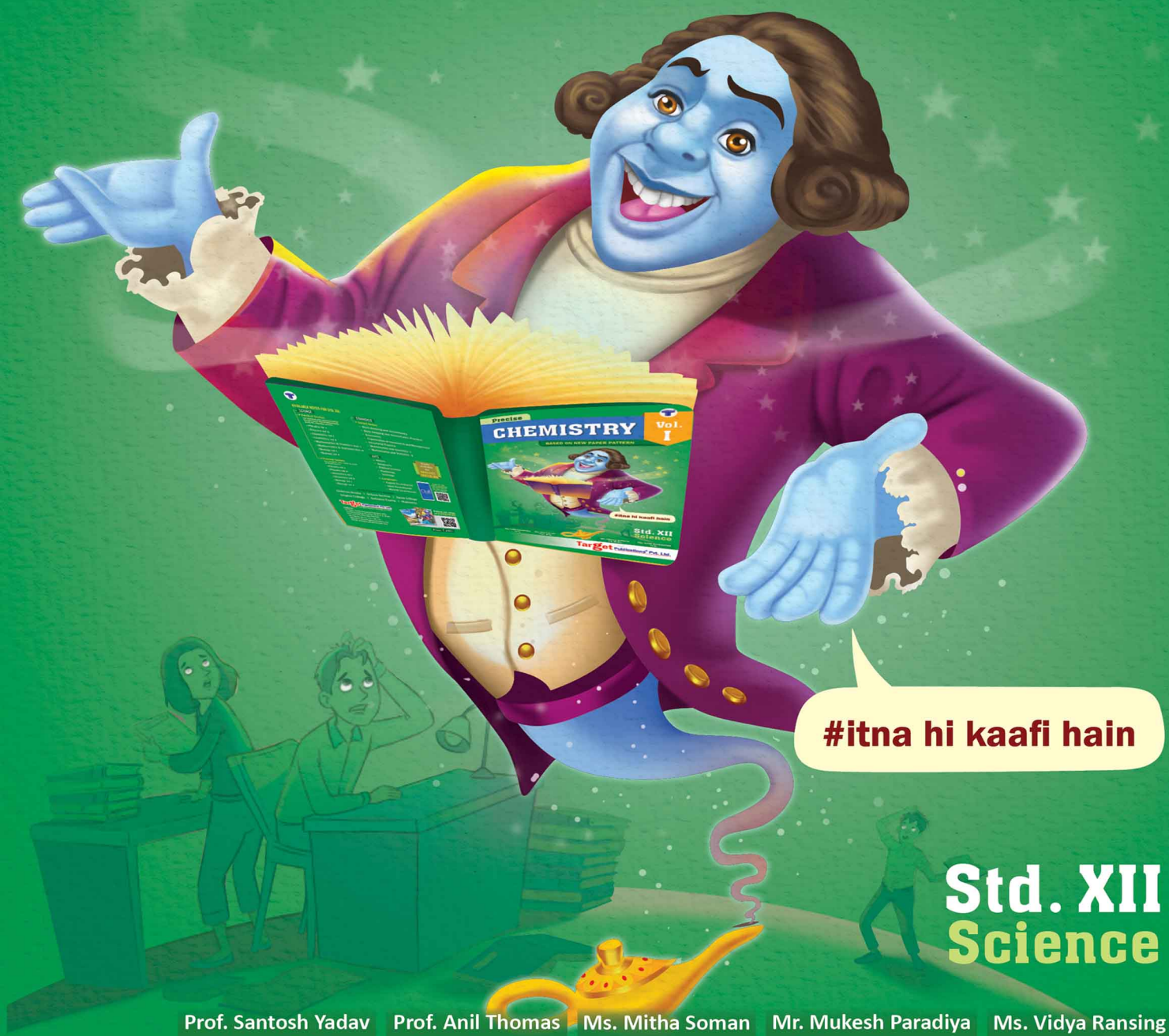
SAMPLE CONTENT

Precise

# CHEMISTRY

Vol. I

BASED ON NEW PAPER PATTERN




Std. XII Science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Precise

# CHEMISTRY (Vol. I)

## Std. XII Sci.



### Salient Features

- Written as per Latest Board Paper Pattern
- Subtopic-wise segregation for powerful concept building
- Complete coverage of Textual Exercise Questions, Intext Questions and Numericals
- Includes selective and relevant Board questions from March 2013 to July 2022
- Includes selective questions from NCERT textbook for practice
- 'Quick Review' of the chapter facilitates quick revision
- 'Important Formulae' and 'Solved Examples' provided to cover numerical aspect of the topic in detail
- Marks provided to the Questions as per relevant weightage wherever deemed necessary
- 'Reading Between the Lines' to elucidate concept
- Video/pdf links provided via QR codes for boosting conceptual retention
- Includes Board Question Paper of March 2023 (Solution in pdf format through QR code)

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# PREFACE

**Precise Chemistry Vol. I, Std. XII Sci.** is intended for every Maharashtra State Board aspirant of Std. XII, Science. The scope, sequence, and level of the book are designed to match the new textbook issued by the Maharashtra State board.

We understand that Board Examinations can be daunting and the stress of cracking the examination can often leave students struggling to make sense of the curriculum. Selective and relevant questions of Board Examination from March 2013 to July 2022 are provided so that students would get an idea about the types of questions that are asked in Board Examinations.

With the examination in focus, the ***Precise Series*** has been specifically designed to make preparation easier, by providing a methodical and organized perspective of the curriculum, thus greatly improving the chances of scoring well.

Chemistry is a science that has the potential to unlock the understanding of the natural world by allowing us to appreciate the changes that characterize matter interactions.

In order to make sure that students fully grasp the nub of the subject, it is important to present such concepts meaningfully and in an easy to read format.

In this vein, the Precise Chemistry book has been crafted to provide an **exam-centric approach** to the curriculum, while **retaining the essence** of the subject. Each chapter is thus structured to provide a **conceptual foundation**, in addition to offering **ample practice** for acing the board examination. **Chemical formulae, bonding structures** and **chemical equations** form the basic building blocks of Chemistry and students are advised to memorise them perfectly.

