Ionic Equilibria

EXERCISE [PAGES 61 - 62]

Exercise | Q 1.1 | Page 61

Choose the most correct answer:

The pH of 10^{-8} M of HCl is ____________

1. 8
2. 7
3. **less than 7**
4. greater than 7

Solution: The pH of 10^{-8} M of HCl is **less than 7.**

Exercise | Q 1.2 | Page 61

Choose the most correct answer:

Which of the following solution will have a pH value equal to 1.0?

1. 50 mL of 0.1M HCl + 50mL of 0.1M NaOH
2. 60 mL of 0.1M HCl + 40mL of 0.1M NaOH
3. 20 mL of 0.1M HCl + 80mL of 0.1M NaOH
4. **75 mL of 0.2M HCl + 25mL of 0.2M NaOH**

Solution: 75 mL of 0.2M HCl + 25mL of 0.2M NaOH

Exercise | Q 1.3 | Page 61

Choose the most correct answer:

Which of the following is a buffer solution?

1. CH_3COONa + NaCl in water
2. CH_3COOH + HCl in water
3. **CH_3COOH + CH_3COONa in water**
4. HCl + NH_4Cl in water

Solution: CH_3COOH + CH_3COONa in water

Exercise | Q 1.4 | Page 61

Choose the most correct answer :

The solubility product of a sparingly soluble salt AX is 5.2×10^{-13}. Its solubility in mol dm^{-3} is ______.

1. **7.2×10^{-7}**

2. 1.35×10^{-4}
3. 7.2×10^{-8}
4. 13.5×10^{-8}

Solution: The solubility product of a sparingly soluble salt AX is 5.2×10^{-13}. Its solubility in mol dm^{-3} is **7.2×10^{-7}**.

Exercise | Q 1.5 | Page 61

Choose the most correct answer :

Blood in the human body is highly buffered at a pH of ________.

1. **7.4**
2. 7.0
3. 6.9
4. 8.1

Solution: Blood in the human body is highly buffered at a pH of **7.4.**

Exercise | Q 1.6 | Page 61

Choose the most correct answer :

The conjugate base of $[Zn(H_2O)_4]^{2\oplus}$ is __________.

1. $[Zn(H_2O)_4]^{2\oplus}NH_3$
2. $[Zn(H_2O)_3]^{2\oplus}$
3. **$[Zn(H_2O)_3OH]^{\oplus}$**
4. $[Zn(H_2O)H]^{3\oplus}$

Solution: The conjugate base of $[Zn(H_2O)_4]^{2\oplus}$ is **$[Zn(H_2O)_3OH]^{\oplus}$**.

Exercise | Q 1.7 | Page 61

Choose the most correct answer :

For pH > 7 the hydronium ion concentration would be _________.

1. 10^{-7}M
2. **< 10^{-7}M**
3. > 10^{-7}M
4. 10^{-7}M

Solution: For pH > 7 the hydronium ion concentration would be **< 10^{-7}M** .

Exercise | Q 2.01 | Page 61

Answer the following in one sentence :

Why cations are Lewis acids?

Solution: Cations are electron-deficient species and can accept an electron pair. Hence, cations are Lewis acids.

Exercise | Q 2.02 | Page 61

Answer the following in one sentence :

Why is KCl solution neutral to litmus?

Solution: KCl, being salt of a strong acid (HCl) and a strong base (KOH), does not undergo hydrolysis. Hence, the KCl solution is neutral to litmus.

Exercise | Q 2.03 | Page 61

Answer the following in one sentence :

How are basic buffer solutions prepared?

Solution: Basic buffer solutions are prepared by mixing aqueous solutions of a weak base and its salt with strong acid.

Exercise | Q 2.04 | Page 61

Answer the following in one sentence :

The dissociation constant of acetic acid is 1.8×10^{-5}. Calculate percent dissociation of acetic acid in 0.01 M solution.

