

constant, say k'

$$\therefore K_c \times k = [H^+][OH^-]$$

$$\underbrace{K_c \times k}_{K_w} = [H^+][OH^-]$$

This K_w is called dissociation constant of H_2O or ionic product of water

K_w at $25^\circ C$ is $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

Pure H_2O , the conc. of hydrogen and hydroxyl ions must be equal to one another, hence:

$$\begin{aligned} [H^+] &= [OH^-] = \sqrt{K_w} = \sqrt{1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}} \\ &= 1 \times 10^{-7} \text{ mol dm}^{-3} \end{aligned}$$

The value of K_w is temp. dependent

$$\begin{aligned} \rho(H_2O) &= 1000 \text{ g/L} \\ \text{m.mass} &= 18.0 \text{ g/mol} \end{aligned}$$

$$[H_2O] = \frac{(1000 \text{ g/L})}{(18.0 \text{ g/mol})} \times (1 \text{ mol/18.0 g}) = 55.55 \text{ M}$$

molarity of pure water is 55.55 M .

The pH Scale:-

The hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale.

" The pH of the solution is defined as the negative logarithm to base 10 of the activity (a_{H^+}) of hydrogen ion."

In dilute solution $< (10^{-4} M)$ $a_{H^+} \approx [H^+]$ (activity has no units)

$$\therefore a_{H^+} = [H^+] / \text{mol L}^{-1}$$

$$\Rightarrow pH = -\log a_{H^+} = -\log \{ [H^+] / \text{mol L}^{-1} \}$$

$\therefore$ an acidic solⁿ of HCl ($10^{-2} M$) will have a pH = 2.

a basic solⁿ of NaOH with $[OH^-] = 10^{-4} M$ and $[H_3O^+] = 10^{-10} M$ will have pH = 10.

At 25°C, pure water has a concentration of hydrogen ions $[H^+] = 10^{-7} M$.

$$pH = -\log(10^{-7}) = 7$$

Acidic solⁿ has pH < 7

Basic " " " > 7

Neutral " " pH = 7

At 298K $K_w = [H_3O^+][OH^-] = 10^{-14}$

$$\begin{aligned} -\log K_w &= -\log \{[H_3O^+][OH^-]\} \\ &= -\log [H_3O^+] - \log [OH^-] \\ &= -\log 10^{-14} \end{aligned}$$

$$pK_w = pH + pOH = 14$$

The scale of pH is from 0 to 14, The conc. of H^+ and $[OH^-]$ ions which are greater than $1M$ are not expressed in terms of pH.

pH test helps in dealing with biological and cosmetic applications. It can be determined using pH strips with 0.5 accuracy. $\Rightarrow$ also pH meters can be used (0.001 precision)

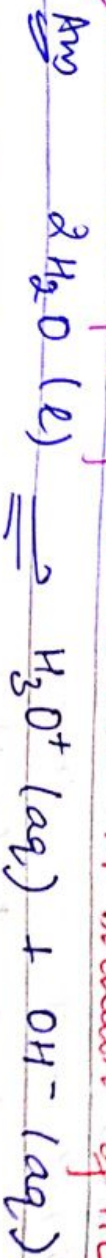
A device that measures the pH-dependent electrical potential of the test solution with 10,001 precision

Quesⁿ The conc. of Hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3}M$. What is its pH?

Ans:-

$$\begin{aligned} pH &= -\log [3.8 \times 10^{-3}] \\ &= -\log [3.8] + \log [10^{-3}] \\ &= \{0.58\} + (-3.0) = 2.42 \end{aligned}$$

Q2 Calculate pH of a $1.0 \times 10^{-8} M$ solution of HCl.



$$K_w = [OH^-][H_3O^+] = 10^{-14}$$

at acidic conc $< 10^{-7}$, Hydrogen ions from water also contributes.

$\therefore$ let $x = [OH^-] = [H_3O^+]$ from H_2O .

then



x ~~10^{-8}~~

x

$$\therefore [H_3O^+] = 10^{-8} + x$$

$$K_w = (10^{-8} + x)(x) = 10^{-14}$$

$$\text{or } x^2 + 10^{-8}x - 10^{-14} = 0$$

$$\therefore x = 9.5 \times 10^{-8} = [OH^-]$$

$$\therefore pOH = 7.02 \text{ and } pH = 6.98$$

Q3 Calculate the pH of a solution obtained by mixing 50 ml of 0.2M HCl with 50 ml of 0.1M KOH.

