

## ACIDS AND BASES

### Topic-2

### Ionisation of acids and bases, ionic product of and concept of P<sup>H</sup>

#### VERY SHORT ANSWER QUESTIONS

1. Explain the ionic product of water?

Ans:

#### Ionic Product of Water:

Pure water is a very weak electrolyte and ionises according to the equation



Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

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

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

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, [H<sub>2</sub>O], may be regarded as constant. Thus, the product # [H<sub>2</sub>O] gives another constant which is designated as K<sub>w</sub>. So,

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

The constant, K<sub>w</sub>, is termed as ionic product of water.

2. Define P<sup>H</sup>.

Ans: The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

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

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

$$\text{or } \text{pH} = -\log [\text{H}^+]$$

$$\text{or } \text{pH} = \log 1/[\text{H}^+]$$

## SHORT ANSWER QUESTIONS

1. Define ionic product of water?

Ans;

### Ionic Product of Water:

Pure water is a very weak electrolyte and ionises according to the equation



Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

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

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules,  $[\text{H}_2\text{O}]$ , may be regarded as constant. Thus, the product  $[\text{H}_2\text{O}]K$  gives another constant which is designated as  $K_w$ . So,

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

The constant,  $K_w$ , is termed as ionic product of water.

The product of concentrations of  $\text{H}^+$  and  $\text{OH}^-$  ions in water at a particular temperature is known as ionic product of water. The value of  $K_w$  increases with the increase of temperature, i.e., the concentration of  $\text{H}^+$  and  $\text{OH}^-$  ions increases with increase in temperature.

Temperature ( $^{\circ}\text{C}$ )    Value of  $K_w$

0                     $0.11 \times 10^{-14}$

10                    $0.31 \times 10^{-14}$

25                    $1.00 \times 10^{-14}$

100                   $7.50 \times 10^{-14}$

The value of  $K_w$  at  $25^{\circ}\text{C}$  is  $1 \times 10^{-14}$ . Since pure water is neutral in nature,  $\text{H}^+$  ion concentration must be equal to  $\text{OH}^-$  ion concentration.

2. Define  $P^H$ . What is the value of  $P^H$  of blood?

**Ans:** The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

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

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

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

or  $pH = \log 1/[H^+]$

pH of a solution is, thus, defined as **the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains or pH of the solution is the logarithm of the reciprocal of  $H^+$  ion concentration.**

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, *i.e.*,

$pOH = -\log [OH^-]$  Considering the relationship,

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

Taking log on both sides, we have

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

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

or  $pH + pOH = PK_w^* = 14$

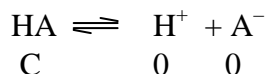
*i.e.*, sum of pH and pOH is equal to 14 in any aqueous solution at 25°C. The above discussion can be summarised in the following manner:

3. What is degree of ionisation of a weak acid and base?

**Ans:**

**$P^H$  of weak acids and weak bases:**

Ionisation of weak acid (HA):



$$K_a = \frac{C - C\alpha}{C - C\alpha} = \frac{C\alpha}{1 - \alpha} = \alpha^2 C \quad (\because \alpha \text{ is very less})$$

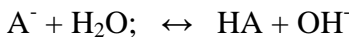
$$K_a = \alpha^2 C; \quad \alpha^2 = K_a / C$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a \cdot V} = \left(\frac{1}{C} = v\right)$$

#### 4. Explain the hydrolysis of the salt of weak acid and strong base?

**Ans: Salt of a weak acid and a Strong base:**

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a **weak acid** and OH<sup>-</sup> ions.



#### **Weak acid**

Consider, for example, the salt CH<sub>3</sub>COONa. It ionises in water completely to give CH<sub>3</sub>COO<sup>-</sup> and Na<sup>+</sup> ions. CH<sub>3</sub>COO<sup>-</sup> ions react with water to form a **weak acid**, CH<sub>3</sub>COOH and OH<sup>-</sup> ions.

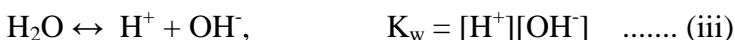
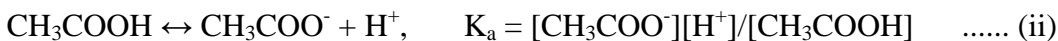


Thus, OH<sup>-</sup> ion concentration increases, the solution becomes alkaline.

