

Calculations of pH of the buffer mixtures

I:- Buffer mixture of weak Acid and its salt.
Weak Acid HA
Completely dissociated Salt NA

So the hydrogen ion concentration of such a solution is given by the equation.

$$[H^+] = K_a \frac{[Acid]}{[Salt]}$$

Taking logs and reversing the sign

$$-\log [H^+] = -\log K_a + \log \left(\frac{[Salt]}{[Acid]} \right)$$

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Henderson-Hasselbalch equation

It enables the calculation of pH of a buffer soln made by mixing known quantities of a weak acid and its salt.

Q2 - Calculate the pH of a solution obtained by mixing 5g of AcH and 7.5g of NaAc and making the vol. equal to 500ml? Dissociation constant of Acetic acid at 25°C is 1.75×10^{-5} ? M.Wt of NaAc = 82, M.Wt of AcH = 60

Ans

$$K_a = 1.75 \times 10^{-5}$$

$$\therefore -\text{p}K_a = -\log K_a = -\log (1.75 \times 10^{-5}) = 4.76$$

$$[\text{Salt}] = \frac{7.5g}{82} \times \frac{1000}{500} = 0.1829 \text{ M}$$

$$[\text{Acid}] = \frac{5g}{60} \times \frac{1000}{500} = 0.1666 \text{ M}$$

$\therefore$ Putting in Henderson - Hasselbalch eqⁿ

$$\text{pH} = 4.76 + \log \frac{0.1829}{0.1666}$$

$$\Rightarrow 4.80$$

Q2 A buffer solⁿ contains 0.2 mole of ACH and 0.25 mole of pot. acetate per litre. Calculate the change in pH of solⁿ.
 If 0.5 ml of 1M HCl is added to it. (The K_a (ACH) at room temp is 1.75×10^{-5} (vol. change on the addⁿ of HCl may be neglected)).

Solⁿ

$$pK_a \text{ of ACH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$pK_a = -\log K_a \\ = -\log 1.75 \times 10^{-5} = 4.76$$

pH of the solution before adding HCl will be given by

$$pH = pK_a + \log \frac{0.25}{0.20}$$

$$= 4.76 + 0.0969 \\ = 4.8569$$

Am^t of HCl added = 0.5 ml of 1M HCl = 0.0005 mole

If we assume that HCl is completely dissociated then.



This means amount of ACH will $\uparrow$ and that of pot. acetate will $\downarrow$ by 0.0005 mole

So, after adding HCl

$$[\text{CH}_3\text{COOH}] = 0.2 \text{ mole} + 0.0005 \text{ mole} = 0.2005 \text{ mole}$$
$$[\text{Pot-Acetate}] = 0.25 \text{ mole} - 0.0005 \text{ mole} = 0.2495$$

$$\text{So } \text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$
$$= 4.76 + \log \frac{0.2495}{0.2005} = 4.8549$$

$$\text{Change of pH} = 4.8569 - 4.8549 = 0.002$$

So there is only a slight change in the pH.

II Buffer Mixture of a weak Base and its Salt:

$$[\text{OH}^-] = K_b \frac{[\text{Base}]}{[\text{Salt}]}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

knowing pOH, pH can be calculated as
 $\text{pOH} + \text{pH} = \text{pK}_w = 14$

HYDROLYSIS OF SALTS.

The phenomenon of the interaction of anions and cations of the salt with H^+ and OH^- ions furnished by water yielding acidic or alkaline (or sometimes even neutral) solutions is known as salt hydrolysis.

Hydrolysis is considered as reverse of neutralization. Neutralization involves combination of H^+ and OH^- ions giving undissociated water.

Hydrolysis leads to formation of H^+ and OH^- ions as discussed.

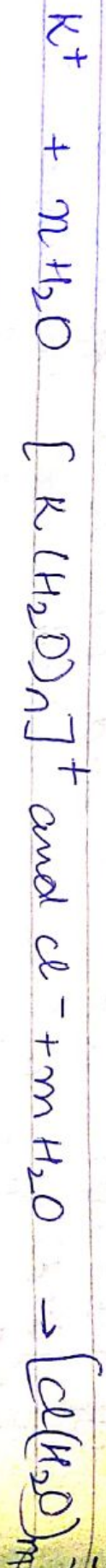
We can divide salt into four categories :-

- 1) Salts of strong acids and strong base i.e. KCl and $NaNO_3$.
- 2) Salts of weak acids and strong bases i.e. KCN and NaAc.
- 3) " " " " weak base i.e. NH_4Cl , Aniline hydrochloride
- 4) " " weak acids " " " i.e. $NH_4CH_3COO^-$.