To quote the Nobel Prize winner, chemist Irving Langmuir, "***A chemist who does not know Mathematics is seriously handicapped!***", a solid theoretical foundation must always be put to the test by solving numericals.
Students should take advantage of the **extensive array of numericals** provided in the book to ascertain their command on problem solving.

**A holistic preparation is the key to mastering any subject and conquering the board examination.**

Our **Precise Chemistry Vol. I, Std. XII Sci.** adheres to our vision and achieves several goals: **building concepts, developing competence to solve numericals, recapitulation and self-study** – all while facilitating effective preparation of the chapter.

Publisher

**Edition:** Fifth

The journey to create a complete book is strewn with triumphs, failures and near misses. If you think we've nearly missed something or want to applaud us for our triumphs, we'd love to hear from you.
Please write to us on: mail@targetpublications.org

# KEY FEATURES

**Reading between the lines**

Reading between the lines provides elaboration or missing fragments of concept which is essential for complete understanding of the concept.

**QR Codes**

QR code provides:

i. Access to a video/PDF in order to boost understanding of a concept or activity

ii. Solutions to Board Question Paper March 2023

**Solved Examples**

Solved Examples offer complete solution to numerical including log calculations (as seemed required).

**Quick Review**

Quick review includes tables/ flow chart to summarize the key points in chapter.

**Important Formulae**

Important Formulae includes all the key formulae in the chapter.

**Exercise**

Exercise includes subtopic-wise additional questions and problems.

**Multiple Choice Questions**

Multiple Choice Questions includes textual as well as additional MCQs.

**Board Questions**

Includes selective and relevant Board questions from March 2013 to July 2022

# PAPER PATTERN

- There will be single question paper of 70 Marks and practical examination of 30 Marks in Chemistry.
- Duration of the question paper will be 3 hours.

**Section A:** **(18 Marks)**

This section will contain Multiple Choice Questions and Very Short Answer(VSA) type of questions.
There will be 10 MCQs and 8 VSA type of questions, each carrying **One** mark.
Students will have to attempt all the questions.