Solution:

Given :

- Dissociation constant (K_a) = 1.8×10-5,
- Concentration (c) = 0.01 M

To find :

- Percent dissociation

Formulae :

1. $K_a = a^2c$
2. Percent dissociation = $\alpha \times 100$

Calculation :

c = 0.01 M = $1 \times 10^{-2} \mathrm{M}$

Using formula (i),

$$\therefore \alpha = \sqrt{\frac{K_a}{c}}$$

$$= \sqrt{\frac{1.8 \times 10^{-5}}{1 \times 10^{-2}}} = \sqrt{1.8 \times 10^{-3}} = \sqrt{18 \times 10^{-4}}$$

$$= 4.242 \times 10^{-2}$$

Using formula (ii),

Percent dissociation = $\alpha \times 100 = 4.242 \times 10^{-2} \times 100 = 4.242\%$

Percent dissociation of 0.01 M acetic acid solution is 4.242%.

Exercise | Q 2.05 | Page 61

Answer the following in one sentence :

Write one property of a buffer solution.

Solution:

Properties of buffer solution:

i. When a small amount of strong acid (or strong base) is added to a buffer solution, there is no significant change in the value of pH.

ii. The pH of a buffer solution is independent of the volume of the solution. Hence, the dilution of a buffer solution will not change its pH.

iii. The pH of a buffer solution does not change even if it is kept for a long time.

Exercise | Q 2.06 | Page 61

Answer the following in one sentence :

The pH of a solution is 6.06. Calculate its $H^{\oplus}$ ion concentration.

Solution:

Given:

pH of solution = 6.06

To find:

H^+ ion concentration

Formula:

pH = $-\log_{10}[H_3O^+]$

Calculation:

From formula,

pH = $-\log_{10}[H_3O^+]$

∴ $\log_{10}[H_3O^+] = -pH$

= -6.06

= -6 - 0.06 + 1 - 1

= (- 6 - 1) + 1 - 0.06

$= -7 + 0.94 = \bar{7}.94$

Thus, $[H_3O^+] = \text{Antilog}_{10}[\bar{7}.94]$

$= 8.710 \times 10^{-7}$ M

The H^+ ion concentration of the solution is 8.710×10^{-7} M.

Exercise | Q 2.07 | Page 61

Answer the following in one sentence :

Calculate the pH of 0.01 M sulphuric acid.

Solution:

Given: Concentration of sulphuric acid = 0.01 M

To find: pH

Formula: pH = $-\log_{10}[H_3O^+]$

Calculation:

Sulphuric acid (H_2SO_4) is a strong acid. It dissociates almost completely in the water as:

$$H_2SO_{4\,(aq)} + 2\,H_2O_{(l)} \longrightarrow 2\,H_3O^+_{(aq)} + SO^{2-}_{4(aq)}$$

Hence, $[H_3O^+] = 2 \times c = 2 \times 0.01\ M = 2 \times 10^{-2}\ M$

From formula (i),

pH = $-\log_{10}[H_3O^+] = -\log_{10}[2 \times 10^{-2}] = -\log_{10}2 - \log_{10}10^{-2}$

= $-\log_{10}2 + 2 = 2 - 0.3010$

pH = 1.699

The pH of 0.01 M sulphuric acid is 1.699.

Exercise | Q 2.08 | Page 61

Answer the following in one sentence :

The dissociation of H_2S is suppressed in the presence of HCl. Name the phenomenon.

Solution:

The phenomenon due to which dissociation of H_2S is suppressed in the presence of HCl is known as the common ion effect.

Exercise | Q 2.09 | Page 61

Answer the following in one sentence :

Why is it necessary to add H_2SO_4 while preparing the solution of $CuSO_4$?

Solution:

i.

The aqueous solution of $CuSO_4$ is turbid due to the formation of sparingly soluble $Cu(OH)_2$ by hydrolysis as shown below:

$$Cu^{2+}_{(aq)} + 4\,H_2O_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2\,H_3O^+_{(aq)}$$

ii.

