Calculation of pH after mixing Weak acid

$$H^+ = \sqrt{(Ka_1 \times C_1) + (Ka_2 \times C_2) + \dots}$$

☼ SALT HYDROLYSIS

- Hydrolysis is a process where salt reacts Water to form acid and base.
- Salt + Water → Acid + Base
- It is the reverse of Neutralisation Reaction.
- Only Weak Acid / 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 OR BASE**

Eg: NaCl, $NaNO_3$, Na_2SO_4, $CuSO_4$ etc.

- Does not undergo hydrolysis, they simply result to the 'ion formation'

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

- pH of that salt (SASB) solution = 7 (Neutral)
  - This is possible when gram equivalent is equal

SALT OF STRONG ACID OR WEAK BASE:

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

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

- **HYDROLYSIS CONSTANT FOR NH_4^+ (K_h)**

In SAWB salt, hydrolysis of NH_4^+ should be carried out so, this type of hydrolysis also called Cationic Hydrolysis.

$NH_4^+(aq) + H_2O \rightarrow NH_4OH(aq) + H^+(aq.)$

$$K_H = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \text{---} (1)$$

- **DISSOCIATION CONSTANT OF WEAK BASE (K_b)**

$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{---} (2)$$

RELATION BETWEEN K_w, K_h and K_b:

Multiply the equation ① and ② :

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

$$\boxed{K_w = K_h \times K_b} \quad \text{—— ③}$$

DEGREE OF HYDROLYSIS FOR STRONG ACID WEAK BASE

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

C — 0 — 0

C-Ch — Ch — Ch

$$\boxed{K_h = Ch^2} \quad \text{or} \quad \boxed{h = \sqrt{\frac{K_h}{C}}} \quad \text{or} \quad \boxed{h = \sqrt{\frac{K_w}{K_b \times C}}} \quad \text{—④}$$

Here, h: degree of hydrolysis.

CALCULATION OF pH FOR SAWB SALT

Here, $H^+ = Ch$

or $H^+ = C\sqrt{\frac{K_w}{K_b \cdot C}}$

$$\boxed{H^+ = \sqrt{\frac{C \times K_w}{K_b}}} \quad \text{—— ⑤}$$

$pH = -\log H^+$

$= -\frac{1}{2}\log\left[\frac{C \times K_w}{K_b}\right]$

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

$$pH = \frac{1}{2}pK_w - \frac{1}{2}\log C - \frac{1}{2}pK_b \quad \text{— (6)}$$

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

Note: Overall pH of SAWB Salt is <7 (Acidic in Nature)

✳ SALT OF STRONG BASE OR WEAK ACID :

Eg : CH_3COONa , $HCOOK$ etc :

$$CH_3COONa + H_2O \longrightarrow CH_3COO^- + Na^+ + H^+ + OH^- + CH_3COOH$$

• HYDROLYSIS CONSTANT (Kh) FOR CH_3COO^-

It is anionic hydrolysis

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

$$K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} \quad \text{— (1)}$$

• DISSOCIATION CONSTANT FOR WEAK ACID

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

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} \quad \text{— (2)}$$

RELATION BTW Kw, Kh, Kb

Multiply eqn ① and ②,

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

$$\boxed{K_w = K_h \times K_a} \quad — ③$$

DEGREE OF HYDROLYSIS FOR SBWA

$$\underset{c}{CH_3COO^-} + H_2O \rightleftharpoons \underset{0}{CH_3COOH} + \underset{0}{OH^-}$$

$$\underset{c-ch}{} \qquad \underset{ch}{} \qquad \underset{ch}{}$$

$$K_h = \frac{c^2h^2}{(1-h)} \Rightarrow \boxed{K_h = ch^2} \quad — ④ \qquad \boxed{h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_a \cdot c}}} \quad — ⑤$$

CALCULATION OF PH FOR SBWA

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

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

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

$$\boxed{[H^+] = \sqrt{\frac{K_w \times K_a}{c}}} \quad — ⑥$$

$$pH = -\log\left(\frac{Kw \times Ka}{c}\right)^{1/2}$$

$$pH = -\frac{1}{2}\log\left(\frac{Kw \times Ka}{c}\right)$$

$$pH = -\frac{1}{2}\log Kw - \frac{1}{2}\log Ka + \frac{1}{2}\log c$$

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

Note: Overall pH of SBWA is more than 7 and it is basic in nature.

SALT OF WEAK ACID OR WEAK BASE:

Eg: CH_3COONH_4, $HCOONH_4$ etc.

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

It is also known as Cationic - Anionic Hydrolysis or Neutral Hydrolysis.

