Salt hydrolysis:

- hydrolysis is a process of where salt reacts water to form acid and base.

- Salt + water ⟶ Acid + 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.) ⟹ 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'.

$$NaCl + H_2O \longrightarrow Na^+ + Cl^- + H^+ + OH^-$$

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

2.) → Salt of weak base and strong acid:

eg: NH_4NO_3, NH_4Cl, $(NH_4)_2SO_4$, etc.

$$NH_4Cl + H_2O \longrightarrow NH_4^+ + Cl^- + NH_4OH + H^+ + OH^-$$

NH_4Cl as it is a weak base → takes part in hydrolysis

NH_4^+ → takes part in hydrolysis

Cl^- → cannot participate in hydrolysis

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

hydrolysis water weak base.

⇒ Relation b/w K_h, K_w and K_b:

(A.)

$$NH_4Cl + H_2O \longrightarrow NH_4^+ + Cl^- + NH_4OH + H^+ + OH^-$$

$$NH_4^+ + H_2O_{(l)} \rightleftharpoons NH_4OH + H^+$$

$$* \quad K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \text{---- eq(I)}$$

hydrolysis constant

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+ + OH^-_{(aq)}$$

$$* \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{---- eq(II)}$$

base constant

eq(I) × eq(II)

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

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

or $\# \quad K_h = \frac{K_w}{K_b}$ — eq(III)

degree of hydrolysis. for.

⇒ ~~pH for~~ weak base and strong acid salt:

(B.)

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

$$C - Ch \qquad\qquad Ch \quad Ch$$

$K_a = C\alpha^2$

here, h = degree of hydrolysis. $\boxed{K_h = Ch^2}$ eq(IV)

putting value of K_h in eq(3).

$$\longrightarrow \underline{K_w = Ch^2 K_b}. \qquad \therefore \boxed{h = \sqrt{\frac{K_w}{K_b \cdot C}}} \text{ eq(V)}.$$

⇒ pH for weak base & strong acid salt:

(C.)

$$H^+ = Ch.$$

putting value of eq(V) in above eqn

$C \times \sqrt{\frac{K_w}{K_b C}}$

$$H^+ = C \times \sqrt{\frac{K_w}{K_b \cdot C}} \qquad \therefore H^+ = \sqrt{\frac{K_w \cdot C}{K_b}}$$

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

multiplying above eqn on both side with -log.

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

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

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

$-\log K_w = pK_w$

$-\log K_b = pK_b$

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

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

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

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

$\longrightarrow \boxed{pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C}$.

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

eg: $HCOONa$, CH_3COONa, $(CH_3COO)_2Ca$, $NaCN$, etc.

- here, in this kind of salt hydrolysis of anion is carried hence it is known as ANIONIC HYDROLYSIS
- pH of solution is basic. ($pH > 7$) due to presence of OH^- ion.

⇒ Relation b/w Kh, Kw and Ka:

(A.)

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ + CH_3COOH + H^+ + OH$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

→ $$Kh = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$ —— eq(1).

→ for Ka:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

→ $$Ka = \frac{[CH_3COO^-] + [H^+]}{[CH_3COOH]}$$ —— eq(11).

eq(1) × eq(11):

$$\frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \times \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = Kw$$

$$\boxed{Kh \times Ka = Kw}$$ —— eq(111)

or $$\boxed{Kh = \frac{Kw}{Ka}}$$ —— eq(111)

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

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

	CH_3COO^-	H_2O	CH_3COOH	OH^-
ini.	c		0	0
mole eq.	c − ch		ch	ch

$$\boxed{K_h = ch^2} \quad \text{— eq (IV)}$$

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

putting eq (V) in eq (III)

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

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

$[OH^-] = ch$ $\quad \because K_w = [H^+][OH^-]$

$H^+ = K_w / OH^-$.

$$\longrightarrow H^+ = \frac{K_w}{ch} \longrightarrow H^+ = \frac{K_w}{c} \times \sqrt{\frac{K_a \cdot c}{K_w}} \qquad H^+ = \sqrt{\frac{K_w \cdot K_a}{c}}$$

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

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

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

$$= \frac{1}{2} pK_a + \frac{1}{2} pK_w + \frac{1}{2}\log c.$$

$$\therefore \boxed{pH = \frac{1}{2}[pK_w + pK_a + \log c]}$$

$pKw = 14$

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

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

or,

$$pH = 7 + \frac{1}{2}(pKa + \log C)$$

4.) ⟹ 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 Ka and Kb
- if $Ka > Kb$; $pKa < pKb$ (acidic). Ka↑ pKa↓
- if $Ka < Kb$; $pKa > pKb$ (basic).

