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 sol^n made by mixing known quantities of a weak acid and its salt

Q:- 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.Mass of NaAc = 82, M.M of AcH = 60

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

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

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

$$[\text{Acid}] = \frac{5g}{60} \times \frac{1000}{500} = 1.666\ M.$$

$\therefore$ putting in Henderson - Hasselbalch eqn

$$pH = 4.76 + \log \frac{0.1829}{1.666}$$

$$\Rightarrow 4.80.$$

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

Sol^n

pKa of AcH = pka + log ([Salt]/[Acid])

pKa = -log Ka

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

pH of the solution before adding HCl will be given by

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

$= 4.76 + 0.0969$

$= 4.8569$

Amt of HCl added = 0.5 ml of 1M HCl = 0.0005 mole

If we assume that HCl is completely dissociated then.

$CH_3COO^- + H^+ \longrightarrow CH_3COOH$.

this means amount of AcH will ↑ and that of pot. acetate ↓ es by 0.0005 mole

So, after adding HCl

$[CH_3COOH]$ = 0.2 mole + 0.0005 mole. = 0.2005 mole

[Pot. Acetate] = 0.25 mole + 0.0005 mole = 0.2495

So $pH = pKa + \log \frac{[salt]}{[Acid]}$

$= 4.76 + \log \frac{0.2495}{0.2005} = 4.8549$

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:

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

$$pOH = pK_b + \log \frac{[salt]}{[Base]}$$

Knowing pOH, pH can be calculated as

$pOH + pOH = pK_w = 14$

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 ie KCl and $NaNO_3$.
2) Salts of weak Acids and strong bases ie KCN and NaAc.
3) " " strong " " weak base ie NH_4Cl, Aniline hydro chloride
4) " " weak Acids " " " ie NH_4CH_3COO.

Now I:- S.A + S.B:- They donot 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 ∴ 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 donot undergo hydrolysis.

$K^+ + n H_2O \rightarrow [K(H_2O)_n]^+$ and $Cl^- + m H_2O \rightarrow [Cl(H_2O)_m]^-$

II). Salts of Weak Acids and strong Bases:-

such category upon hydrolysis give alkaline solutions.

so $CH_3COONa \longrightarrow CH_3COO^- + Na^+$

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

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:

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

which is $CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$.

Unhydrolysed — Free base — Free Acid

Acc to law of chem. eqlbm: (taking the conc. of H_2O as constt)

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

↓

hydrolysis constant.

apart from the above eqlbm, the two eqlbm:-

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

$$H_2O \rightleftharpoons H^+ + OH^-$$

$\therefore K_a = \frac{[H^+]\cdot[CH_3COO^-]}{[CH_3COOH]}$ (1) & $K_w = [H^+][OH^-]$ (2).

do (2) ÷ by (1)

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

$$\boxed{K_h = K_w/K_a}$$

So 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 equilibrium.

Let c moles per litre be the initial conc. of NaAc
Let x be degree of hydrolysis.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
$$C(1-x) \qquad\qquad Cx \qquad Cx$$

$$K_h = \frac{Cx \cdot Cx}{C(1-x)} = \frac{Cx^2}{1-x}.$$

x is small compared to 1 ∴

$$K_h = Cx^2 \quad \text{or} \quad x = \sqrt{K_h/C}$$

But $K_h = K_w/K_a$

$$\therefore \quad x = \sqrt{\frac{K_w}{(K_a \times C)}} \rightarrow (1)$$

So x can be known by knowing K_a at any conc. 'c'.

∴ 1) degree of hydrolysis ↑es with ↑ in temp
2) " " ↑es with ↑ in dilution
3) Weaker the acid, greater is 'x' (degree of hydrolysis).

pH of the hydrolysed salt solutions:-

during hydrolysis of CH_3COONa, $[OH^-] = Cx$.

to using eq (1)

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

taking negative logs on both side

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

$\because$ $pH + pOH = 14$

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

III Salts of weak Base 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. $\therefore$ Sol^n becomes acidic.

Hydrolysis constant:-

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

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

(unhydrolysed salt) — free base — free Acid

So by Law of chem Eqlbm.. -

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]}$$

The other Eqlbm that exists are

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

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

$$H_2O \rightleftharpoons H^+ + OH^-$$

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

$$\frac{K_w}{K_b} = \frac{[H^+][NH_4OH]}{[NH_4^+]} = K_h$$

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