**Applying law of mass action,**

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3CO^-]} = \frac{(Cx \times Cx)}{C(1-x)} = \frac{(Cx^2)}{(1-x)} \dots\dots (i)$$

Other equations present in the solution are:



From eqs. (ii) and (iii),

$$\log [OH^-] = \log K_w - \log K_a + \log[\text{salt}]/[\text{acid}]$$

$$-pOH = -pK_w + pK_a + \log[\text{salt}]/[\text{acid}]$$

$$pK_w - pOH = pK_a + \log[\text{salt}]/[\text{acid}]$$

$$pH = pK_a + \log[\text{salt}]/[\text{acid}]$$

Considering eq. (i) again,

$$K_h = cx^2/(1-x) \quad \text{or} \quad K_h = Ch^2/(1-h)$$

When h is very small, (1-h)  $\rightarrow$  1

$$\text{or} \quad h^2 = K_h/C$$

$$\text{or} \quad h = \sqrt{K_h/C}$$

$$[\text{OH}^-] = h \times C = \sqrt{CK_h} = \sqrt{C \cdot K_w/K_a}$$

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

$$= K_w/\sqrt{C \cdot K_w/K_a} = \sqrt{(K_a \cdot K_w)/K_c}$$

$$-\log [\text{H}^+] = -1/2 \log K_w - 1/2 \log K_a + 1/2 \log C$$

$$pH = 1/2 pK_w + 1/2 pK_a + 1/2 \log C$$

$$= 7 + 1/2 pK_a + 1/2 \log C.$$

## LONG ANSWER QUESTIONS

### 1. Explain the concept of ionisation acid and base?

#### P<sup>H</sup> of weak acids and weak bases:

Ionisation of weak acid (HA):

$$\begin{array}{ccc} \text{HA} & \rightleftharpoons & \text{H}^+ + \text{A}^- \\ \text{C} & & \text{0} \quad \text{0} \\ \text{C} - \text{C}\alpha & & \text{C}\alpha \quad \text{C}\alpha \\ \mathbf{K_a} = \frac{\text{C}\alpha \cdot \text{C}\alpha}{\text{C} - \text{C}\alpha} = \frac{\alpha^2 \text{C}}{(1-\alpha)} = \alpha^2 \text{C} \quad (\because \alpha \text{ is very less}) \end{array}$$

$$\begin{aligned} \mathbf{K_a} &= \alpha^2 \text{C}; \quad \alpha^2 = \mathbf{K_a} / \text{C} \\ \alpha &= \sqrt{\frac{\mathbf{K_a}}{\text{C}}} = \sqrt{\mathbf{K_a} \cdot V} = \left( \frac{1}{\text{C}} = v \right) \end{aligned}$$

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.

$$[\text{H}^+] = C\alpha$$

$$[\text{H}^+] = C \sqrt{\frac{k_a}{C}}; [\text{H}^+] = \sqrt{K_a \cdot C}$$

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

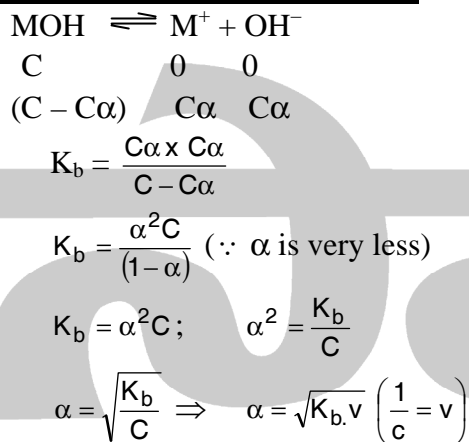
$$\log[\text{H}^+] = \frac{1}{2} \log K_a + \frac{1}{2} \log C$$

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.

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

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

**Ionisation of weak bases (MOH):**



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

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

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

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

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

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

**For weak acids:**

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

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

**For weak bases:**

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

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

**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**

## 2. Explain Ionic product of water.

### Ionic Product of Water:

Pure water is a very weak electrolyte and ionises according to the equation



Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

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

$$\text{or } [H^+][OH^-] = K[H_2O]$$

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules,  $[H_2O]$ , may be regarded as constant. Thus, the product  $[H^+][OH^-]$  gives another constant which is designated as  $K_w$ . So,

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

The constant,  $K_w$ , is termed as ionic product of water.

The product of concentrations of  $H^+$  and  $OH^-$  ions in water at a particular temperature is known as ionic product of water. The value of  $K_w$  increases with the increase of temperature, i.e., the concentration of  $H^+$  and  $OH^-$  ions increases with increase in temperature.

Temperature ( $^{\circ}C$ )    Value of  $K_w$

0                     $0.11 \times 10^{-14}$

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25                    $1.00 \times 10^{-14}$

100                   $7.50 \times 10^{-14}$

The value of  $K_w$  at  $25^\circ\text{C}$  is  $1 \times 10^{-14}$ . Since pure water is neutral in nature,  $\text{H}^+$  ion concentration must be equal to  $\text{OH}^-$  ion concentration.

$$[\text{H}^+] = [\text{OH}^-] = x$$

$$\text{or } [\text{H}^+][\text{OH}^-] = x^2 = 1 \times 10^{-14}$$

$$\text{or } x = 1 \times 10^{-7} \text{ M}$$

$$\text{or } [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol litre}^{-1}$$

This shows that at  $25^\circ\text{C}$ , in 1 litre only  $10^{-7}$  mole of water is in ionic form out of a total of approximately 55.5 moles.