If H_2SO_4, that is H_3O^+ ions are added, the hydrolytic equilibrium shifts to the left. Turbidity of $Cu(OH)_2$ dissolves to give a clear solution. Hence, it is necessary to add H_2SO_4 while preparing the solution of $CuSO_4$.

Exercise | Q 2.1 | Page 61

Answer the following in one sentence :

Classify the following buffers into different types :

a. $CH_3COOH + CH_3COONa$

b. $NH_4OH + NH_4Cl$

c. Sodium benzoate + benzoic acid

d. $Cu(OH)_2 + CuCl_2$

Solution:

	Buffer	**Type**
i.	$CH_3COOH + CH_3COONa$	Acidic buffer
ii.	$NH_4OH + NH_4Cl$	Basic buffer
iii.	Sodium benzoate + benzoic acid	Acidic buffer
iv.	$Cu(OH)_2 + CuCl_2$	Basic buffer

Exercise | Q 3.01 | Page 62

Answer the following in brief :

What are acids and bases according to Arrhenius theory?

Solution:

According to Arrhenius theory, acids and bases are defined as follows:

i.

Acid: An acid is a substance that contains hydrogen and gives H^+ ions in an aqueous solution.

e.g.

$$HCl_{(aq)} \xrightarrow{\text{water}} H^+_{(aq)} + Cl^-_{(aq)};$$

$$CH_3COOH_{(aq)} \overset{\text{water}}{\rightleftharpoons} H^+_{(aq)} + CH_3COO^-_{(aq)}$$

ii.

Base: A base is a substance that contains the OH group and produces hydroxide ions (OH^- ions) in aqueous solution.

e.g.

$$NaOH_{(aq)} \xrightarrow{\text{water}} Na^+_{(aq)} + OH^-_{(aq)};$$

$$NH_4OH_{(aq)} \overset{\text{water}}{\rightleftharpoons} NH^+_{4(aq)} + OH^-_{(aq)}$$

Exercise | Q 3.02 | Page 62

Answer the following in brief :

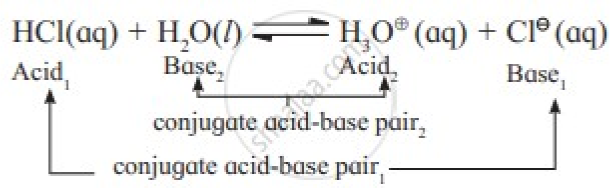
What is meant by conjugate acid-base pair?

Solution:

i. The base produced by accepting the proton from acid is the conjugate base of that acid.

ii. Similarly, the acid produced when a base accepts a proton is called the conjugate acid of that base.

iii. A pair of an acid and a base differing by a proton is said to be a conjugate acid-base pair.



Exercise | Q 3.03 | Page 62

Answer the following in brief :

Label the conjugate acid-base pair in the following reaction:

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

Solution:

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Cl^-}$$

Exercise | Q 3.03 | Page 62

Answer the following in brief :

Label the conjugate acid-base pair in the following reaction:

$$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$$

Solution:

$$\underset{\text{Base}_1}{CO_3^{2-}} + \underset{\text{Acid}_2}{H_2O} \rightleftharpoons \underset{\text{Base}_2}{OH^-} + \underset{\text{Acid}_1}{HCO_3^-}$$

Exercise | Q 3.04 | Page 62

Answer the following in brief :

Write a reaction in which water acts as a base.

Solution:

$$\underset{\text{(Base)}}{H_2O_{(l)}} + HCl_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Exercise | Q 3.05 | Page 62

Answer the following in brief :

Ammonia serves as a Lewis base whereas $AlCl_3$ is Lewis acid. Explain.

Solution:

i.

