

Salt hydrolysis:

- hydrolysis is a process of where salt reacts water to form acid and base.
- $\text{Salt} + \text{Water} \longrightarrow \text{Acid} + \text{Base}.$
- salt hydrolysis is the reverse of neutralisation reaction.

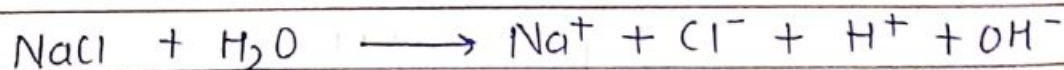
★ - Only weak acid or weak base are involved in hydrolysis of salt.

- nature of aqueous solution of salt depends upon relative strength of acid and base formed.
- on the basis of strength of acid or base there are 4 kinds of salts:

1.) $\Rightarrow$ Salt of strong acid and base:

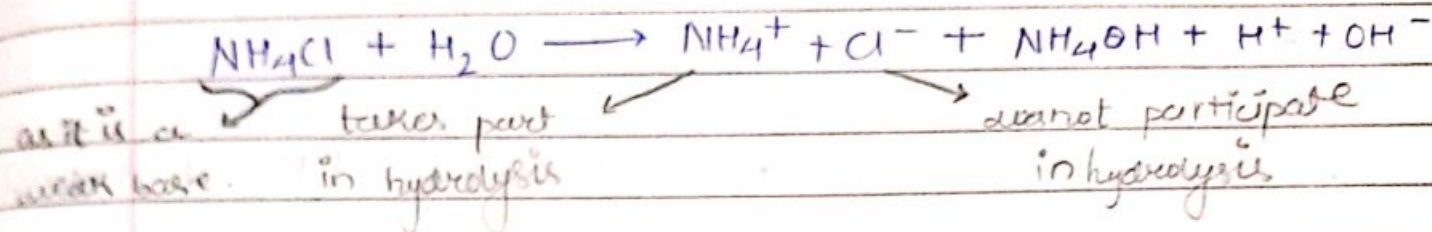
eg: NaCl , NaNO_3 , Na_2SO_4 , CuSO_4 , etc.

- this type of salt ~~do~~^{does} not undergo hydrolysis, they simply result to the 'ion formation'.



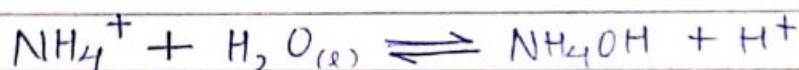
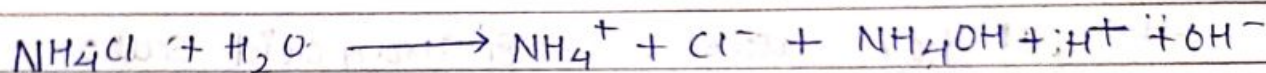
pH of that salt solution = 7. (neutral).

2.) $\Rightarrow$ Salt of weak base and strong acid
 eg: NH_4NO_3 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, etc.

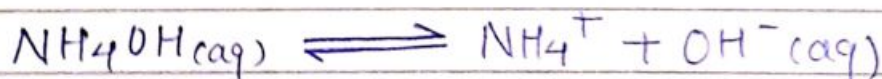


- here, in this hydrolysis only cation reacts to water
 hence it is also called CATIONIC HYDROLYSIS.

$\Rightarrow$ Relation b/w K_h , K_w and K_b
 (A.)



$$* K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \text{--- eq (I)} \quad \text{hydrolysis constant}$$



$$* K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{--- eq (II)} \quad \text{base constant}$$

eq (I) $\times$ eq (II)

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

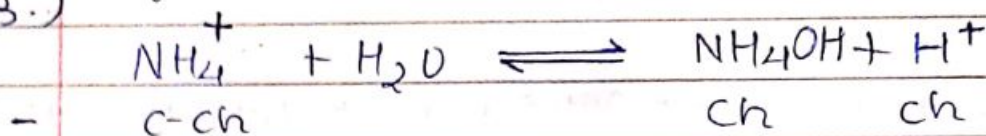
$$\boxed{K_h \times K_b = K_w}$$

$$\text{or } K_h = \frac{K_w}{K_b} \quad \text{--- eq (III)}$$

degree of hydrolysis. for.

⇒ pH for weak base and strong acid salt

(B.)



