

## Ionic Equilibria

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### 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.  $\text{CH}_3\text{COONa} + \text{NaCl}$  in water
2.  $\text{CH}_3\text{COOH} + \text{HCl}$  in water
- 3.  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  in water**
4.  $\text{HCl} + \text{NH}_4\text{Cl}$  in water

**Solution:**  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  in water

#### Exercise | Q 1.4 | Page 61

Choose the most correct answer :

The solubility product of a sparingly soluble salt AX is  $5.2 \times 10^{-13}$ . Its solubility in mol  $\text{dm}^{-3}$  is \_\_\_\_\_.

- 1.  $7.2 \times 10^{-7}$**

2.  $1.35 \times 10^{-4}$
3.  $7.2 \times 10^{-8}$
4.  $13.5 \times 10^{-8}$

**Solution:** The solubility product of a sparingly soluble salt AX is  $5.2 \times 10^{-13}$ . Its solubility in mol dm<sup>-3</sup> is  $7.2 \times 10^{-7}$ .

**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  $[\text{Zn}(\text{H}_2\text{O})_4]^{2\oplus}$  is \_\_\_\_\_.

1.  $[\text{Zn}(\text{H}_2\text{O})_4]^{2\oplus}\text{NH}_3$
2.  $[\text{Zn}(\text{H}_2\text{O})_3]^{2\oplus}$
3.  **$[\text{Zn}(\text{H}_2\text{O})_3\text{OH}]^\oplus$**
4.  $[\text{Zn}(\text{H}_2\text{O})\text{H}]^{3\oplus}$

**Solution:** The conjugate base of  $[\text{Zn}(\text{H}_2\text{O})_4]^{2\oplus}$  is  $[\text{Zn}(\text{H}_2\text{O})_3\text{OH}]^\oplus$ .

**Exercise | Q 1.7 | Page 61**

**Choose the most correct answer :**

For pH > 7 the hydronium ion concentration would be \_\_\_\_\_.

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

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

**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  $1.8 \times 10^{-5}$ . Calculate percent dissociation of acetic acid in 0.01 M solution.

**Solution:**

**Given :**

- Dissociation constant ( $K_a$ ) =  $1.8 \times 10^{-5}$ ,
- Concentration (c) = 0.01 M

**To find :**

- Percent dissociation

**Formulae :**

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

**Calculation :**

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

Using formula (i),

$$\begin{aligned}\therefore \alpha &= \sqrt{\frac{K_a}{c}} \\ &= \sqrt{\frac{1.8 \times 10^{-5}}{1 \times 10^{-2}}} = \sqrt{1.8 \times 10^{-3}} = \sqrt{18 \times 10^{-4}} \\ &= 4.242 \times 10^{-2}\end{aligned}$$

Using formula (ii),

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

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  $\text{H}^+$  ion concentration.

**Solution:**

**Given:**

pH of solution = 6.06

**To find:**

$\text{H}^+$  ion concentration

**Formula:**

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

**Calculation:**

From formula,

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

$$\therefore \log_{10}[\text{H}_3\text{O}^+] = -\text{pH}$$

$$= -6.06$$

$$= -6 - 0.06 + 1 - 1$$

$$= (-6 - 1) + 1 - 0.06$$

$$= -7 + 0.94 = \underline{\underline{7.94}}$$

$$\text{Thus, } [\text{H}_3\text{O}^+] = \text{Antilog}_{10}[7.94]$$

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

The  $\text{H}^+$  ion concentration of the solution is  $8.710 \times 10^{-7} \text{ M}$ .

### Exercise | Q 2.07 | Page 61

**Answer the following in one sentence :**

Calculate the pH of 0.01 M sulphuric acid.

**Solution:**

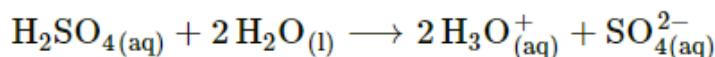
**Given:** Concentration of sulphuric acid = 0.01 M

**To find:** pH

**Formula:**  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$

**Calculation:**

Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) is a strong acid. It dissociates almost completely in the water as:



$$\text{Hence, } [\text{H}_3\text{O}^+] = 2 \times c = 2 \times 0.01 \text{ M} = 2 \times 10^{-2} \text{ M}$$

From formula (i),

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}[2 \times 10^{-2}] = -\log_{10}2 - \log_{10}10^{-2}$$

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

$$\text{pH} = 1.699$$

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  $\text{H}_2\text{S}$  is suppressed in the presence of  $\text{HCl}$ . Name the phenomenon.