According to Lewis's theory, an acid is a substance that can accept a share in an electron pair. In the $AlCl_3$ molecule, the octet of Al is incomplete. Therefore, it can accept an electron pair to complete its octet. Hence, $AlCl_3$ acts as a Lewis acid.

ii.

According to Lewis's theory, a base is a substance that can donate an electron pair. In the ammonia (NH_3) molecule, the nitrogen atom has one lone pair of electrons to donate. Hence, NH_3 acts as a Lewis base.

Exercise | Q 3.06 | Page 62

Answer the following in brief :

Acetic acid is 5% ionised in its decimolar solution. Calculate the dissociation constant of acid.

Solution:

Given: Percent dissociation = 5%, Concentration (c) = 1 decimolar

To find: Dissociation constant of acid (K_a)

Formulae:

i. Percent dissociation = $\alpha \times 100$

ii. $K_a = \alpha^2 c$

Calculation:

Using formula (i),

$$\alpha = \frac{\text{Percent dissociation}}{100} = \frac{5}{100} = 0.05$$

c = 1 decimolar = 0.1 M

Using formula (ii),

$K_a = (0.05)^2 \times (0.1)$

$= 2.5 \times 10^{-4}$

Dissociation constant of acid is 2.5×10^{-4}.

Exercise | Q 3.07 | Page 62

Answer the following in brief :

Derive the relation pH + pOH = 14.

Solution:

Relationship between pH and pOH:

The ionic product of water is given as:

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

Now, $K_w = 1 \times 10^{-14}$ at 298 K

Thus, $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Taking the logarithm of both the sides, we write

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

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

Now, $pH = -\log_{10}[H_3O^+]$ and $pOH = -\log_{10}[OH^-]$

$\therefore pH + pOH = 14$

Exercise | Q 3.08 | Page 62

Answer the following in brief :

The aqueous solution of sodium carbonate is alkaline whereas the aqueous solution of ammonium chloride is acidic. Explain.

Solution:

i.

Sodium carbonate (Na_2CO_3) is a salt of weak acid H_2CO_3 and strong base NaOH. When dissolved in water, it dissociates completely.

$$Na_2CO_{3\,(aq)} \longrightarrow 2\,Na^+_{(aq)} + CO^{2-}_{3(aq)}$$

ii.

The Na^+ ions of salt have no tendency to react with OH^- ions of water since the possible product of the reaction is NaOH, a strong electrolyte.

iii.

On the other hand, the reaction of CO_3^{2-} ions of salt with the H_3O^+

ions from water produces unionized H_2CO_3.

$$CO^{2-}_{3(aq)} + 2\,H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + 2\,OH^-_{(aq)}$$

Thus, the hydrolytic equilibrium for Na_2CO_3 is,

$$Na_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + 2\,Na^+_{(aq)} + 2\,OH^-_{(aq)}$$

iv.

As a result of excess OH^- ions produced, the resulting solution of Na_2CO_3 is alkaline.

v.

Similarly, ammonium chloride (NH_4Cl) is salt of strong acid HCl and weak base NH_4OH. When NH_4Cl is dissolved in water, it dissociates completely as,

$$NH_4Cl_{(aq)} \longrightarrow NH^{+}_{4(aq)} + Cl^{-}_{(aq)}$$

vi.

$Cl^{-}_{(aq)}$ ions of salt have no tendency to react with water because the possible product HCl is a strong electrolyte.

vii.

The reaction of NH_4^+ ions with OH^- ions form unionized NH_4OH.

The hydrolytic equilibrium for NH_4Cl is then written as,

$$NH^{+}_{4(aq)} + 2\,H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_3O^{+}_{(aq)}$$

viii.

Due to the presence of an excess of H_3O^+ ions, the resulting solution of NH_4Cl is acidic.

Exercise | Q 3.09 | Page 62

Answer the following in brief :

The pH of a weak monobasic acid is 3.2 in its 0.02 M solution. Calculate its dissociation constant.