*Ka: ca 2

here, h = degree of hydrolysis. | $K_h = ch^2$ eq(IV)

putting value of K_h in eq(3).

$$\rightarrow K_w = ch^2 K_b. \quad \therefore, h = \sqrt{\frac{K_w}{K_b \cdot c}} \text{ eq(V).}$$

⇒ pH for weak base & strong acid salt

(C.)

$$\text{H}^+ = ch.$$

putting value of eq(V) in above eqⁿ

$$c \times \sqrt{\frac{K_w}{K_b \cdot c}}$$

$$\text{H}^+ = c \times \sqrt{\frac{K_w}{K_b \cdot c}}$$

$$\therefore, \text{H}^+ = \sqrt{\frac{K_w \cdot c}{K_b}}$$

$$\text{or } \text{H}^+ = \left(\frac{K_w \cdot c}{K_b} \right)^{1/2}$$

multiplying above eqⁿ on both side with -log.

$$-\log \text{H}^+ = -\log \left[\frac{K_w \cdot c}{K_b} \right]^{1/2}$$

$$\text{pH} = -\frac{1}{2} \log \left(\frac{K_w \cdot c}{K_b} \right)$$

$$\therefore, pH = \frac{-1}{2} (\log K_w + \log C - \log K_b)$$

$$-\log K_b = pK_b$$

$$-\log K_b = pK_b$$

$$\rightarrow pH = \frac{-1}{2} \log K_w - \frac{1}{2} \log C - \frac{1}{2} (-\log K_b)$$

$$\therefore, pH = \frac{1}{2} pK_w - \frac{1}{2} \log C - \frac{1}{2} pK_b$$

$$\rightarrow pH = \frac{1}{2} (pK_w - pK_b - \log C)$$

$$\therefore, pH = 7 - \frac{1}{2} \log C - \frac{1}{2} pK_b \quad \text{[} \because pK_w = 14 \text{ @ } 25^\circ\text{C} \text{]}$$

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

3.) $\Rightarrow$ Salt of weak acid and strong base:

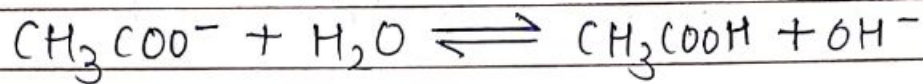
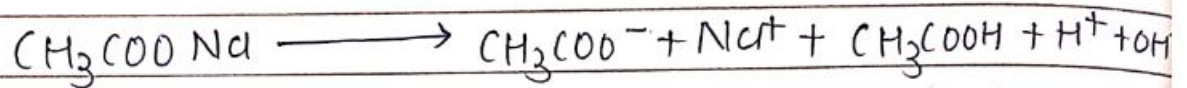
eg: HCOONa , CH_3COONa , $(\text{CH}_3\text{COO})\text{Ca}$, NaCN , etc.

- here, in this kind of salt hydrolysis of anion is covered hence it is known as ANIONIC HYDROLYSIS

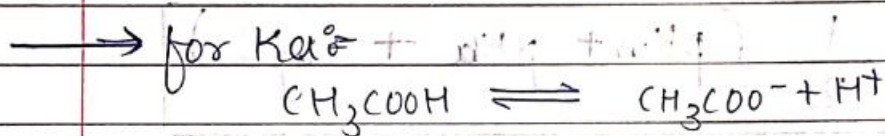
- pH of solution is basic. ($pH > 7$) due to presence of OH^- ion.



⇒ Relation b/w K_h , K_w and K_a
(A.)



$$\rightarrow K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \text{--- eq (I)}$$



$$\rightarrow K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{--- eq (II)}$$

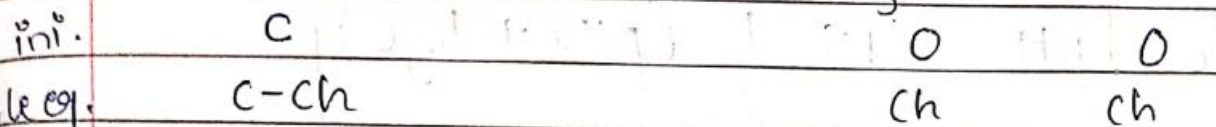
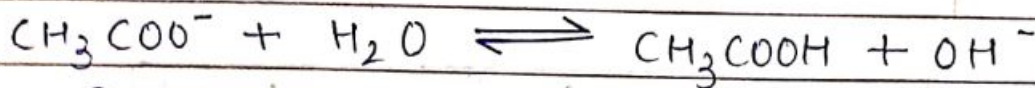
eq (I) $\times$ eq (II):

$$\frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = K_w$$

$$\boxed{K_h \times K_a = K_w} \quad \text{--- eq (III)}$$

$$\text{or } \boxed{K_h = \frac{K_w}{K_a}} \quad \text{--- eq (IV)}$$

⇒ Degree of hydrolysis for weak acid, strong base salt:
(B.)



