DETERMINATION OF pH OF ACIDS AND BASES

Strong Acid

Let's examine a scenario involving a strong acid, denoted as HA, with a concentration of C M. The concentration of hydrogen ions ($[H^+]$) contributed by the acid is also C, and an additional amount (x) arises from the self-ionization of water.

The dissociation of the strong acid is represented as:

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

Simultaneously, water undergoes self-ionization:

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

The total pH of the solution is given by the negative logarithm of the total hydrogen ion concentration:

$$Ph = -\log[H^+]\text{ Total} = -\log([H^+]\text{Acid} + [H^+]\text{Water})$$

Substituting the expressions, we get:

$$pH = -\log(C + x)$$

Since the concentration of the acid (C) is usually much greater than the contribution from the self-ionization of water (x),

when, $C \geq 10^{-6}$

we can simplify the equation to: $C + x \approx C$

Thus, the pH is approximately equal to $-\log C$.

Weak Acid,

A weak acid does not completely undergo dissociation, necessitating the calculation of its degree of dissociation using the acid's dissociation constant, Ka. This involves the application of Ostwald's Dilution Law, as derived previously.

	$HA \longrightarrow$	H^+	$+ \quad A^-$
$t = 0$	C	0	0
t_{eq}	$C(1 - \alpha)$	$C\alpha$	$X\alpha$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{Ca^2}{1-\alpha}$$

If, $\alpha << 1$

$\Rightarrow$ $(1 - \alpha) \approx 1$

$\Rightarrow$ $K_a \approx C\alpha^2$

$\Rightarrow$ $\alpha =$ (is valid if $\alpha < 0.1$ or 10%)

$$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$$

So, $pH = \frac{1}{2}(pK_a - \log C)$

valid only if $\alpha <<< 1$.

on increasing the dilution

$\Rightarrow$ $C\downarrow \; = \alpha\uparrow$ and $[H^+]\downarrow$

$\Rightarrow$ $pH\uparrow$

Mixture of two Weak Acids,

Both acids will dissociate partially.

Let the acid are HA_1 & HA_2 and their final concentrations are C_1 & C_2 respectively, then

$$\begin{array}{lllllll} & HA_1 \longrightarrow & H^+ + & A_1^- & HA_2 \longrightarrow & H^+ + & A_2^- \\ t = 0 & C_1 & 0 & 0 & C_2 & 0 & 0 \\ \text{At eq.} & C_1(1-\alpha_1) & C_1\alpha_1 + C_2\alpha_2 & C_1\alpha_1 & C_2(1-\alpha_2) & C_2\alpha_2 + C_1\alpha_1 & C_2\alpha_2 \end{array}$$

$$K_{a_1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)} \qquad K_{a_2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

(Since α_1, α_2 both are small in comparison to unity)

$$= (C_1\alpha_1 + C_2\alpha_2)\alpha_1 \ ; \ = (C_1\alpha_1 + C_2\alpha_2)\alpha_2$$

$$\Rightarrow \qquad \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1\ K_{a_1}}{\sqrt{C_1\ K_{a_1} + C_2\ K_{a_2}}} + \frac{C_2\ K_{a_2}}{\sqrt{C_1\ K_{a_1} + C_2\ K_{a_2}}}$$

$$\Rightarrow \qquad [H^+] = \sqrt{C_1\ K_{a_1} + C_2\ K_{a_2}}$$

If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

So, $[H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$

Polyprotic Weak Acid

A diprotic acid is an acid that can release two protons per molecule when dissolved in water. Consider a weak diprotic acid (H_2A) in an aqueous solution with a concentration of c M.

In an aqueous solution, following equilibria exist.

α_1 = degree of ionization of H_2A in presence of HA^-	K_{a_1} = first ionisation constant of H_2A
α_2 = degree of ionisation of HA^- in presence of H_2A	K_{a_2} = second ionisation constant of H_2A
$H_2A + H_2O\ HA^- + H_3O^+$	$HA^- + H_2O\ A^{2-} + H_3O^+$
at eq. $C - x$ $\quad x - y$ $\quad x + y$ at eq. $x - y$ $\quad y$ $\quad x + y$	
$(K_{eq})_1\ [H_2O] = \frac{[H_3O^+][HA^-]}{[H_2\ A]} = K_{a_1}$	$(K_{eq})_2\ [H_2O] = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = K_{a_2}$
$\therefore \quad K_{a_1} = \frac{(x-y)(x+y)}{(C-x)}$	$K_{a_2} = \frac{(y)(x+y)}{(x-y)}$

Approximation

For diprotic acids, << and y would be even smaller than x.

$\therefore \qquad y <<< x$

$\Rightarrow \qquad x - y\ x$ and $x + y\ x$

Thus, equation (i) can be reduced to $K_{a_1} = \frac{x^2}{C-x}$, $K_{a_2} = y$

This is expression similar to the expression for a weak monoprotic acid.

Hence, for a diprotic acid (or a polyprotic acid) the $[H_3O^+]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} << K_{a_1}$

pH of a Mixture of a Polyprotic Weak Acid and a Strong Acid

For the initial approximation of pH, it is sufficient to consider the concentration of the strong acid. However, for a more accurate calculation, we should focus solely on the first dissociation constant of the weak polyprotic acid, as indicated by the equations we've discussed thus far. These same procedures can also be applied to determine the pOH for weak bases and their combinations, with the only modification being to replace Ka with Kb.