**Section B:** **(16 Marks)**

This section will contain 12 Short Answer (SA-I) type of questions, each carrying **Two** marks.
Students will have to attempt any 8 questions.

**Section C:** **(24 Marks)**

This section will contain 12 Short Answer (SA-II) type of questions, each carrying **Three** marks.
Students will have to attempt any 8 questions.

**Section D:** **(12 Marks)**

This section will contain 5 Long Answer (LA) type of questions, each carrying **Four** marks.
Students will have to attempt any 3 questions.

**Distribution of Marks According to the Type of Questions**

| Type of Questions | | |
|---|---|---|
| MCQ | 1 Mark each | 10 Marks |
| VSA | 1 Mark each | 8 Marks |
| SA - I | 2 Marks each | 16 Marks |
| SA - II | 3 Marks each | 24 Marks |
| LA | 4 Marks each | 12 Marks |

# CONTENTS



**[Reference:** Maharashtra State Board of Secondary and Higher Secondary Education, Pune - 04**]**

**Note:**
1. * mark represents Textual question.
2. # mark represents Intext question.
3. + mark represents Textual examples.
4. 🔔 symbol represents textual questions that need external reference for an answer.
5. Chapters 10 to 16 are a part of Precise Chemistry Vol. II, Std. XII Sci.

# 3 Ionic Equilibria

## Contents and Concepts



## 3.1 Introduction

**Q.1. Define ionic equilibrium. Give four examples of ionic equilibrium.** **[3 Marks]**

**Ans:** *The equilibrium between ions and unionized molecules in solution is called* ***ionic equilibrium****.*

**e.g.**

i. Equilibrium between $H^+$ and $OH^-$ ions and unionized water molecules.
ii. Ionization of weak acids and weak bases.
iii. Reactions between ions of salt and ions of water.
iv. Solid salt and its ions in water.

## 3.2 Types of electrolyte

**Q.2. Define electrolytes.** **[1 Mark]**

**Ans:** *The substances which give rise to ions when dissolved in water are called* ***electrolytes****.*

**Q.3. Define nonelectrolytes.** **[1 Mark]**

**Ans:** *The substances which do not ionize and exist as molecules in aqueous solutions are called* ***non-electrolytes****.*

**Q.4. How are electrolytes classified?** **[2 Marks]**

**Ans:** The electrolytes are classified into strong and weak electrolytes. This classification is based on their extent of ionization in dilute aqueous solutions.

**i.** **Strong electrolyte:** *The electrolytes ionizing completely or almost completely are* ***strong electrolytes****.*
**e.g.** Strong acids, strong bases and salts

**ii.** **Weak electrolyte:** *The electrolytes which dissociate to a smaller extent in aqueous solution are* ***weak electrolytes****.*
**e.g.** Weak acids and weak bases

**Q.5. Explain the dissociation of weak electrolytes in water.** **[2 Marks]**

**Ans:**

i. Weak electrolytes are partially dissociated in dilute aqueous solutions. Hence, an equilibrium exists between the ions and the nonionized molecules.

ii. A double arrow ($\rightleftharpoons$) between the ions and nonionized molecules of the weak electrolyte is used to represent the ionization reaction.

**Q.6. Use your brain power** *(Textbook Page no. 47)*
**Which of the following is a strong electrolyte?** **[1 Mark]**
**HF, AgCl, $CuSO_4$, $CH_3COONH_4$, $H_3PO_4$**

**Ans:** HF is a weak electrolyte while others are strong electrolytes.

***Q.7. Define degree of dissociation.** **[1 Mark]**

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

**Q.8. Write a short note on degree of dissociation.** **[2 Marks]**

**Ans:**

i. Definition: *Refer Q.7.*

ii. It is denoted by symbol α and given by

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Total number of moles}}$$

iii. Percent dissociation = α × 100

iv. If c is the molar concentration of an electrolyte $X^+Y^-$, the equilibrium concentration of cation or anion is (α × c) mol $dm^{-3}$.