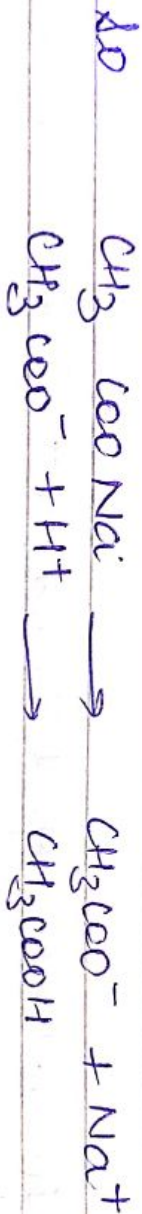
New I:- S.A + S.B:- They don't hydrolyse. e.g.

KCl when dissolved in H_2O have no tendency to react with H^+ or OH^- because the possible product KOH and HCl are themselves completely dissociated i.e. there is

no change in the conc. of H^+ and OH^- and the solution continues to remain neutral. ∴ the salts of S.A & S.B do not undergo hydrolysis.

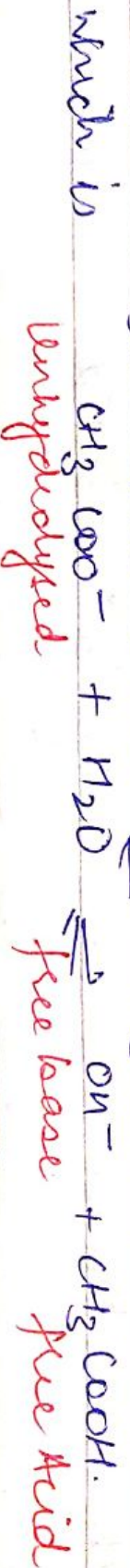


II). Salts of weak Acids and strong Bases:-
such category upon hydrolysis give alkaline solutions.



The undissociated H_2O further dissociates to maintain the constant value of K_w . The H^+ ions are further taken up of CH_3COO^- so eventually this leads to ↑ in amt of OH^- ions making solution alkaline.

Hydrolysis constant:-
the hydrolytic reaction of sod. Acetate may be written as:-

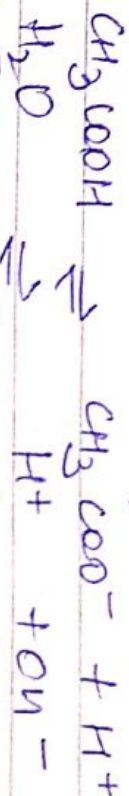


Acc to law of chem. eqbm: (taking the conc. of H_2O as const)

$$K_h = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$$

↓
hydrolysis constant.

apart from the above eqbm, the 2nd eqbm:-



$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad (1) \quad K_b = [H^+][OH^-] \quad (2)$$

do (2) ÷ (1) by

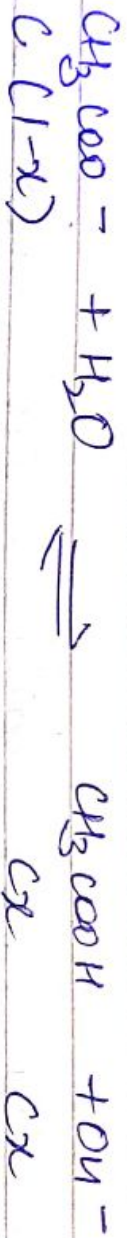
$$\frac{K_b}{K_a} = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$$

$$K_h = K_b/K_a$$

As weaker the acid, greater the hydrolysis constant of the salt.

Degree of hydrolysis: The fraction of the total salt that has undergone hydrolysis on the attainment of carbon.