**Solution:**

The phenomenon due to which dissociation of  $\text{H}_2\text{S}$  is suppressed in the presence of  $\text{HCl}$  is known as the common ion effect.

**Exercise | Q 2.09 | Page 61**

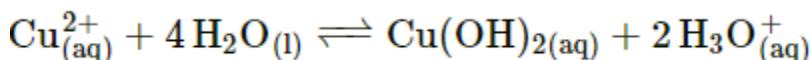
**Answer the following in one sentence :**

Why is it necessary to add  $\text{H}_2\text{SO}_4$  while preparing the solution of  $\text{CuSO}_4$ ?

**Solution:**

i.

The aqueous solution of  $\text{CuSO}_4$  is turbid due to the formation of sparingly soluble  $\text{Cu}(\text{OH})_2$  by hydrolysis as shown below:



ii.

If  $\text{H}_2\text{SO}_4$ , that is  $\text{H}_3\text{O}^+$  ions are added, the hydrolytic equilibrium shifts to the left. Turbidity of  $\text{Cu}(\text{OH})_2$  dissolves to give a clear solution. Hence, it is necessary to add  $\text{H}_2\text{SO}_4$  while preparing the solution of  $\text{CuSO}_4$ .

### Exercise | Q 2.1 | Page 61

Answer the following in one sentence :

Classify the following buffers into different types :

- a. CH<sub>3</sub>COOH + CH<sub>3</sub>COONa
- b. NH<sub>4</sub>OH + NH<sub>4</sub>Cl
- c. Sodium benzoate + benzoic acid
- d. Cu(OH)<sub>2</sub> + CuCl<sub>2</sub>

**Solution:**

	Buffer	Type
i.	CH <sub>3</sub> COOH + CH <sub>3</sub> COONa	Acidic buffer
ii.	NH <sub>4</sub> OH + NH <sub>4</sub> Cl	Basic buffer
iii.	Sodium benzoate + benzoic acid	Acidic buffer
iv.	Cu(OH) <sub>2</sub> + CuCl <sub>2</sub>	Basic buffer

### Exercise | Q 3.01 | Page 62

Answer the following in brief :

What are acids and bases according to Arrhenius theory?

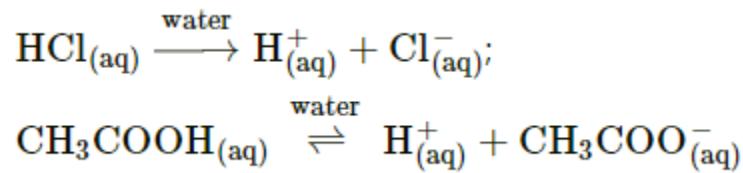
**Solution:**

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

i.

**Acid:** An acid is a substance that contains hydrogen and gives H<sup>+</sup> ions in an aqueous solution.

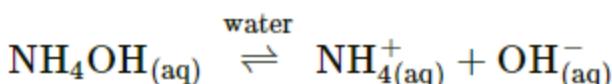
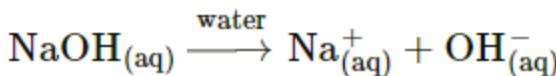
e.g.



ii.

**Base:** A base is a substance that contains the OH group and produces hydroxide ions (OH<sup>-</sup> ions) in aqueous solution.

**e.g.**



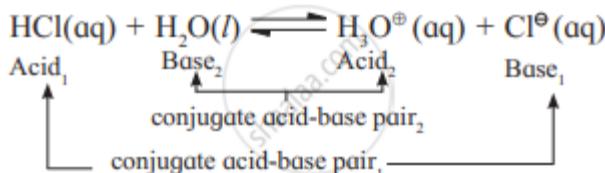
### Exercise | Q 3.02 | Page 62

**Answer the following in brief :**

What is meant by conjugate acid-base pair?

**Solution:**

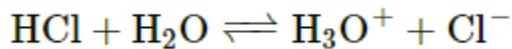
- i. The base produced by accepting the proton from acid is the conjugate base of that acid.
- ii. Similarly, the acid produced when a base accepts a proton is called the conjugate acid of that base.
- iii. A pair of an acid and a base differing by a proton is said to be a conjugate acid-base pair.



