Lewis concept :-

Acids :- species capable of accepting a pair of e^-

Bases :- " " " donating " " "

i) BF_3 + NH_3 $\longrightarrow$ F_3BNH_3
(acid) (base)

ii) $BF_3 + F^- \longrightarrow BF_4^-$

iii) $Cu^{+2} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-}$

This definitn attribute acidity to e^- arrangement

Ionic Product Of H_2O.

Water is dissociated into H^+ & OH^- into (to a small extent)

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

Applying law of chemical Eqlbm :-

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

as the dissociation takes place to a very small extent, the conc. of undissociated water, $[H_2O]$, may be regarded as

Constant, say 'k'

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

$$K_w = [H^+][OH^-]$$

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

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

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

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

The value of K_w is temp. dependent

$\rho(H_2O) = 1000\ g/L$

m. mass $= 18.0\ g/mol$

$$[H_2O] = (1000\ g/L) \times (1\ mol/18.0\ g) = 55.55\ M.$$

~~$(1\ mol/18.0\ g)$~~

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 $< (0.01\,M)$ $a_{H^+} \simeq [H^+]$ (activity has no units)

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

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

∴ an acidic sol^n of HCl (10^{-2} M) will have a pH = 2.

a basic sol 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 sol^n has pH < 7

Basic " " " > 7

Neutral " " pH = 7

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

$$-\log K_w = -\log \{[H_2O^+][OH^-]\}$$
$$= -\log [H_3O^+] - \log [OH^-]$$
$$= -\log 10^{-14}$$

$$pK_w = pH + pOH = 14$$

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 soln helps in dealing with biological and cosmetic applications. It can be determined using pH strips ~ 0.5 accuracy.
⇒ also pH meters can be used (0.001 precision)

⇓

A device that measures the pH-dependent electrical potential of the test solution with ±0.001 precision

Ques^n The conc. of Hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?

Ans:- $pH = -\log [3.8 \times 10^{-3}] = -\log [3.8] + \log [10^{-3}]$
$= -\{(0.58) + (-3.0)\} = 2.42$

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

Ans $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$K_w = [OH^-][H_3O^+]$

$= 10^{-14}$

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

∴ Let $x = [OH^-] = [H_3O^+]$ from H_2O.

then

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

x 10^{-8} x x

∴ $[H_3O^+] = 10^{-8} + x$

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

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

∴ $x = 9.5 \times 10^{-8} = [OH^-]$

So pOH $= 7.02$ and pH $= 6.98$.

Q3 Calculate the pH of a solution obtained by mixing 50mL of 0.2M HCl with 50 mL of 0.1M NaOH.?

Ans. No. of m.mol of acid in soln $= 50\text{mL} \times 0.2\text{M} = 10$ m mol

" " " " alkali " $= 50 \times 0.1\text{M} = 5$ 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 mL

∴ i.e. 5 mmol in 100 mL of soln (acid)

or 0.05 mole / L of soln

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

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

Q4 (for practise 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 $K_w = 10^{-14}$ mol^2 dm^{-6}?

Ans = 13.0

DISSOCIATION OF WEAK ACIDS AND BASES

I Weak Acid:-

Let there be a weak monobasic HA in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Acc to law of Chem eqlbm,

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

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

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

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

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

⇒ This K_a is characteristic of acid and is known as dissociation constant of the acid.

⇒ It varies only with temperature.

⇒ The dissociation constant of a weak acid can be expressed in terms of degree of dissociation (α) and molar conc (c)

	CH_3COOH	$\rightleftharpoons$	H^+	+	CH_3COO^-
original conc	c		0		0
Eqbm conc	$c(1-\alpha)$		$c\alpha$		$c\alpha$

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

for weak acids, α is very small

so $1-\alpha$ is 1

$$K_a = c\alpha^2$$

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

for two weak acids K_{a_1}, K_{a_2} at same conc C.

$$\therefore \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

And this is nothing but

$$\frac{\text{Strength of one Acid } HA_1}{\text{" " another " } HA_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} \rightarrow (1)$$

The dissociation constants of weak acids can be determined by Eq → 1 Since α, can also be determined from conductance measurements as $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$

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 0.100 M 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 ion 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 0.20M = 0.009486

$[H^+] = \sqrt{cK_a}$

$= \sqrt{0.2 \times 1.8 \times 10^{-5}}$

$= 0.001897$ mol dm^{-3}.