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Deg-I(H) Physical (paper-II)

Chapter - Ionic Equilibrium

Topics - Ionic-product of water & pH, p(OH) & pKw

Ionic Product of water & Ionization Constant for water.

Conductivity measurement of water indicates that water is very weak electrolytes. At pure water is likely to be non-ionic & It is weakly ionised to give $H^+(aq)$ & $OH^-(aq)$ ions

$$\underset{(l)}{H_2O} \rightleftharpoons \underset{(aq)}{H^+} + \underset{(aq)}{OH^-}$$

Its ionization constant may be expressed as

$$K_a(H_2O) = \frac{[H^+][OH^-]}{[H_2O]}$$

water concentration is very high ab

55.5 mol/lit & very small fraction of it undergoes ionization, therefore concentration of H_2O may be taken as constant & combines with $K_a(H_2O)$ to give another constant called K_w.

$$K_a(H_2O) \times [H_2O] = [H^+][OH^-]$$

$$\boxed{K_w = [H^+][OH^-]}$$

K_w is known as Ionic-product of water.

In pure water $[H^+]$ is found experimentally equal to 1×10^{-7} at 298K. In water $[H^+] = [OH^-]$

Thus, $[H^+] = [OH^-] = 1 \times 10^{-7}$ at 298K

Thus $K_w = 1 \times 10^{-7} \times 1 \times 10^{-7}$

$K_w = 1 \times 10^{-14}\ mol^2/lit^2$

Thus degree of dissociation of water, $\cancel{K_a(H_2O)} = \frac{1 \times 10^{-7}}{55.5} = 1.8 \times 10^{-9}$

The value of Kw is Temp^t. dependence thus it has different value at diff. Temp^t.

Temp (K)	Kw
273	0.113×10^{-14}
283	0.292×10^{-14}
298	1.008×10^{-14}
323	5.474×10^{-14}
373	56×10^{-14}

$$pKw = -\log Kw$$
$$= -\log 1 \times 10^{-14}$$
$$= -x -14 \log 10$$
$$\boxed{pKw = 14} \text{ at } 298K.$$

pH :- Concept of Kw unable to classify solution either acidic, basic or neutral.

Thus if $[H^+]$ is expressed upon log-scale, the nature of solution may be decided.

Definition - The pH is defined as negative log of activity / Concentration of $[a_{H^+}]$ / $[H^+]$

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

Taking log both side,

$$\log[H^+] = -pH \log 10$$

or, $\log[H^+] = -pH \times 1$

$\therefore$ $\boxed{pH = -\log[H^+]}$

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

Similiarly, for base which gives $[OH^-]$

$$\boxed{p(OH) = -\log[OH^-]}$$

In ~~pure~~ water $[H^+] = [OH^-] = 1 \times 10^{-7}$

Thus pH & p(OH) for water is 7 (for neutral)

Thus $\boxed{pH + p(OH) = 14}$

or, $pH + p(OH) = pK_w$.

Remarks, $[H^+]$ for Acid $> 10^{-7}$, pH < 7

$[OH^-]$ for base $< 10^{-7}$, pH > 7

For neutral $[H^+] = [OH^-] = 10^{-7}$

pH = 7.

— x — x —