

Chapter - 2

IONIC EQUILIBRIA

DEGREE OF DISSOCIATION OR DEGREE OF IONISATION (α)

The degree of ionisation is defined as the fraction of the total electrolyte that ionises at equilibrium in solution. Thus if α mole ionises out of one mole of the dissolved electrolyte, the degree of ionisation is α . If $x\%$ of an electrolyte is ionised in the solution, the degree of ionisation is $x/100$. "The degree of ionisation is α ", means that out of every mole of the electrolyte α mole ionises and $(1 - \alpha)$ mole is left unionised in the solution.

OSTWALD'S DILUTION LAW

The law states that – at a given temperature the degree of ionisation of a weak electrolyte is inversely proportional to the square root of the concentration of the solution or directly proportional to the square root of the volume of the solution containing one gram mole of the solute. It further states that, at a constant temperature, a weak electrolyte in solution gets more ionised with the increase of dilution.

Mathematical deduction :

If one mole of M A is dissolved in 'V' litre of solution and if C and α be the molar concentration and degree of ionisation respectively at this dilution,

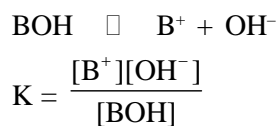
	M A \rightleftharpoons	M ⁺	A ⁻
Amounts at equilibrium :	(1 - α) moles	α gm-ion	α gm-ion
Concentration at equilibrium :	C(1 - α) moles	C α gm-ion	C α gm-ion
or	$\frac{(1 - \alpha)}{V}$ moles per litre	$\frac{\alpha}{V}$ gm-ion litre	$\frac{\alpha}{V}$ gm-ion per litre

Applying law of mass action,

$$K = \frac{[M^+][A^-]}{[MA]} \quad \dots\dots(1)$$

If M A is a weak acid, K is called ionisation or dissociation constant of the acid and is symbolised as K_a .

Similarly is case of a base BOH



Here K is called the dissociation constant of the base and is represented as K_b .

Now putting the values in terms of concentrations (1),

$$K = \frac{C\alpha \times C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha}$$

If α is small in comparison to 1 i.e., for a weak electrolyte the dissociation is very small. $(1 - \alpha) \approx 1$ then,

$$K = C\alpha^2 \quad \text{or,} \quad \alpha = \sqrt{K/C} \quad \dots\dots(2)$$

Again,
$$K = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V} \quad \text{as } (1-\alpha) \approx 1; \quad K = \alpha^2/V \quad \text{or,} \quad \alpha = \sqrt{K \cdot V} \quad \dots\dots(3)$$

Both the equations (2) and (3) are mathematical expression for the Ostwald's dilution law.

Discussion

- (i) From eq. (2) it is evident that the degree of ionisation (α) must increase with the decrease of concentration. Thus, as the solution becomes more and more dilute the extent of dissociation is more. Hence at infinite dilution a weak electrolyte behaves like a strong electrolyte.
- (ii) The law is applicable only to weak electrolyte i.e., weak acids, weak bases etc.

IONIC PRODUCT OF WATER (K_w)

Kohlrausch and Heydweiller showed from the conductance measurement that pure water may be regarded as a very weak electrolyte dissociating as



Applying law of mass action,

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

K is called the ionisation constant of water.

$$\text{or } K [\text{H}_2\text{O}] = [\text{H}^+] [\text{OH}^-]$$

Since $[\text{H}_2\text{O}]$ is constant at concentration temperature and K is also constant, therefore,

$$K[\text{H}_2\text{O}] = K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

The product of ionic concentration $[\text{H}^+] \cdot [\text{OH}^-]$ is constant at constant temperature. K_w is called ionic product of water, because it is equal to the product of the ionic concentration of the H^+ and OH^- ions of water. Like any equilibrium constant, K_w also depends on temperature. At 298 K the value of $K_w = 1.04 \times 10^{-14}$. With the rise of temperature the value of K_w increases.

Temperature K	273	298	303	313	373
K_w	0.05×10^{-14}	1.04×10^{-14}	1.89×10^{-14}	3.8×10^{-14}	4.8×10^{-14}

pH and pOH

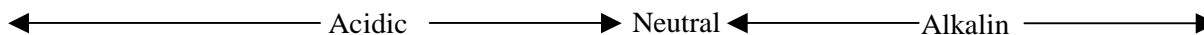
pH and pOH are the two scales of expressing the concentrations of H^+ and OH^- ions respectively in dilute solution. Normally the concentration of H^+ and OH^- ions of dilute solution are expressed in gram eq./litre. A very convenient method was proposed by *Sorensen*. According to him,

$$\text{pH} = \log \frac{1}{[\text{H}^+]}, \quad \text{or } \text{pH} = -\log [\text{H}^+] \quad \text{or, } [\text{H}^+] = 10^{-\text{pH}}$$

Thus pH is the negative logarithm to the base 10 of the hydrogen ion concentration in the solution. Most aqueous solutions have hydrogen ion concentration between 1M and 1×10^{-14} M. These solutions have pH between 0 and 14 and so it is more convenient to express the acidity in terms of pH rather than $[\text{H}^+]$. This avoids using negative exponents or fractions.

- (i) Neutral solution has pH = 7, pure water has pH = 7.
- (ii) An acidic solution has pH less than 7.
- (iii) An alkaline solution has pH greater than 7.