Ans. No. of m.mol of acid in soln = $50 \text{ ml} \times 0.2 M = 10 \text{ m.mol}$
" " " alkali " = $50 \times 0.1 M = 5 \text{ m.mol}$

∴ No. of millimoles of acid left in the soln after addn of alkali = $10 - 5 = 5$
Total volume of soln = $50 + 50 = 100 \text{ mL}$

∴ 5 mmol in 100 mL of soln (acid)

or 0.05 mole / L of soln

Conc. of H^+ ions = 0.05 mol dm^{-3} .

$$\text{pH} = -\log [\text{H}^+] = -\log (0.05) = 1.30$$

Q4 (for practice only)

Calculate the pH of a solution obtained by mixing 25 mL of 0.2 M HCl with 50 mL of 0.25 M NaOH. Take $K_{\text{a}} = 10^{-14} \text{ mol dm}^{-6}$?

$$\text{Ans} = 13.0$$

DISSOCIATION OF WEAK ACIDS AND BASES

I Weak Acid: —

Let there be a weak monobasic HA in water,



Acc to law of chem eqbm,

$$K_{\text{c}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

Since water is present in large excess in dilute soln, it can be taken as constant 'K'

$$K_c = \frac{[H^+][A^-]}{[HA] \times \gamma} \quad (\text{assuming the activity coeff equal to unity}).$$

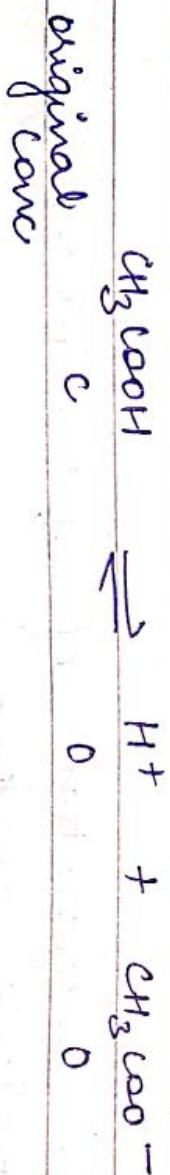
the product of two constants is a const, let it be K_a

$$\therefore K_a = \frac{[H^+][A^-]}{[HA]}$$

$\Rightarrow$ This K_a is characteristic of acid and is known as dissociation constant of the acid.

$\Rightarrow$ It varies only with temperature.

$\Rightarrow$ The dissociation constant of a weak acid can be expressed in terms of degree of dissociation (α) and molar conc (C)



$$\begin{array}{ccc} \text{eqm conc} & C(1-\alpha) & C\alpha \qquad C\alpha \end{array}$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

for weak acids, α is very small
so $1-\alpha \approx 1$

$$K_a = C\alpha^2$$

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

for two weak acids K_{a1} , K_{a2} at same conc C .

$$\therefore \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

but this is not true but

$$\frac{\text{Strength of one Acid } HA_1}{\text{another " } HA_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} \rightarrow \textcircled{1}$$

The dissociation constant of weak acids can be determined by
Eq $\rightarrow$ 1 twice α , can also be determined from conductance
measurements as $\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$

calculation of hydrogen ion concentration of aq. solution of
acids whose dissociation constants are known.

$$[H^+] = C\alpha = C\sqrt{K_a/C} = \sqrt{CK_a}$$

Q. A solution of 0.100M acetic Acid is found to be dissociated to
the extent of 1.33 percent at the room temperature. Calculate
the dissociation constant of the acid at this temperature.

% dissociation of Acetic Acid = 1.33
degree of dissociation of Acetic Acid, $\alpha = 0.0133$

Dissociation constant of Acetic Acid, $K_a = \frac{C\alpha^2}{1-\alpha}$

α is very small, hence $K_a = C\alpha^2$
 $= 0.1 \times (0.0133)^2$
 $= 1.77 \times 10^{-5}$

Q2:- A monobasic acid has a dissociation constant equal to 1.8×10^{-5} at 25°C . Calculate its degree of dissociation at a conc. of 0.20M at the same temperature. What will be the conc. of hydrogen ions furnished by it?

Ans:- $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.2}} = 0.009486$

degree of dissociation of $0.20\text{M} = 0.009486$
 $[H^+] = \sqrt{C K_a}$
 $= \sqrt{0.2 \times 1.8 \times 10^{-5}}$
 $= 0.001897 \text{ mol dm}^{-3}$