Solution:

Given:

pH of weak monobasic acid = 3.2,

Concentration of solution (c) = 0.02 M

To find: Dissociation constant (K_a)

Formula:

i. $pH = -\log_{10}[H_3O^+]$

ii. $K_a = \alpha^2 c$

Calculation:

From the formula (i),

$pH = -\log_{10}[H_3O^+]$

$\therefore \log_{10}[H_3O^+] = -3.2$

= - 3 - 0.2 + 1 - 1

= (-3 - 1) + 1 - 0.2

= -4 + 0.8 = $\bar{4}.8$

$\therefore [H_3O^+] = \text{Antilog}_{10}[\bar{4}.8]$

$= \mathbf{6.310 \times 10^{-4}}$ M

A weak monobasic acid HA dissociates as:

$$\mathbf{HA + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}}$$

$\therefore [H_3O^+] = \alpha \times c$

$$\alpha = \frac{[H_3O^+]}{c} = \frac{6.310 \times 10^{-4}}{0.02} = 3.16 \times 10^{-2}$$

From formula (ii),

$$K_a = \alpha^2 c = (3.16 \times 10^{-2})^2 \times 0.02 = 2.0 \times 10^{-5}$$

The dissociation constant of the acid is $\mathbf{2.0 \times 10^{-5}}$.

Exercise | Q 3.1 | Page 62

Answer the following in brief :

In NaOH solution $[OH^-]$ is 2.87×10^{-4}. Calculate the pH of the solution.

Solution:

Given: $[OH^-] = 2.87 \times 10^{-4}$ M

To find: pH of the solution

Formulae:

i. $pOH = -\log_{10}[OH^-]$

ii. pH + pOH = 14

Calculation:

From formula (i),

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

$\therefore pOH = -\log_{10}[2.87 \times 10^{-4}] = -\log_{10}2.87 - \log_{10}10^{-4}$

$= -\log_{10}2.87 + 4 = 4 - 0.4579$

pOH = 3.5421

From formula (ii),

pH + pOH = 14

pH = 14 - pOH = 14 - 3.5421 = 10.4579,

pH of the solution is 10.4579

Exercise | Q 4.01 | Page 62

Answer the following :

Define the degree of dissociation

Solution:

The degree of dissociation (α) of an electrolyte is defined as a fraction of the total number of moles of the electrolyte that dissociates into its ions when the equilibrium is attained.

Exercise | Q 4.01 | Page 62

Answer the following :

Derive Ostwald's dilution law for the CH_3COOH.

Solution:

i.

Consider an equilibrium of weak acid CH_3COOH that exists in solution partly as the undissociated species CH_3COOH and partly H^+ and CH_3COO^- ions. Then

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

ii.

The acid dissociation constant is given as:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad ....(1)$$

iii.

Suppose 1 mol of acid CH_3COOH is initially present in volume V dm^3 of the solution. At equilibrium, the fraction dissociated would be α, where α is the degree of dissociation of the acid. The fraction of an acid that remains undissociated would be (1 - α).

$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$			
The amount present at equilibrium (mol)	(1 - α)	α	α
Concentration at equilibrium (mol dm^{-3})	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

iv.

Thus, at equilibrium $[CH_3COOH] = \frac{1-\alpha}{V}$ mol dm^{-3},

$[H^+] = [CH_3COO^-] = \frac{\alpha}{V}$ mol dm^{-3}

v.

Substituting these in equation (1),

$$K_a = \frac{\frac{\alpha}{V}\frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{1-\alpha\,V} \quad ...(2)$$

vi.

If c is the initial concentration of CH_3COOH in mol dm^{-3} and V is the volume in dm^3 mol^{-1} then c = 1/V. Replacing 1/V in equation (2) by c,

we get

$$K_a = \frac{\alpha^2 c}{1 - \alpha} \quad ...(3)$$

vii.

