [\text{B}^+]_0 = [\text{B}^+] + [\text{BOH}]$$

$$c = [\text{A}^-]_0 = [\text{A}^-] + [\text{HA}]$$

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

Charge balance equation

$$[\text{B}^+] + [\text{H}_3\text{O}^+] = [\text{A}^-] + [\text{OH}^-] \quad (6)$$

from (1)

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

from (2)

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

using (7) in (5)

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

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

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

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

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

(8)

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

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

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

(9)

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

(9)



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

$$A \leftarrow A \leftarrow C \leftarrow C$$

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

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  $k_{ac}$  &  $k_{ba}$  are very small.

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

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

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

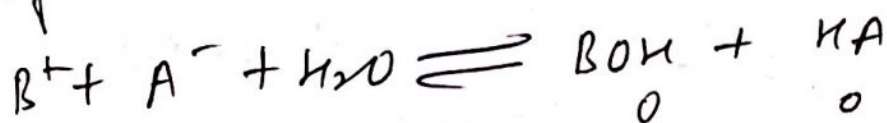
$$[H_3O^+] = \sqrt{\frac{k_w k_a}{k_b}}$$

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

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

$$\boxed{pH = \frac{1}{2} p k_w + \frac{1}{2} p k_a - \frac{1}{2} p k_b}$$

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.



At C C  
 Ev ~~C(H)C(H)~~  
 At ~~C(H)C(H)~~  
 Ev C(H)C(H)  
 At t

ch ch

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

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

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

If  $h \ll 1$ ,

$$h = \sqrt{K_h} = \sqrt{\frac{k_w}{k_a k_b}}$$

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

So equation (10) becomes -

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

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

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

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

$$pH = \frac{1}{2} p k_w + \frac{1}{2} p k_a - \frac{1}{2} p k_b$$

$$\left. \begin{aligned} k_a &= \frac{[A^-][H_3O^+]}{[HA]} \\ \frac{[HA]}{[A^-]} &= \frac{[H_3O^+]}{k_a} \end{aligned} \right\}$$