⟹ Relation b/w Ka, Kb, Kw & Kh:

(A.)

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

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

diss. const. for weak acid (Ka_1)

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

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

diss^n. constant for weak base (K_b),

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

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

eq(I) x eq(II) x eq(III).

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

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

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

(B.) Degree of hydrolysis:

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

ini.	c	c	0	0
m.eq.	c(1-h)	c(1-h)	ch	ch

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

$$\boxed{K_h = h^2} \quad \text{or:} \quad \boxed{h = \sqrt{K_h}} \longrightarrow \boxed{h = \sqrt{\frac{K_w}{K_a \times K_b}}}$$

(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].

(C.) ⟹ **pH:**

from eq(II).

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

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

$$\Longrightarrow [H^+] = \frac{K_a \cdot ch}{c(1-h)} \qquad (h<<1).$$

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

putting value of h from eq(VI)

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

now, putting -log.

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

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

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

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

$-\log K_b \rightarrow pK_b.$

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

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

	K_h	h	H^+	pH	nature
SASB.	–	–	10^{-7}	7	neutral.
SAWB.	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b \cdot C}}$ $\sqrt{K_h/C}$	$H^+ = \sqrt{\frac{K_w \cdot C}{K_b}}$	$7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$.	acidic.
WASB.	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a \cdot C}}$ $\sqrt{K_h/C}$	$H^+ = \sqrt{\frac{K_w \cdot K_a}{C}}$	$7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$	basic.
WAWB.	$K_h = \frac{K_w}{K_a \times K_b}$	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$ 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:

$pKa + pKb = 14$ @ 25°C.

$Ka \times Kb = 10^{-14}$ @ 25°C.

Q:16 pKb for CN^- @ 25°C is 4.7. pH of 0.5M NaCN?

→ NaCN → weak acid; strong base.

$pKa + pKb = 14$. $14 - 4.7$

$\therefore pKa = 9.3$.

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

$$pH = 7 + \frac{pKa}{2} + \frac{\log c}{2}$$

$$= 7 + \frac{9.3}{2} + \frac{0.7}{2}$$

$$= 7 + 4.6 + 0.35$$

$$=$$

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

$\log 5 + \log 1$

0.7

$$pH = 7 + \frac{pKa}{2} + \frac{\log c}{2}$$

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

$$= 7 + 4.6 - 0.15$$

$$= 11.55$$

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

$-1 + 0.7$

-0.3

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ω A ; SB .

Q:17 0.1 M acetate ; $K_a = 1.8 \times 10^{-5}$; at 298K,

→ 298K → 25°C ; $pK_w = 14$. $K_w = 10^{-14}$.

$$H^+ = \sqrt{\frac{K_w}{K_a \cdot c}} \longrightarrow \sqrt{\frac{10^{-14}}{18 \times 10^{-6} \times 10^{-1}}} \quad \sqrt{\frac{10^{-7}}{18}} \quad \frac{10^{-6-1}}{} = \frac{10^{-1}}{} = \frac{1}{10}.$$

$$\longrightarrow 10^{-3} \sqrt{\frac{1}{180}} \longrightarrow 10^{-3} \times \frac{1}{13.5}$$

$$H^+ = \frac{10^{-3} \times 10}{135}$$

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

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

135) 100 (0.07
9.65

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

→

$$K_h = \frac{K_w}{K_a \cdot K_b} \longrightarrow \frac{1 \times 10^{-14}}{1.75 \times 10^{-5} \times 1.8 \times 10^{-5}}$$

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

$$h = \sqrt{K_h} \longrightarrow (3.175 \times 10^{-5})^{1/2}$$

$$\longrightarrow (31.75 \times 10^{-6})^{1/2}$$

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