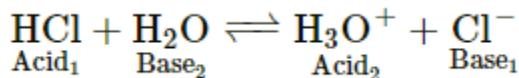
### Exercise | Q 3.03 | Page 62

**Answer the following in brief :**

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



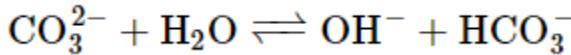
**Solution:**



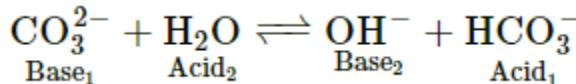
### Exercise | Q 3.03 | Page 62

**Answer the following in brief :**

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



**Solution:**

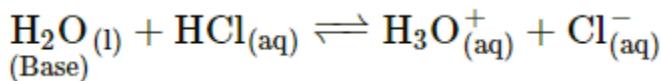


### Exercise | Q 3.04 | Page 62

**Answer the following in brief :**

Write a reaction in which water acts as a base.

**Solution:**



**Exercise | Q 3.05 | Page 62**

**Answer the following in brief :**

Ammonia serves as a Lewis base whereas  $\text{AlCl}_3$  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  $\text{AlCl}_3$  molecule, the octet of Al is incomplete. Therefore, it can accept an electron pair to complete its octet. Hence,  $\text{AlCl}_3$  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 ( $\text{NH}_3$ ) molecule, the nitrogen atom has one lone pair of electrons to donate. Hence,  $\text{NH}_3$  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  $2.5 \times 10^{-4}$ .

### Exercise | Q 3.07 | Page 62

**Answer the following in brief :**

Derive the relation  $\text{pH} + \text{pOH} = 14$ .

**Solution:**

**Relationship between pH and pOH:**

The ionic product of water is given as:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

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

$$\text{Thus, } [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Taking the logarithm of both the sides, we write

$$\log_{10}[\text{H}_3\text{O}^+] + \log_{10}[\text{OH}^-] = -14$$

$$-\log_{10}[\text{H}_3\text{O}^+] + \{-\log_{10}[\text{OH}^-]\} = 14$$

$$\text{Now, pH} = -\log_{10}[\text{H}_3\text{O}^+] \text{ and pOH} = -\log_{10}[\text{OH}^-]$$

$$\therefore \text{pH} + \text{pOH} = 14$$

### Exercise | Q 3.08 | Page 62

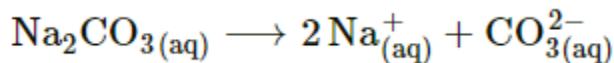
**Answer the following in brief :**

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

**Solution:**

i.

Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is a salt of weak acid  $\text{H}_2\text{CO}_3$  and strong base  $\text{NaOH}$ . When dissolved in water, it dissociates completely.

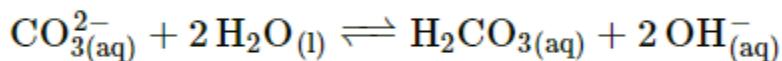


ii.

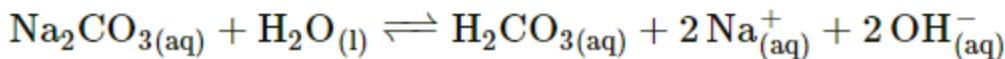
The  $\text{Na}^+$  ions of salt have no tendency to react with  $\text{OH}^-$  ions of water since the possible product of the reaction is  $\text{NaOH}$ , a strong electrolyte.

iii.

On the other hand, the reaction of  $\text{CO}_{3}^{2-}$  ions of salt with the  $\text{H}_3\text{O}^+$  ions from water produces unionized  $\text{H}_2\text{CO}_3$ .



Thus, the hydrolytic equilibrium for  $\text{Na}_2\text{CO}_3$  is,

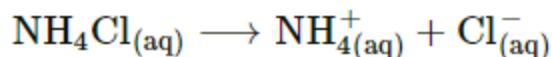


iv.

As a result of excess  $\text{OH}^-$  ions produced, the resulting solution of  $\text{Na}_2\text{CO}_3$  is alkaline.

v.

Similarly, ammonium chloride ( $\text{NH}_4\text{Cl}$ ) is salt of strong acid  $\text{HCl}$  and weak base  $\text{NH}_4\text{OH}$ . When  $\text{NH}_4\text{Cl}$  is dissolved in water, it dissociates completely as,



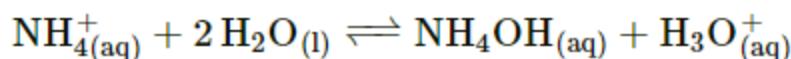
**vi.**

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

**vii.**

The reaction of  $\text{NH}_4^+$  ions with  $\text{OH}^-$  ions form unionized  $\text{NH}_4\text{OH}$ .

