

Similarly

$$pOH = -\log [OH^-]$$

Note : * As per thermodynamics pH has no unit, pH is defined as

$$pH = -\log a_{H^+}$$

Where, a_{H^+} is the hydrogen ion activity. The H^+ activity is obtained by multiplying $[H^+]$ by a suitable activity coefficient (γ) based on thermodynamic measurements. They approach 1.0 for very dilute solutions but get smaller as concentration increases.

* for concentrate solution pH values greater than 14 are possible for concentrated strong base and negative pH values are possible for concentrated strong acids.

* pH of very dilute ($\sim 10^{-8}M$ or Lower) acids (or bases) is nearly 7 (not simply $-\log[\text{acid}]$ etc. due to ionization of water.

* At $25^\circ C$, if $pH = 7$, then solution is neutral, $pH > 7$ then solution is basic.

Ionisation Constants

* For dissociation of weak acids (eg. HCN), $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$ the equilibrium

constant expression is written as $K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$

* For the Polyprotic acids (e.g. H_3PO_4), successive ionisation constants are denoted by K_{a1} , K_{a2} , K_{a3} etc. For H_3PO_4 ,

$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} ; \quad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} ; \quad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

Similarly, K_b denotes basic dissociation constant for a base.

Also, $pK_b = -\log_{10} K_b$, $pK = -\log_{10} K_a$

pH CALCULATION :-

Case (i)

A weak acid in water :

(a) if $\alpha = \sqrt{\frac{K_a}{C}}$ is < 0.05 , then $[H^+] \approx \sqrt{K_a C}$.

(b) **General Expression :** $[H^+] = 0.5(-K_a + \sqrt{K_a^2 + 4K_a C})$

Similarly for a weak base, substitute $[OH^-]$ and K_b instead of $[H^+]$ and K_a respectively in these expressions.

Case (ii)

(a) **A weak acid and a strong acid :** $[H^+]$ is entirely due to dissociation of strong acid may be both depend on conditions.

(b) **A weak base and a strong base :** $[OH^-]$ is entirely due to dissociation of strong base may be both depend on conditions.

Neglect the contribution of weak acid/base if α is negligible.

Case (iii)

Two (or more) weak acids

If acids dissociate to a negligible extent, $[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$