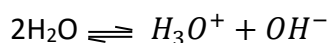### Ionic product of water :

Pure water is weak electrolyte that is just one molecule out of 556 million of water molecules will ionize.

- Ionization of water :

$$H_2O \rightleftharpoons H^+ + OH^- \text{ (or)}$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

By applying law of mass action to the above ionization reaction.

$$K = \frac{[H^+][OH^-]}{[H_2O]} \text{ (or) } \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

since the molar concentration of $[H_2O]$ is practically a constant and therefore

K or $K_w = [H^+] \ [OH^-]$

$K_w \rightarrow$ ionic product of water.

- K_w is defined as the product of molar concentration of H^+ and OH^- ions.
- At 25^0C, $K_w = 1 \times 10^{-14}$ mol^2 / lit^2.
- "with an increase in temperature the value of k_w increase as the extent of ionization of water increases"
- At a given temperature the value of K_w remains constant for any given dilute aqueous solution. i.e. neutral (or) acidic (or) basic.

  In pure water (or) neutral aqueous solution.

  $[H^+] = [OH^-] = 10^{-7}$ mol/lit

  $[H^+] = 10^{-7}$ mol/lit

  $[OH^-] = 10^{-7}$ mol / lit

  $K_w = 1 \times 10^{-14}$ mol/ lit

  In acidic solution :

  $[H^+] > [OH^-]$

  $[H^+] > 10^{-7}$

  $[OH^-] < 10^{-7}$

  $K_w = 10^{-14}$
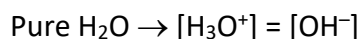
  In basic solution

  $[OH^-] > 10^{-7}$

  $[H^+] < 10^{-7}$

  $K_w = 10^{-14}$

- At 90^0C the concentration of H_3O^+ ions is 10^{-6} mole/ lit in pure water. The value of K_w is

  Pure $H_2O \rightarrow [H_3O^+] = [OH^-]$

  $1 \times 10^{-6} = 1 \times 10^{-6}$

  $K_w = 1 \times 10^{-12}$ mol^2 / lit^2

p^H of solutions:

It was introduced by Sorensen to calculate lower concentrations of H$^+$ ion.

- p^H is –ve logarithm of H$^+$ ion concentration.

  p^H is logarithmic reciprocal of H$^+$ ion concentration.

  P^H is the negative power rised on ten in order to express H$^+$ ion concentration.

  p^H = – log[H$^+$]

  p^H = $log \frac{1}{[H^+]}$

  [H$^+$] = 10^{-pH}

  Even OH$^-$ ion concentration can be expressed on p^H scale.

  p^{OH} = – log(OH$^-$)

  [OH$^-$] = $10^{-P^{OH}}$

  For any dilute solution; [H$^+$] [OH$^-$]= 10^{-14} mol^2/ litre^2

  P^{K_w} = p^H + p^{OH} = 14

- Other similar expressions:

$$p^{OH} = - log[\, OH^-]$$

Similarly

$$p^{k_a} = - log \quad k_a$$

$$p^{k_b} = - log \quad k_b$$
$$p^{k_\omega} = - log \quad k_\omega$$
$$p^k = - log \quad k$$

$p^M = - log[\, M^+]$ $\qquad$ M$^+ \rightarrow$ metal ion concentration

p^H scale $\qquad 1 \xrightarrow{acids} 7 \xrightarrow{bases} 14$
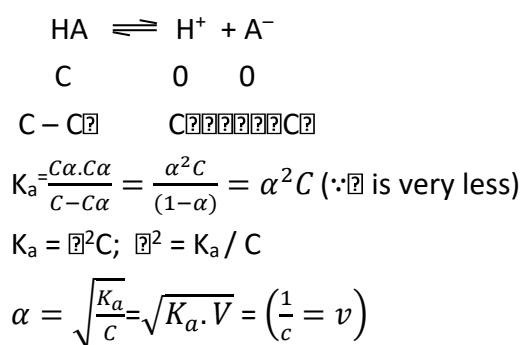
$\qquad\qquad\qquad\qquad$ neutral

- The maximum concentration of H$^+$ ion that could be expressed on p^H scale is 0.1 M. When [H$^+$] = 0.1; p^H = 1. If [H$^+$] = more than 0.1 p^H is less than 1

  [no provision for less than 1 on scale]

- The maximum concentration of OH$^-$ ion that could be expressed on p^H scale is 1M. When [OH$^-$] =1M; p^{OH} = 0; p^H = 14 if [OH$^-$] = more than 1M; p^{OH} < 0 and p^H > 14 [no provision for more than 14 on p^H scale]

- P^H scale is applicable for dilute solutions.

- With increase in the concentration of [H$^+$], p^H value decreases, p^{OH} value increases.