HYDROLYSIS CONSTANT FOR WAWB:

$$\boxed{Kh = \frac{[CH_3COOH]\,[NH_4OH]}{[CH_3COO^-][NH_4^+][H_2O]}} \quad \text{---(1)}$$

DISSOCIATION CONSTANT OF WAWB:

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad \text{—— (2)}$$

$$NH_4OH + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{—— (3)}$$

RELATION BTW Kw, Ka, Kb and Kh

After multiplying the equation (1), (2) & (3)

$$K_w = K_a \times K_b \times K_h \quad \text{—— (4)}$$

CALCULATION OF DEGREE OF HYDROLYSIS

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

C	C	0	0
C - Ch	C - Ch	Ch	Ch
or	or		
C(1 - h)	C(1 - h)		

$$K_h = \frac{C^2h^2}{C^2(1-h)^2} \quad \text{or} \quad \boxed{K_h = h^2} \ (5) \quad \text{or} \quad h = \sqrt{K_h}$$

NOTE Degree of hydrolysis for WAWB salt does not depends on initial concentration of salt. It depends only on temperature

$$h = \sqrt{\frac{Kw}{Ka \times Kb}} \quad \text{---} \ (6)$$

- CALCULATION OF pH

From eqn: 02

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

$$H^+ = \frac{Ka \times h}{\underbrace{c(1-h)}_{\text{Approx} = 1}} \qquad H^+ = Ka \times h$$

$$H^+ = Ka \sqrt{\frac{Kw}{Ka \times Kb}}$$

$$H^+ = \sqrt{\frac{Kw \times Ka}{Kb}}$$

$$pH = \frac{1}{2} pKw - \frac{1}{2} pKb + \frac{1}{2} pKa$$

SASB: Neutral Salt : (pH = 07)

	K_h	h	H^+	pH
	$K_h = ch^2$	$h = \sqrt{K_h/c}$	$H^+ = ch$	$pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log c$
(NH_4Cl)	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b \times c}}$	$H^+ = \sqrt{\frac{K_w \times c}{K_b}}$	
	$K_H = ch^2$	$h = \sqrt{\frac{K_w}{K_a \times c}}$	$H^+ = \sqrt{\frac{K_w \times K_a}{c}}$	$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c$
(CH_3COONa)	$K_h = \frac{K_w}{K_a}$			
	$K_h = h^2$	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$H^+ = \sqrt{\frac{K_w \times K_a}{K_b}}$	$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_b + \frac{1}{2}pK_a$
(CH_3COONH_4)				

Note: In case of WAWB salt,
if $pK_a > pK_b$: Basic in nature ($K_a < K_b$)
if $pK_a < pK_b$: Acidic in nature ($K_a > K_b$)
if $pK_a = pK_b$: Neutral

Que: 9 DPP: 05 What is the pH of an aqueous solution of Ammonium acetate ($K_a = K_b = 1.8 \times 10^{-5}$)
7.0 (Neutral))

Que: 12 DPP: 05 $K_H = 6.25 \times 10^{-8}$
0.5M ammonium benzoate ($C_6H_5COONH_4$)
% Hydrolysis of salt = ?
$K_h = h^2 \Rightarrow h = \sqrt{6.25 \times 10^{-6}} = 0.25 \times 10^{-3}$

Que 13 DPP05

0.10M NaZ

pH = 8.90

Ka of HZ = ?

$\log(10) = 10^{-2}$

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

$$8.9 = 7 + \frac{pKa}{2} + \frac{1}{2}(-1)$$

$$8.9 = 7 - 1 + \frac{pKa}{2}$$

$$8.9 = \frac{12 + pKa}{2}$$

$$17.8 = 12 + pKa$$

$$pKa = 17.8 - 12.0$$

$$pKa = 5.8$$

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

$$8.90 = 7 + \frac{1}{2}pKa + \frac{1}{2} \times \log 10^{-1}$$

$$8.90 = 7 + \frac{1}{2}pKa - \frac{1}{2}$$

$$8.90 - 7 + 0.5 = \frac{1}{2}pKa$$

$$9.4 = \frac{1}{2}pKa$$

$$4.8 = pKa$$

$$\boxed{Ka = 1.6 \times 10^{-5}}$$

Note

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ Ka_1

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$ Ka_2

$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$ Ka_3

$Ka_1 >>> Ka_2 >>> Ka_3$

$$\boxed{Ka = Ka_1 \times Ka_2 \times Ka_3}$$

Que 13 DPPO4

pH = ?

0.01 M H_3PO_4

$[PO_4^{-3}] = 10^{-5}$ M

$Ka_1 = 10^{-4}$

$Ka_2 = 10^{-6}$

$Ka_3 = 10^{-8}$

$Ka = Ka_1 \times Ka_2 \times Ka_3 = 10^{-18}$

H_3PO_4 = Weak acid

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$

$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$

$H_3PO_4 \rightleftharpoons H^+ + PO_4^{-3}$

(10^{-2}) (10^{-5})

$$Ka = \frac{[PO_4^{-3}][H^+]}{[H_3PO_4]}$$

$$10^{-18} = \frac{[10^{-5}][H^+]}{[10^{-2}]} \Rightarrow \frac{10^{-36}}{10^{-5}} = [H^+]$$