Let c moles per litre be the initial conc. of Mn^{2+}
Let x be degree of hydrolysis.



$$k_h = \frac{cx}{x(1-x)} = \frac{cx^2}{1-x}$$

x is small compared to 1 i.e.

$$k_1 = \frac{c x_2}{x_1} \quad \text{or} \quad x_1 = \sqrt{k_5 / c}$$

But $k_h = k_{w0}/k_a$

$$x = \sqrt{\frac{K_w}{(K_a x_c)}}$$

do x can be known by
knowing ka. at any time.
(c) d

degree of hydrolysis $\propto$ with $\uparrow$ in Temp

2) $\begin{matrix} 0 & 0 & 0 \\ \parallel & \parallel & \parallel \\ \uparrow & \text{ex} & \uparrow \end{matrix}$ in deletion

3) weaker the acid, greater is 'x' (degree of hydrolysis) -

pH of the hydrolysed salt solution:-

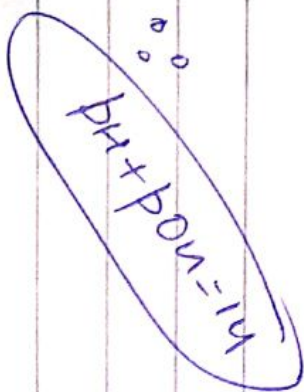
during hydrolysis of CH_3COONa , $[\text{CN}^-] = cx$.
so using eq (1)

$$[\text{CN}^-] = c \left(\frac{K_w}{K_a c} \right)^{1/2} = \left(\frac{K_w \times c}{K_a} \right)^{1/2}$$

taking negative logs on both side

$$-p[\text{CN}^-] = \frac{1}{2} pK_w - \frac{1}{2} \log c - \frac{1}{2} pK_a$$

$$\text{pH} = 14 - \frac{1}{2} pK_w + \frac{1}{2} \log c + \frac{1}{2} pK_a$$



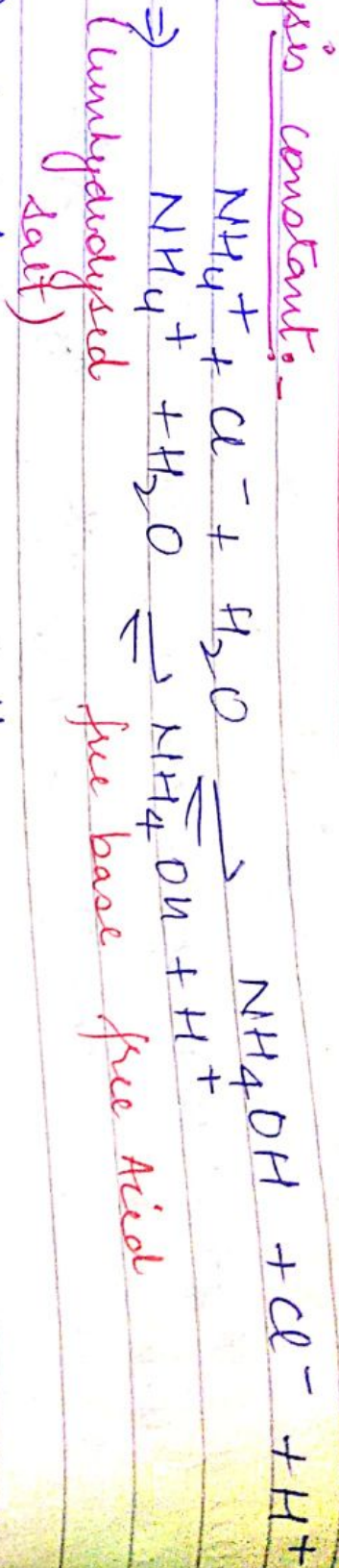
III Salts of weak Bases and strong Acids:-

e.g. NH_4Cl .

In water this form NH_4OH .

This undissociated H_2O further dissociates so as to maintain the constant value of K_w . This causes an increase in the conc. of hydrogen ions and a decrease in the conc. of hydroxyl ions. $\therefore$ solⁿ becomes acidic.

Hydrolysis constant:-



So by law of Chem Equilibrium..

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

The other Equilibrium that exists are

$$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

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



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

$$\frac{K_w}{K_b} = \frac{[\text{H}^+][\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = K_h$$

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