For the weak acid CH_3COOH, α is very small, or $(1 - \alpha) \cong 1$. With this equation (2) and (3) becomes:

$$K_a = \frac{\alpha^2}{V} \text{ and } K_a = \alpha^2 c \quad ...(4)$$

$$\alpha = \frac{\sqrt{K_a}}{c} \text{ or } \alpha = \sqrt{K_a . V} \quad ...(5)$$

Equation (5) implies that the degree of dissociation of a weak acid (CH_3COOH) is inversely proportional to the square root of its concentration or directly proportional to the square root of the volume of the solution containing 1 mol of the weak acid.

Exercise | Q 4.02 | Page 62

Answer the following :

Define pH and pOH.

Solution:

i.

The pH of a solution is defined as the negative logarithm to the base 10, of the concentration of H^+ ions in solution in mol dm^{-3}.

pH is expressed mathematically as

$pH = -\log_{10}[H^+]$ or $pH = -\log_{10}[H_3O^+]$

ii.

Similarly, pOH of a solution can be defined as the negative logarithm to the base 10, of the molar concentration of OH^- ions in solution.

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

Exercise | Q 4.02 | Page 62

Answer the following :

Derive the relationship between pH and pOH.

Solution:

Relationship between pH and pOH:

The ionic product of water is given as:

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

Now, $K_w = 1 \times 10^{-14}$ at 298 K

Thus, $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Taking the logarithm of both the sides, we write

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

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

Now, $pH = -\log_{10}[H_3O^+]$ and $pOH = -\log_{10}[OH^-]$

$\therefore$ pH + pOH = 14

Exercise | Q 4.03 | Page 62

Answer the following :

What is meant by hydrolysis?

Solution:

Hydrolysis of salt is defined as the reaction in which cations or anions or both ions of a salt react with ions of water to produce acidity or alkalinity (or sometimes even neutrality).

Exercise | Q 4.03 | Page 62

Answer the following :

A solution of CH_3COONH_4 is neutral. why?

Solution:

i.

CH_3COONH_4 is a salt of a weak acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$), and weak base, NH_4OH ($K_b = 1.8 \times 10^{-5}$). When the salt CH_3COONH_4 is dissolved in water, it undergoes hydrolysis:

$$CH_3COO^-_{(aq)} + NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons \underset{\text{(weak acid)}}{CH_3COOH_{(aq)}} + \underset{\text{(weak base)}}{NH_4OH_{(aq)}}$$

ii.

The ions of the salt react with water as

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)} \quad ...(1)$$

$$NH^{4+}_{(aq)} + 2\,H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_3O^+_{(aq)} \quad ...(2)$$

iii.

As $K_a = K_b$, the relative strength of acid and base produced in hydrolysis is the same.

iv.

Therefore, the solution is neutral. Hydrolysis of NH_4^+ produces as many H_3O^+ ions as that of CH3COO$^-$ produces OH^- ions.

Exercise | Q 4.04 | Page 62

Answer the following :

The dissociation of HCN is suppressed by the addition of HCl. Explain.

Solution:

i. HCN and HCl both dissociate to produce H^+ ions which are common to both.

ii. HCN is a weak electrolyte. It dissociates to a little extent.

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-$$

iii. HCl is a strong electrolyte. It undergoes complete dissociation.

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Both HCN and HCl provide H^+ ions.

iv. The concentration of H^+ ions in the solution increases due to the complete dissociation of HCl.

v. According to Le-Chatelier's principle, the effect of the stress (the addition of H^+ ions from HCl) applied to the ionization equilibrium of HCN is reduced by shifting the equilibrium in the backward direction.

vi. H^+ ions combine with CN^- ions to produce unionized HCN. Thus, the dissociation of HCN is suppressed by the addition of HCl.

Exercise | Q 4.05 | Page 62

Answer the following :

Derive the relationship between the degree of dissociation and dissociation constant in weak electrolytes.