## 3.3 Acids and bases

***Q.9. What are acids and bases according to Arrhenius theory?** **[2 Marks]**

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

**i. Acid:** *An **acid** is a substance which contains hydrogen and gives $H^+$ ions in 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 which contains OH group and produces hydroxide ions ($OH^-$ ions) in aqueous solution.*

**e.g.** $NaOH_{(aq)} \xrightarrow{\text{water}} Na^+_{(aq)} + OH^-_{(aq)}$ ; $NH_4OH_{(aq)} \overset{\text{water}}{\rightleftharpoons} NH^+_{4(aq)} + OH^-_{(aq)}$

**Note:** i. Although, Arrhenius described $H^+$ ions in water as bare ions, we now know that they are hydrated in aqueous solutions and are represented as hydronium ions, $H_3O^+$. However, we will conveniently represent them as $H^+$.

ii. Acids and bases are familiar chemical compounds. Acetic acid is found in vinegar, citric acid in lemons, magnesium hydroxide in antacids, ammonia in household cleaning products. The tartaric acid is present in tamarind paste.

iii. Hydrochloric acid, HCl present in the gastric juice is secreted by our stomach and is essential for digestion of food.

**Q.10. What are the limitations of Arrhenius theory?** **[2 Marks]**

**Ans: Limitations of Arrhenius theory:**

i. Arrhenius theory accounts for properties of different acids and bases but is applicable only to aqueous solutions.

ii. It does not account for the basicity of $NH_3$ and $Na_2CO_3$ which do not have OH group.

**Q.11. Give a brief account of Bronsted-Lowry theory of acids and bases.** **[2 Marks]**

**Ans: Bronsted-Lowry theory:** J. N. Bronsted and T. M. Lowry (1923) proposed a more general theory known as the Bronsted-Lowry proton transfer theory.

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

**Acid:** ***Acid** is a substance that donates a proton ($H^+$) to another substance.*

**Base:** ***Base** is a substance that accepts a proton ($H^+$) from another substance.*

**e.g.** $\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{NH_3} \rightleftharpoons \underset{\text{Acid}_2}{NH_4^+} + \underset{\text{Base}_1}{Cl^-}$

In the above reaction, HCl and $NH_4^+$ are proton donors and act as acids. The $NH_3$ and $Cl^-$ are proton acceptors and act as bases. From the above reaction, it is clear that the products of the Bronsted-Lowry acid-base reactions are acids and bases.

**Q.12. What is a conjugate base?** **[1 Mark]**

**Ans:** *The base produced by accepting the proton from an acid is the **conjugate base** of that acid.*

**e.g.** $Cl^-$ is a conjugate base of acid HCl.

**Q.13. What is a conjugate acid?** **[1 Mark]**

**Ans:** *The acid produced when a base accepts a proton is called the **conjugate acid** of that base.*

**e.g.** $H_3O^+$ is a conjugate acid of base $H_2O$.

Page no. **78** to **98** are purposely left blank.

To see complete chapter buy **Target Notes** or **Target E-Notes**

Ionic product in the solution is given by

$[Mg^{2+}][C_2O_4^{2-}] = 0.05 \times 0.15 = 0.0075 = 7.5 \times 10^{-3}$

$K_{sp}$ value for $MgC_2O_4$ at 293 K is $8.56 \times 10^{-5}$.

As ionic product is greater than $K_{sp}$, **precipitation will take place**.

**Ans:** $MgC_2O_4$ **will precipitate** out from the solution.

**+Q.97. If 20.0 cm$^3$ of 0.050 M $Ba(NO_3)_2$ are mixed with 20.0 cm$^3$ of 0.020 M NaF, will $BaF_2$ precipitate? $K_{sp}$ of $BaF_2$ is $1.7 \times 10^{-6}$ at 298 K.** *(Problem 3.13 of Textbook page no. 59-60)* **[3 Marks]**

***Solution:***

*Given:* Volume of $Ba(NO_3)_2$ solution = 20.0 cm$^3$ , Concentration of $Ba(NO_3)_2$ solution = 0.050 M,
Volume of NaF solution = 20.0 cm$^3$, Concentration of NaF solution = 0.020 M,
$K_{sp}$ of $BaF_2 = 1.7 \times 10^{-6}$