∴, $\boxed{K_h = ch^2}$ — eq (IV)

$\boxed{h = \sqrt{\frac{K_h}{c}}}$ — eq (V).

putting eq (V) in eq (III)

$$K_h = \sqrt{\frac{K_w}{K_a \cdot c}}$$

$$\rightarrow K_h = \left(\frac{K_w}{K_a \cdot c} \right)^{1/2}$$

⇒ pH for strong base, weak acid salt:
(C.)

$$[\text{OH}^-] = ch$$

$$\therefore K_w = [\text{H}^+][\text{OH}^-]$$

$$\text{H}^+ = K_w / \text{OH}^-$$

$$\rightarrow \text{H}^+ = \frac{K_w}{ch}$$

$$\rightarrow \text{H}^+ = \frac{K_w \times \sqrt{\frac{K_a \cdot c}{K_w}}}{c}$$

$$\text{H}^+ = \sqrt{\frac{K_w \cdot K_a}{c}} \quad (1)$$

now, $-\log \text{H}^+ = -\log \left(\frac{K_a \cdot K_w}{c} \right)^{1/2}$

$$\text{pH} = -\frac{1}{2} (\log K_a + \log K_w - \log c)$$

$$= -\frac{1}{2} \log K_a - \frac{1}{2} \log K_w - \frac{1}{2} (-\log c)$$

$$= \frac{1}{2} \text{p}K_a + \frac{1}{2} \text{p}K_w + \frac{1}{2} \log c$$

∴, $\boxed{\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]}$

$$pK_w = 14$$

$$\frac{14}{2} = 7$$

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

$$o.o., \quad pH = 7 + \frac{1}{2} (pK_a + \log C)$$

4.) $\Rightarrow$ Salt of weak acid and weak base:

eg: CH_3COONH_4 , $HCOONH_4$, NH_4CN , $(NH_4)_2CO_3$, etc.

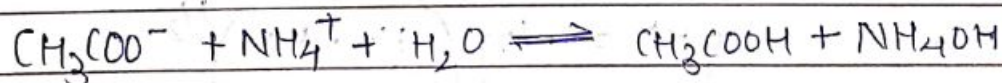
- in this category, both cation and anion participates in hydrolysis. hence it is called cationic-anionic hydrolysis or neutral hydrolysis.

- pH of that salt is decided by value of K_a and K_b

- if $K_a > K_b$; $pK_a < pK_b$ (acidic). $K_a \uparrow$ $pK_a \downarrow$
- if $K_a < K_b$; $pK_a > pK_b$ (basic).

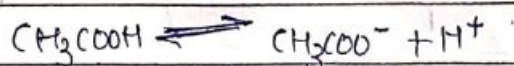
$\Rightarrow$ Relation b/w K_a , K_b , K_w & K_h :

(A.)



$$\rightarrow K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \quad \text{--- eq (1)}$$

disso. const. for weak acid (K_a)



$$\rightarrow K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \text{ --- eq(II).}$$

disso. constant for weak base (K_b),



$$\rightarrow K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \text{ --- eq(III)}$$

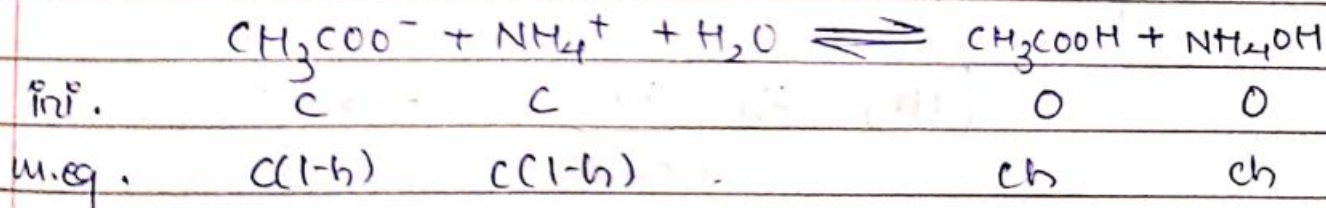
$$\text{eq(I)} \times \text{eq(II)} \times \text{eq(III).}$$

$$\Rightarrow \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \times \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_w$$

$$\therefore, K_h \times K_a \times K_b = K_w \text{ --- eq(IV)}$$

$$K_h = \frac{K_w}{K_a \times K_b} \text{ --- eq(V).}$$

⇒ Degree of hydrolysis:
(B.)



$$K_h = \frac{c^2 h^2}{c^2 (1-h)^2} \quad (\text{here, } h \ll 1)$$

$$K_h = h^2 \quad \text{or} \quad h = \sqrt{K_h} \quad \rightarrow \quad h = \sqrt{\frac{K_w}{K_a \times K_b}} \quad (\text{eq(VI)})$$

NOTE:

- for w. acid, w. base salt degree of hydrolysis
(h) does not depend upon initial concentration
(C) of the salt.
[concentration independent].