The hydrolytic equilibrium for  $\text{NH}_4\text{Cl}$  is then written as,



**viii.**

Due to the presence of an excess of  $\text{H}_3\text{O}^+$  ions, the resulting solution of  $\text{NH}_4\text{Cl}$  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.  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$

ii.  $K_a = \alpha^2 c$

**Calculation:**

From the formula (i),

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

$$\therefore \log_{10}[\text{H}_3\text{O}^+] = -3.2$$

$$= -3 - 0.2 + 1 - 1$$

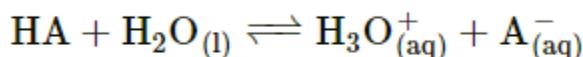
$$= (-3 - 1) + 1 - 0.2$$

$$= -4 + 0.8 = \bar{4.8}$$

$$\therefore [\text{H}_3\text{O}^+] = \text{Antilog}_{10}[\bar{4.8}]$$

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

A weak monobasic acid HA dissociates as:



$$\therefore [\text{H}_3\text{O}^+] = \alpha \times c$$

$$\alpha = \frac{[\text{H}_3\text{O}^+]}{c} = \frac{6.310 \times 10^{-4}}{0.02} = 3.16 \times 10^{-2}$$

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  $2.0 \times 10^{-5}$ .

### Exercise | Q 3.1 | Page 62

**Answer the following in brief :**

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

**Solution:**

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

**To find:** pH of the solution

**Formulae:**

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

ii.  $\text{pH} + \text{pOH} = 14$

**Calculation:**

From formula (i),

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

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

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

$$\text{pOH} = 3.5421$$

From formula (ii),

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - \text{pOH} = 14 - 3.5421 = 10.4579,$$

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 ( $\alpha$ ) 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

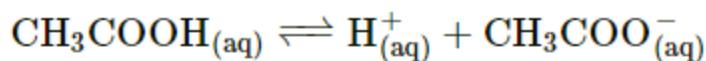
**Answer the following :**

Derive Ostwald's dilution law for the  $\text{CH}_3\text{COOH}$ .

**Solution:**

i.

Consider an equilibrium of weak acid  $\text{CH}_3\text{COOH}$  that exists in solution partly as the undissociated species  $\text{CH}_3\text{COOH}$  and partly  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$  ions. Then



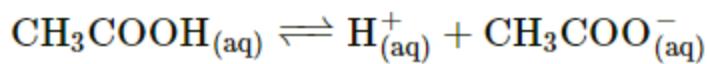
ii.

The acid dissociation constant is given as:

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \dots(1)$$

iii.

Suppose 1 mol of acid  $\text{CH}_3\text{COOH}$  is initially present in volume  $V \text{ dm}^3$  of the solution. At equilibrium, the fraction dissociated would be  $\alpha$ , where  $\alpha$  is the degree of dissociation of the acid. The fraction of an acid that remains undissociated would be  $(1 - \alpha)$ .



The amount present at equilibrium (mol)	$(1 - \alpha)$	$\alpha$	$\alpha$
Concentration at equilibrium (mol dm <sup>-3</sup> )	$\frac{1 - \alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

**iv.**

Thus, at equilibrium  $[\text{CH}_3\text{COOH}] = \frac{1 - \alpha}{V}$  mol dm<sup>-3</sup>,

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] = \frac{\alpha}{V} \text{ mol dm}^{-3}$$

**v.**

Substituting these in equation (1),

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

**vi.**

If  $c$  is the initial concentration of  $\text{CH}_3\text{COOH}$  in mol dm<sup>-3</sup> and  $V$  is the volume in dm<sup>3</sup> mol<sup>-1</sup> then  $c = 1/V$ . Replacing  $1/V$  in equation (2) by  $c$ , we get

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

vii.

For the weak acid  $\text{CH}_3\text{COOH}$ ,  $\alpha$  is very small, or  $(1 - \alpha) \cong 1$ . With this equation (2) and (3) becomes:

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

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

Equation (5) implies that the degree of dissociation of a weak acid ( $\text{CH}_3\text{COOH}$ ) 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  $\text{H}^+$  ions in solution in  $\text{mol dm}^{-3}$ .

pH is expressed mathematically as

$$\text{pH} = -\log_{10}[\text{H}^+] \text{ or } \text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

ii.