*To find:* Whether $BaF_2$ will precipitate out or not

*Calculation:* Final volume of solution is 20 + 20 = 40 cm$^3$

$$[Ba(NO_3)_2] = \frac{0.050 \times 20}{40} = 0.025 \text{ M}$$

$$[NaF] = \frac{0.020 \times 20}{40} = 0.010 \text{ M}$$

$\therefore$ $[Ba^{2+}] = 0.025$ M and $[F^-] = 0.010$ M

These ions would react to form sparingly soluble salt $BaF_2$ in accordance with reaction

$$Ba^{2+}_{(aq)} + 2F^-_{(aq)} \rightleftharpoons BaF_{2(s)}$$

Ionic product of $BaF_2$ is

$IP = [Ba^{2+}][F^-]^2 = 0.025 \times (0.01)^2$
$= 2.5 \times 10^{-6}$

$K_{sp}$ $(BaF_2) = 1.7 \times 10^{-6}$

Thus, $K_{sp} < IP$

Ionic product in the solution is greater than $K_{sp}$. Hence, $BaF_2$ **will precipitate** from the solution.

**Ans:** $BaF_2$ **will precipitate** out from the solution.

**+Q.98. The solubility product of AgBr is $5.2 \times 10^{-13}$. Calculate its solubility in mol dm$^{-3}$ and g dm$^{-3}$. (Molar mass of AgBr = 187.8 g mol$^{-1}$)** *(Problem 3.12 of Textbook page no. 59)* **[3 Marks]**

***Solution:***

*Given:* Solubility product ($K_{sp}$) of AgBr = $5.2 \times 10^{-13}$
Molar mass of AgBr = 187.8 g mol$^{-1}$

*To find:* Solubility in mol dm$^{-3}$ and g dm$^{-3}$

*Formulae:* i. $K_{sp} = x^x y^y S^{x+y}$
ii. Solubility (g dm$^{-3}$) = Molar solubility (mol dm$^{-3}$) × Molar mass (g mol$^{-1}$)

*Calculation:* The solubility equilibrium of AgBr is:

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$$

$x = 1, y = 1$

$K_{sp} = x^x y^y S^{x+y} = (1)^1 (1)^1 S^{1+1} = S^2$

$S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}}$

$= \mathbf{7.2 \times 10^{-7}}$ **mol dm$^{-3}$**

Solubility (g dm$^{-3}$) = Molar solubility (mol dm$^{-3}$) × Molar mass (g mol$^{-1}$)

$S = 7.2 \times 10^{-7}$ mol dm$^{-3}$ × 187.8 g mol$^{-1}$

$= \mathbf{1.35 \times 10^{-4}}$ **g dm$^{-3}$**

**Ans:** Solubility in mol dm$^{-3}$ is $\mathbf{7.2 \times 10^{-7}}$ **mol dm$^{-3}$** and solubility in g dm$^{-3}$ is $\mathbf{1.35 \times 10^{-4}}$ **g dm$^{-3}$**.

**Q.99. Solubility product of AgCl is $1.8 \times 10^{-10}$. Calculate its molar solubility and solubility in g dm$^{-3}$. Molar mass of AgCl is 143.5 g mol$^{-1}$.** **[3 Marks]**

***Solution:***

*Given:* Solubility product of AgCl = $K_{sp} = 1.8 \times 10^{-10}$
Molar mass of AgCl = 143.5 g mol$^{-1}$

*To find:* i. Molar solubility (S) ii. Solubility in g dm$^{-3}$

*Formulae:* i. $K_{sp} = x^x y^y S^{x+y}$
ii. Solubility (g dm$^{-3}$) = Molar solubility (mol dm$^{-3}$) × Molar mass (g mol$^{-1}$)

*Calculation:* Solubility equilibrium for AgCl is:

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

$x = y = 1$

$K_{sp} = x^x y^y S^{x+y} = 1^1 1^1 S^{1+1} = S^2$

The molar solubility S of AgCl is given by

$S = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}}$

$= \mathbf{1.342 \times 10^{-5}\ mol\ dm^{-3}}$

Solubility (g $dm^{-3}$) = molar solubility (mol $dm^{-3}$) × Molar mass (g $mol^{-1}$)

