HENDERSON'S EQUATION (pH OF A BUFFER)

(i) Acidic buffer:

It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, HA, can be shown by the equation

$HA \leftrightarrow H^+ + A^-$

Applying law of mass action,

$K_a = H^+A^-/[HA]$

It can be assumed that concentration of $\boldsymbol{A^-}$ ions from complete ionisation of the salt ***BA*** is too large to be compared with concentration of $\boldsymbol{A^-}$ ions from the acid HA.

$BA \leftrightarrow B^+ + \boldsymbol{A^-}$

Thus, ***[HA]*** = Initial concentration of the acid as it is feebly ionised in presence of common ion

and $\boldsymbol{[A^-]}$ = Initial concentration of the salt as it is completely ionised.

So $[H^+] = Ka \cdot [Acid]/[Salt]$ ..... (iii)

Taking logarithm and reversing sign,

$-\log [H^+] = -\log K_a - \log[Acid]/[Salt]$

or $pH = \log[Salt]/[Acid] - \log K_a$

or $pH = pK_a + \log[Salt]/[Acid]$ ..... (iv)

This is known as Henderson's equation.

When [Salt]/[Acid] = 10 , then

$pH = 1 + pK_a$

and when [Salt]/[Acid] , then

$pH = pK_a - 1$

So weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a - 1$. The acetic acid gas a pK_a of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the ranges 3.8 to 5.8.

(ii) Basic offer:

It consists of a weak base and its salt with strong acid. Ionization of a weak base, BOH, can be represented by the equation.

$BOH \leftrightarrow B^+ + OH^-$

Applying law of mass action,

$K_b = [B^+][OH^-]/[BOH]$ ..... (i)

or $[OH^-] = K_b [BOH]/[B^+]$ ..... (ii)

As the salt is completely ionized, it can be assumed that whole of B^+ ion concentration comes from the salt and contribution of weak base to B^+ ions can be ignored.

$BA \leftrightarrow B^+ + A^-$ (Completely ionised)

So $[OH^-] = K_b[Base]/[Salt]$ .... (iii)

or $pOH = \log[Salt]/[Base]$ $\log K_b$

or $pOH = pKb + \log[Salt]/[Base]$ ..... (iv)

Knowing pOH, pH can be calculated by the application of the formula.

$pH + pOH = 14$

Source : http://ciseche10.files.wordpress.com/2013/12/ionic-equilibrium.pdf