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

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

### 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

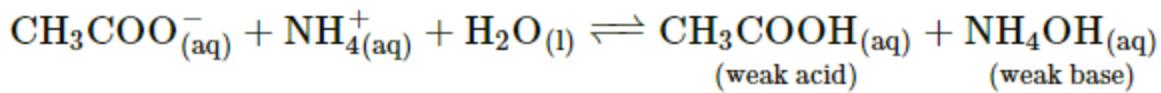
**Answer the following :**

A solution of  $CH_3COONH_4$  is neutral. why?

**Solution:**

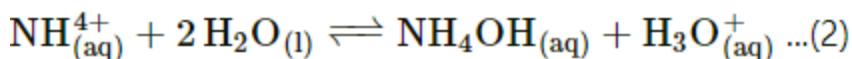
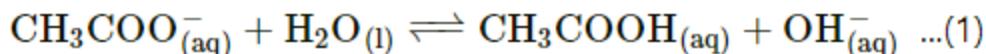
i.

$CH_3COONH_4$  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:



iii.

The ions of the salt react with water as



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  $\text{NH}_4^+$  produces as many  $\text{H}_3\text{O}^+$  ions as that of  $\text{CH}_3\text{COO}^-$  produces  $\text{OH}^-$  ions.

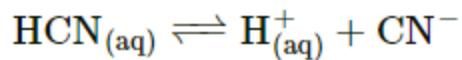
**Exercise | Q 4.04 | Page 62**

## **Answer the following :**

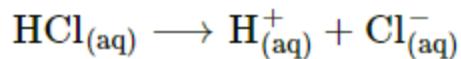
The dissociation of HCN is suppressed by the addition of HCl. Explain.

## 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.



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



Both HCN and HCl provide H<sup>+</sup> ions.

**iv.** The concentration of H<sup>+</sup> 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<sup>+</sup> ions from HCl) applied to the ionization equilibrium of HCN is reduced by shifting the equilibrium in the backward direction.

**vi.** H<sup>+</sup> ions combine with CN<sup>-</sup> ions to produce unionized HCN. Thus, the dissociation of HCN is suppressed by the addition of HCl.

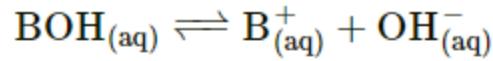
### Exercise | Q 4.05 | Page 62

**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<sup>3</sup> of solution. The base dissociates partially as



ii. The base dissociation constant is:

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

iii. Let the fraction dissociated at equilibrium is  $\alpha$  and that remains undissociated is  $(1 - \alpha)$ .

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

iv. at equilibrium,

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

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

v. Substituting these concentrations in equation (1),

$$K_b = \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{1 - \alpha V} \dots(2)$$

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

we get

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

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

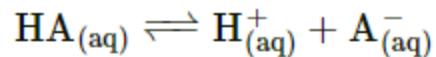
$$K_b = \frac{\alpha^2}{V} \text{ and } K_b = \alpha^2 c$$

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

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  $\text{H}^+$  and  $\text{A}^-$  ions. Then



ii. The acid dissociation constant is given as:

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

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

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

iv. Thus, at equilibrium,

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

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

v. Substituting these in equation (1),

$$K_a = \frac{\frac{\alpha}{V} \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{1 - \alpha V} \dots(2)$$

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

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

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

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

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

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:**

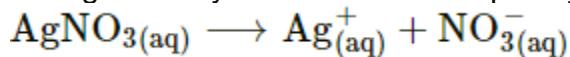
- i. The presence of a common ion affects the solubility of a sparingly soluble salt.
- ii. Consider, the solubility equilibrium of  $AgCl$ ,



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.



- 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<sup>+</sup> ion concentration

ii. Percent dissociation

**Formula:**

i. pH = -log<sub>10</sub>[H<sub>3</sub>O<sup>+</sup>]

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

**Calculation:** From the formula (i),

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

$$\therefore \log_{10}[\text{H}_3\text{O}^+] = -5.1$$

$$= -5 - 0.1 + 1 - 1$$

$$= (-5 - 1) + 1 - 0.1$$

$$= -6 + 0.9 = \bar{6.9}$$

$$\therefore [\text{H}_3\text{O}^+] = \text{Antilog}_{10}[\bar{6.9}]$$

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

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



$$\therefore [\text{H}_3\text{O}^+] = \alpha$$

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

From formula (ii),

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

i. H<sup>+</sup> ion concentration is  $7.943 \times 10^{-6} \text{ M}$

ii. Percent dissociation is  $7.943 \times 10^{-4}$ .

### 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.