Solution1:

i. Consider 1 mol of weak base BOH dissolved in V dm^3 of solution. The base dissociates partially as

$$BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$$

ii. The base dissociation constant is:

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad ....(1)$$

iii. Let the fraction dissociated at equilibrium is α and that remains undissociated is (1 − α).

$BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$			
Amount present at equilibrium	$(1 - \alpha)$	α	α
Concentration at equilibrium	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

iv. at equilibrium,

$$[BOH] = \frac{1-\alpha}{V} \text{ mol dm}^{-3},$$

$$[B^+] = [OH^-] = \frac{\alpha}{V} \text{ mol dm}^{-3}$$

v. Substituting these concentrations in equation (1),

$$K_b = \frac{\frac{\alpha}{V}\frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{1-\alpha\, V} \quad ...(2)$$

vi. If c is the initial concentration of base in mol dm^{-3} and V is the volume in dm^3 mol^{-1} then c = 1/V. Replacing 1/V in equation (2) by c,

we get

$$K_b = \frac{\alpha^2 c}{1-\alpha} \quad ...(3)$$

vii. For the weak acid base, α is very small, or $(1 - \alpha) \cong 1$. With this equation (2) and (3) becomes:

$$K_b = \frac{\alpha^2}{V} \text{ and } K_b = \alpha^2 c$$

$$\alpha = \sqrt{\frac{K_b}{c}} \text{ or } \alpha = \sqrt{K_b.V} \quad ...(4)$$

The degree of dissociation of a weak base is inversely proportional to square root of its concentration and is directly proportional to square root of volume of the solution containing 1 mol of weak base.

Solution2:

i. Consider an equilibrium of weak acid HA that exists in solution partly as the undissociated species HA and partly H^+ and A^- ions. Then

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

ii. The acid dissociation constant is given as:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad ....(1)$$

iii. Suppose 1 mol of acid HA is initially present in volume V dm^3 of the solution. At equilibrium, the fraction dissociated would be α, where α is the degree of dissociation of the acid. The fraction of an acid that remains undissociated would be (1 − α).

$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$			
Amount present at equilibrium (mol)	(1 - α)	α	α
Concentration at equilibrium (mol dm^{-3})	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

iv. Thus, at equilibrium,

$[HA] = \frac{1-\alpha}{V}$ mol dm^{-3},

$[H^+] = [A^-] = \frac{\alpha}{V}$ mol dm^{-3}

v. Substituting these in equation (1),

$$K_a = \frac{\frac{\alpha}{V}\frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{1-\alpha\,V} \quad ...(2)$$

vi. If c is the initial concentration of acid in mol dm^{-3} and V is the volume in $dm^3\ mol^{-1}$ then c = 1/V. Replacing 1/V in equation (2) by c, we get

$$K_a = \frac{\alpha^2 c}{1-\alpha} \quad ...(3)$$

vii. For the weak acid HA, α is very small, or $(1 - \alpha) \cong 1$. With this equation (2) and (3) becomes:

$$K_a = \frac{\alpha^2}{V} \text{ and } K_a = \alpha^2 c \quad ...(4)$$

$$\alpha = \frac{\sqrt{K_a}}{c} \text{ or } \alpha = \sqrt{K_a . V} \quad ...(5)$$

The equation (5) implies that the degree of dissociation of a weak acid is inversely proportional to the square root of its concentration or directly proportional to the square root of volume of the solution containing 1 mol of the weak acid.

Exercise | Q 4.06 | Page 62

Answer the following :

Sulfides of the cation of group II are precipitated in acidic solution (H_2S + HCl) whereas sulfides of cations of group IIIB are precipitated in the ammoniacal solution of H_2S. Comment on the relative values of the solubility product of sulfides of these.