When an acid or a base is added to water, the ionic concentration product,  $[\text{H}^+][\text{OH}^-]$ , remains constant, i.e., equal to  $K_w$  but concentrations of  $\text{H}^+$  and  $\text{OH}^-$  ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases, i.e.,

$$[\text{H}^+] > [\text{OH}^-]; \quad (\text{Acidic solution})$$

Similarly, when a base is added, the  $\text{OH}^-$  ion concentration increases while  $\text{H}^+$  ion concentration decreases,

$$\text{i.e.,} \quad [\text{OH}^-] > [\text{H}^+]; \quad (\text{Alkaline or basic solution})$$

$$\text{In neutral solution,} \quad [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$$

$$\text{In acidic solution,} \quad [\text{H}^+] > [\text{OH}^-]$$

$$\text{or} \quad [\text{H}^+] > 1 \times 10^{-7} \text{ M}$$

$$\text{and} \quad [\text{OH}^-] < 1 \times 10^{-7} \text{ M}$$

$$\text{In alkaline solution,} \quad [\text{OH}^-] > [\text{H}^+]$$

$$\text{or} \quad [\text{OH}^-] > 1 \times 10^{-7} \text{ M}$$

$$\text{and} \quad [\text{H}^+] < 1 \times 10^{-7} \text{ M}$$

Thus, if the hydrogen ion concentration is more than  $1 \times 10^{-7} \text{ M}$ , the solution will be acidic in nature and if less than  $1 \times 10^{-7} \text{ M}$ , the solution will be alkaline.

$$[\text{H}^+] = 10^{-0} \ 10^{-1} \ 10^{-2} \ 10^{-3} \ 10^{-4} \ 10^{-5} \ 10^{-6} \quad (\text{Acidic})$$

$$[\text{H}^+] = 10^{-7} \quad (\text{Neutral})$$



$$[\text{H}^+] = 10^{-14} \ 10^{-13} \ 10^{-12} \ 10^{-11} \ 10^{-10} \ 10^{-9} \ 10^{-8} \quad (\text{Alkaline})$$

We shall have the following table if  $\text{OH}^-$  ion concentration is taken into account.

$$[\text{OH}^-] = 10^{-14} \ 10^{-13} \ 10^{-12} \ 10^{-11} \ 10^{-10} \ 10^{-9} \ 10^{-8} \quad (\text{Acidic})$$

$$[\text{OH}^-] = 10^{-7} \quad (\text{Neutral})$$

$$[\text{OH}^-] = 10^{-6} \ 10^{-5} \ 10^{-4} \ 10^{-3} \ 10^{-2} \ 10^{-1} \ 10^0 \quad (\text{Alkaline})$$

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both  $\text{H}^+$  and  $\text{OH}^-$  ions. The product of their concentrations is always constant, equal to  $1 \times 10^{-14}$  at  $25^\circ\text{C}$ . If one increases, the other decrease accordingly so that the product remains  $1 \times 10^{-14}$  at  $25^\circ\text{C}$ .

If  $[\text{H}^+] = 10^{-2} \text{ M}$ , then  $[\text{OH}^-] = 10^{-12} \text{ M}$ ; the product,  $[\text{H}^+][\text{OH}^-] = 10^{-2} \times 10^{-12} = 10^{-14}$ ; the solution is acidic.

If  $[\text{H}^+] = 10^{-10} \text{ M}$ , then  $[\text{OH}^-] = 10^{-4} \text{ M}$ ; the product,  $[\text{H}^+][\text{OH}^-] = 10^{-10} \times 10^{-4} = 10^{-14}$ ; the solution is alkaline.

### 3. Explain the concept of $\text{P}^{\text{H}}$ in detail?

Ans:

#### **HYDROGEN ION CONCENTRATION-pH SCALE:**

It is clear from the above discussion that nature of the solution (acidic, alkaline or neutral) can be represented in terms of either hydrogen ion concentration or hydroxyl ion concentration but it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only. Since  $\text{H}^+$  ion concentration can vary within a wide range from 1 mol per litre to about  $1.0 \times 10^{-14}$  mol per litre, a logarithmic notation has been devised **by Sorensen**, in 1909, to simplify the expression of these quantities. The notation used is termed as the pH scale.

The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

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

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

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

or  $\text{pH} = \log 1/[\text{H}^+]$

pH of a solution is, thus, defined as the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains or pH of the solution is the logarithm of the reciprocal of  $\text{H}^+$  ion concentration.

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, i.e.,

$\text{pOH} = -\log [\text{OH}^-]$  Considering the relationship,

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

Taking log on both sides, we have

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

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

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

i.e., sum of pH and pOH is equal to 14 in any aqueous solution at 25°C. The above discussion can be summarized in the following manner:

	$[\text{H}^+]$	$[\text{OH}^-]$	pH	pOH
Acidic solution	$>10^{-7}$	$<10^{-7}$	$<7$	$>7$
Neutral solution	$10^{-7}$	$10^{-7}$	7	7
Basic solution	$<10^{-7}$	$>10^{-7}$	$>7$	$<7$