$\Rightarrow$ pH:

from eq (II).

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a [CH_3COOH]}{[CH_3COO^-]}$$

$$\Rightarrow [H^+] = \frac{K_a \cdot h}{1-h} \quad (h \ll 1).$$

$$\therefore, [H^+] = K_a \cdot h.$$

putting value of h from eq (VI)

$$[H^+] = K_a \sqrt{\frac{K_w}{K_a \cdot K_b}} \rightarrow \sqrt{\frac{K_w \cdot K_a}{K_b}}$$

now, putting $-\log$.

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



$$pH = -\frac{1}{2} (\log K_w + \log K_a - \log K_b)$$

$$= -\frac{1}{2} (+\log K_w) + \left(-\frac{1}{2}\right) (\log K_a) - \frac{1}{2} (-\log K_b)$$

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

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

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

	K_h	h	H^+	pH	nature
<u>SASB.</u>	—	—	10^{-7}	7	neutral.
<u>SAWB.</u>	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b \cdot c}}$	$H^+ = \sqrt{\frac{K_w \cdot c}{K_b}}$	$7 - \frac{1}{2} pK_b - \frac{1}{2} \log c$	acidic.
<u>WASB.</u>	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a \cdot c}}$	$H^+ = \sqrt{\frac{K_w \cdot K_a}{c}}$	$7 + \frac{1}{2} pK_a + \frac{1}{2} \log c$	basic.
<u>WAWB.</u>	$K_h = \frac{K_w}{K_a \times K_b}$	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$ or $h = \sqrt{K_h}$	$H^+ = \sqrt{\frac{K_w \cdot K_a}{K_b}}$	$7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$	depends upon conc of K_a/K_b .

NOTE:

$$pK_a + pK_b = 14 \text{ @ } 25^\circ\text{C}.$$

$$K_a \times K_b = 10^{-14} \text{ @ } 25^\circ\text{C}.$$

Q: 16 pK_b for CN^- @ 25°C is 4.7. pH of 0.5M NaCN ?
 $\text{NaCN} \rightarrow$ weak acid; strong base.

$$pK_a + pK_b = 14.$$

$$14 - 4.7$$

$$\therefore pK_a = 9.3.$$

$$C = 5 \times 10^{-1}.$$

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

$$= 7 + \frac{9.3}{2} + \frac{\log 0.5}{2}$$

$$= 7 + 4.6 + 0.95$$

=

$$\log 5 \times 10^{-1}$$

$$\log 5 + \log 1$$

$$0.3.$$

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

$$\log(5) + (-1)$$

$$-1 + 0.7$$

$$= 7 + \frac{9.3}{2} - \frac{0.3}{2}$$

$$-0.3$$

$$= 7 + 4.6 - 0.15$$

$$= 11.55$$

WA, SB.

Q:17 0.1 M acetate $K_a = 1.8 \times 10^{-5}$ at 298K. $\rightarrow 298K \rightarrow 25^\circ C$ $pK_w = 14$ $K_w = 10^{-14}$ 10^{-6-1}

$$H^+ = \sqrt{\frac{K_w}{K_a \cdot c}}$$

$$\rightarrow \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 10^{-1}}}$$

$$\sqrt{\frac{10^{-7}}{1.8}} \leftarrow \frac{10^{-1}}{1.8} = \frac{1}{1.8} \times 10^{-1}$$

$$\rightarrow 10^{-3} \sqrt{\frac{1}{1.8}}$$

$$\rightarrow 10^{-3} \times \frac{1}{1.35}$$

$$H^+ = \frac{10^{-3} \times 10}{1.35}$$

$$= 10^{-3} \times 0.07$$

$$= 7 \times 10^{-5}$$

$$135 \overline{) 1000}$$

$$9.65$$

Q:18 % hydrolysis of decimolal (0.1N) of ammonium acetate.
Given that value of $K_a = 1.75 \times 10^{-5}$ $K_b = 1.8 \times 10^{-5}$ $\rightarrow$

$$K_h = \frac{K_w}{K_a \cdot K_b}$$

$$\rightarrow$$

$$1 \times 10^{-14}$$

$$1.75 \times 10^{-5} \times 1.8 \times 10^{-5}$$

$$3.175 \times 10^{-5}$$

$$\rightarrow$$

$$3.175 \times 10^{-5}$$

$$h^+ = \sqrt{K_h}$$

$$\rightarrow$$

$$(3.175 \times 10^{-5})^{1/2}$$

$$\rightarrow (3.175 \times 10^{-6})^{1/2}$$

$$\rightarrow$$

$$5.63 \times 10^{-3}$$