Solution:

Group II and group IIIB cations are precipitated as their sulphides. However, the solubility product of sulphides of group II cations is lower than group IIIB cations. Therefore, for the precipitation of cations of group II, only a small concentration of sulphide ion is required. This is achieved by passing H_2S gas in the presence of strong electrolyte HCl, which has a common ion (H^+) with H_2S. Due to the common ion effect, the dissociation of H_2S is suppressed and thus, the concentration of S^{2-} ions decreases.

This results only in the precipitation of sulphides of group II while sulphides of the higher group remain in solution as they require a higher concentration of S^{2-} ions for precipitation.

Exercise | Q 4.07 | Page 62

Answer the following :

The solubility of a sparingly soluble salt gets affected in the presence of a soluble salt having one common ion. Explain.

Solution:

i. The presence of a common ion affects the solubility of a sparingly soluble salt.

ii. Consider, the solubility equilibrium of AgCl,

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

The solubility product of AgCl is

$$K_{sp} = [Ag^+][Cl^-]$$

iii. Suppose $AgNO_3$ is added to the saturated solution of AgCl. The salt $AgNO_3$ being a strong electrolyte dissociates completely in the solution.

$$AgNO_{3(aq)} \longrightarrow Ag^+_{(aq)} + NO^-_{3(aq)}$$

iv. The dissociation of AgCl and $AgNO_3$ produce a common Ag^+ ion. The concentration of Ag^+ ion in the solution increases owing to complete dissociation of $AgNO_3$.

v. According to Le-Chatelier's principle, the addition of Ag^+ ions from $AgNO_3$ to the solution of AgCl shifts the solubility equilibrium of AgCl from right to left. The reverse reaction in which AgCl precipitates is favoured until the solubility equilibrium is re-established.

vi. However, the value of K_{sp} remains the same since it is an equilibrium constant. Thus, the solubility of a sparingly soluble compound decreases with the presence of a common ion in solution.

Exercise | Q 4.08 | Page 62

Answer the following :

The pH of rainwater collected in a certain region of Maharashtra on a particular day was 5.1. Calculate the H^+ ion concentration of the rainwater and its percent dissociation.

Solution:

Given: pH of rainwater = 5.1

To find:

i. H^+ ion concentration

ii. Percent dissociation

Formula:

i. pH = $-\log_{10}[H_3O^+]$

ii. Percent dissociation = $\alpha \times 100$

Calculation: From the formula (i),

pH = $-\log_{10}[H_3O^+]$

$\therefore \log_{10}[H_3O^+] = -5.1$

= -5 - 0.1 + 1 - 1

= (-5 - 1) + 1 - 0.1

$= -6 + 0.9 = \bar{6}.9$

$\therefore [H_3O^+] = \text{Antilog}_{10}[\bar{6}.9]$

$= 7.943 \times 10^{-6}$ M

Considering that the pH of rainwater is due to the dissociation of a monobasic strong acid (HA), we have

$$HA_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

$\therefore [H_3O^+] = \alpha$

$\alpha = 7.943 \times 10^{-6}$

From formula (ii),

Percent dissociation = $7.943 \times 10^{-6} \times 100 = 7.943 \times 10^{-4}$

i. H^+ ion concentration is 7.943×10^{-6} M

ii. Percent dissociation is 7.943×10^{-4}.

Exercise | Q 4.09 | Page 62

Answer the following :

Explain the relation between ionic product and solubility product to predict whether a precipitate will form when two solutions are mixed?

Solution:

Condition of precipitation:

The ionic product (IP) of an electrolyte is defined in the same way as solubility product (K_{sp}). The only difference is that the ionic product expression contains a concentration of ions under any condition whereas the expression of K_{sp} contains only equilibrium concentrations. If,

i. IP = K_{sp}; the solution is saturated and solubility equilibrium exists.

ii. IP > K_{sp}; the solution is supersaturated and hence precipitation of the compound will occur.

iii. If IP < K_{sp}, the solution is unsaturated and precipitation will not occur.