[H] →	10 ⁰	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁸	10 ⁻⁹	10 ⁻¹⁰	10 ⁻¹¹	10 ⁻¹²	10 ⁻¹³	10 ⁻¹⁴
pH →	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14



It is observed that the greater the value of [H⁺], the smaller will be the value of pH and vice versa. A neutral solution is one in which [H⁺] = [OH⁻].

In a similar manner, pOH is the negative logarithm to the base 10 of the OH⁻ ion concentration in the solution.

$$\text{pOH} = -\log [\text{OH}^-]$$

or $[\text{OH}^-] = 10^{-\text{pOH}}$

We know, [H⁺] [OH⁻] = K_w = 1 × 10⁻¹⁴

Taking log on both sides,

$$\log [\text{H}^+] + \log [\text{OH}^-] = \log K_w = \log (1 \times 10^{-14})$$

or $-\log [\text{H}^+] - \log [\text{OH}^-] = -\log K_w = -\log (1 \times 10^{-14})$

or $\text{pH} + \text{pOH} = \text{p}K_w = 14$

In a neutral solution pH = pOH = 7

i.e., [H⁺] = [OH⁻] = 1 × 10⁻⁷ gram-ion/litre.

BUFFER SOLUTION

Buffer solutions are those solutions which resist change in their pH value on adding small quantities of acids or alkalis to them. They retain practically a constant pH value.

A buffer solution is said to possess reserve acidity and reserve alkalinity. It consists of either a mixture of weak acid and its salt with strong base or a weak base and its salt with strong acid.

Examples of buffer solution : (i) CH₃COOH and CH₃COONa, (ii) NH₄OH and NH₄Cl, (iii) H₂CO₃ and NaHCO₃.

pH of buffer solution

The pH of a buffer solution is calculated by applying **Henderson's equation**.

Let us consider a buffer solution containing a weak acid HA and its salt BA (with strong base BOH).



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad [\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

Taking log on both sides,

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

$$\text{or } -\log [H^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$$\text{or } \text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]}$$

i.e., $\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$ This is called Henderson's equation.

Here salt provides the negative ion A^- which is the conjugate base of the acid HA.

Similarly in case of mixture of weak base and its salt with strong acid, the form of Henderson's equation is -

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Application of Buffers :

- (i) **In biochemistry :** Blood and various other human fluids are highly buffered with bicarbonate, carbonic acid and proteins. pH of human blood is 7.4 – slightly alkaline. If the pH of blood falls to 7 or rise to 7.7, the result may be fatal.
- (ii) **In chemical analysis :** Buffer solutions of different pH values are used in the qualitative and quantitative analysis e.g., Fe^{+++} , Cr^{+++} and Al^{+++} are precipitated in Gr III A hydroxides by adding NH_4Cl and NH_4OH .

ASSIGNMENT

I. Multiple Choice Questions

- pH of 0.1 M CH_3COOH (weak electrolyte) is
 - 1
 - zero
 - less than one
 - more than one
- pKa values of three acids A, B and C are 4.5, 3.5 and 6.5 respectively. The correct order of acidic strength is
 - $A > B > C$
 - $C > A > B$
 - $B > A > C$
 - $C > B > A$
- The units of K_w are
 - mol L^{-1}
 - L mol^{-1}
 - $\text{mol}^2\text{L}^{-2}$
 - $\text{L}^2 \text{mol}^{-2}$
- Which of the following solutions can act as acidic buffer ?
 - NH_4Cl and NH_4OH
 - HCl and NaCl
 - HCOOH and HCOONa
 - HNO_3 and NH_4NO_3
- In a Buffer solution the ratio of salt to acid is increased ten times. The pH of solution
 - Increases by 10
 - Decreases by 10
 - Decreases by 1
 - Increases by 1

II. Fill in the blanks

- The K_w for water at 298 K is _____.
- Lower is the $\text{p}K_b$ _____ will be the base.
- Degree of ionisation decreases with increase in _____.
- The reaction between an acid and base is called _____.
- $K_a \times K_b =$ _____.

III. True / False

- $\text{p}K_w = \log K_w$.
- With decrease in pH acidic character increases.
- pH of 10^{-8} M KOH is 6.
- Vinegar is acidic in nature.
- pH of 10^{-8} HCl is very close to 7.

IV. Subjective Types Questions

- At 90°C pure water has $[\text{H}^+] = 10^{-6}$ M. What is the value of K_w at this temp. ?
- What is the pH of 0.5 M HF solution ($K_a = 2 \times 10^{-4}$) ?
- What will be the value of hydroxyl ion concentration in solution of pH = 3?
- Predict the pH of a solution obtained by mixing 0.1 M NaA and 0.1 M HA ($K_a = 1 \times 10^{-6}$) ?
- The pH of neutral water decreases with increasing temperature. Explain why ?

ANSWERS

I. Multiple Choice Questions :

1. (d) 2. (c) 3. (c) 4. (c) 5. (d)

II. Fill in the blanks :

- (i) 1×10^{-14} .
(ii) stronger
(iii) concentration
(iv) neutralisation
(v) K_w

III. True / False

- (i) False
(ii) True
(iii) False
(iv) True
(v) True

IV. Subjective Type Questions

- (i) 10^{-12}
(ii) 2
(iii) 10^{-11}
(iv) 6