- With increase in the [OH$^-$] the p^H value increases, and p^{OH} value decreases.

- With increase in temperature p^H value decreases. At higher temperature, the extent of ionization increases and H$^+$ ion concentration increases. There fore p^H value decreases. Similarly OH$^-$ ion concentration also increases and p^{OH} decreases and thus the entire p^H scale contracts.

- If [H$^+$] ion concentration is increased by 10^n times p^H value decreases by n units.

- If [H$^+$] ion concentration is decreased by 10^n times p^H value increases by n units.

- If acid solution is diluted by 10^n times, p^H value increases by n units.
- If basic solution is diluted by 10^n times, p^H value decreases by n units.

P^H of weak acids and weak bases :

Ionisation of weak acid(HA) :

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

$$C \qquad 0 \quad 0$$

$$C - C\alpha \qquad C\alpha \qquad C\alpha$$

$K_a = \dfrac{C\alpha.C\alpha}{C - C\alpha} = \dfrac{\alpha^2 C}{(1-\alpha)} = \alpha^2 C$ ($\because \alpha$ is very less)

$K_a = \alpha^2 C; \quad \alpha^2 = K_a / C$

$$\alpha = \sqrt{\dfrac{K_a}{C}} = \sqrt{K_a.V} = \left(\dfrac{1}{c} = v\right)$$

Ostwald's law of dilution explains the variation of degree of ionisation with concentration. The degree of ionisation is inversely proportional to its square root of its concentration (or) directly proportional to square root of its dilution.

$[H^+] = C\alpha$

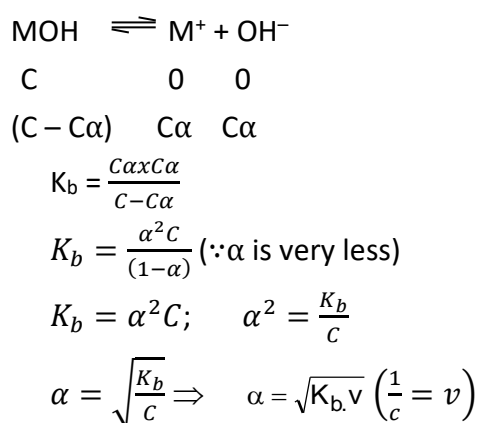$[H^+] = C\sqrt{\dfrac{k_a}{C}}; \quad [H^+] = \sqrt{K_a.C}$

$\log [H^+] = \log \sqrt{K_a.C}$

$\log[H^+] = \dfrac{1}{2}\log K_a + \dfrac{1}{2}\log C$

- Ostwald's law of dilution is applicable for weak electrolytes (weak acid and weak base) it is not applicable to strong electrolytes because they completely ionise at moderate concentration.

- The behaviour of strong electrolytes is explained by Debye – Huckel's theory.

$-\log [H^+] = -\dfrac{1}{2}\log \quad k_a - \dfrac{1}{2}\log C$

$p^H = \dfrac{1}{2}p^{k_a} - \dfrac{1}{2}\log C$

Ionization of weak bases (MOH) :

$$MOH \rightleftharpoons M^+ + OH^-$$

$$C \qquad 0 \quad 0$$

$$(C - C\alpha) \quad C\alpha \quad C\alpha$$

$K_b = \dfrac{C\alpha \times C\alpha}{C - C\alpha}$

$K_b = \dfrac{\alpha^2 C}{(1-\alpha)}$ ($\because \alpha$ is very less)

$K_b = \alpha^2 C; \quad \alpha^2 = \dfrac{K_b}{C}$

$\alpha = \sqrt{\dfrac{K_b}{C}} \Rightarrow \quad \alpha = \sqrt{K_b.v}\left(\dfrac{1}{c} = v\right)$

$$[OH^-] = C\alpha = C\sqrt{\frac{K_b}{C}}$$

$$[OH^-] = \sqrt{K_b.C}$$

$$-log[OH]^- = -\frac{1}{2}log\,K_b - \frac{1}{2}log\,C$$

$$p^{OH} = \frac{1}{2}p^{K_b} - \frac{1}{2}log\,C$$

$$p^H = K_w - p^{OH}$$

$$p^H = k_w - \frac{1}{2}p^{K_b} + \frac{1}{2}log\,C$$

For weak acids :

$$[H^+] = C\alpha \; ; [H^+] = \sqrt{K_a.C}$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

For weak bases :

$$[OH^-] = C\alpha; \; [OH^-] = \sqrt{K_b.C}$$

$$\alpha = \sqrt{\frac{K_b}{C}}$$

For strong acids ; $[H^+]$ = N of acid

For weak acids ; $[H^+]$ < N of acid

For strong bases; $[OH^-]$ = N of base

For weak bases; $[OH^-]$ < N of base