Solubility = $1.342 \times 10^{-5}$ (mol $dm^{-3}$) × 143.5 (g $mol^{-1}$)

$= 1.342 \times 143.5 \times 10^{-5}$

$\therefore$ $\mathbf{S = 192.5 \times 10^{-5}}$ *(Using log table)*

$\mathbf{= 1.925 \times 10^{-3}\ g\ dm^{-3}}$

Calculation using log table:

$\sqrt{1.8}$ = Antilog$_{10}$ [log$_{10}$ $\sqrt{1.8}$ ]

= Antilog$_{10}$[ $\frac{1}{2}$ × log$_{10}$ 1.8]

= Antilog$_{10}$ [ $\frac{1}{2}$ × 0.2553]

= Antilog$_{10}$ [0.1277] = **1.342**

(1.342 × 143.5) = Antilog$_{10}$ [log$_{10}$ 1.342 + log$_{10}$ 143.5]

= Antilog$_{10}$ [0.1277 + 2.1568]

= Antilog$_{10}$ [2.2845] = **192.5**

**Ans:** Molar solubility of AgCl is $\mathbf{1.342 \times 10^{-5}\ mol\ dm^{-3}}$ and solubility in g $dm^{-3}$ is $\mathbf{1.925 \times 10^{-3}\ g\ dm^{-3}}$.

## 3.10 Common ion effect

**Q.100. What is common ion effect? Explain with an example.** **[2 Marks]**

**Ans:**

i. Consider a solution of weak acid $CH_3COOH$ and its soluble ionic salt $CH_3COONa$. $CH_3COOH$ is weak acid, dissociates only slightly in solution

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

$CH_3COONa$ being a strong electrolyte dissociates almost completely in solution.

$CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$

ii. Both the acid and the salt produce $CH_3COO^-$ ions in solution. $CH_3COONa$ dissociates completely. Therefore, it provides high concentration of $CH_3COO^-$ ions.

iii. According to Le-Chatelier principle, the addition of $CH_3COO^-$ from $CH_3COONa$ to the solution of $CH_3COOH$, shifts equilibrium of dissociation of $CH_3COOH$ to left. Thus, the reverse reaction is favoured in which $CH_3COO^-$ ions combines with $H^+$ ions to form unionised $CH_3COOH$. Hence, dissociation of $CH_3COOH$ is suppressed due to presence of $CH_3COONa$ containing a common $CH_3COO^-$ ion.

iv. The common ion effect states that the ionization of a weak electrolyte is suppressed in presence of a strong electrolyte containing an ion common to the weak electrolyte.

**Note:** Common ion effect is a special case of Le-Chatelier's principle in which the stress applied to an equilibrium system is an increase in the concentration of one of the product (ions). The effect of this stress is reduced by shifting the equilibrium to the reactant side.

**Q.101. Can you tell?** *(Textbook Page no. 60)*

**How does the ionization of $NH_4OH$ suppressed by addition of $NH_4Cl$ to the solution of $NH_4OH$?** **[2 Marks]**

**Ans:**

i. $NH_4OH$ is a weak electrolyte. It dissociates to a little extent.

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

ii. $NH_4Cl$ is a strong electrolyte, It undergoes complete dissociation.

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

Both $NH_4OH$ and $NH_4Cl$ provide $NH_4^+$ ions. The concentration of $NH_4^+$ ions in the solution increases due to the complete dissociation of $NH_4Cl$.

iii. According to Le-Chatelier's principle, the effect of the stress (the addition of $NH_4^+$ ions from $NH_4Cl$) applied to the ionization equilibrium of $NH_4OH$ is reduced by shifting the equilibrium in the backward direction. Thus, $NH_4^+$ ions combine with $OH^-$ ions to produce unionized $NH_4OH$ molecules.

iv. The ionization of $NH_4OH$ is suppressed due to the presence of $NH_4Cl$ which contains a common $NH_4^+$ ion.

***Q.102. The dissociation of $H_2S$ is suppressed in the presence of HCl. Name the phenomenon. [1 Mark]**

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

**Reading between the lines**

*Both $H_2S$ and HCl produce common ion ($H^+$) on dissociation.*
*The $H^+$ ions combine with $S^{2-}$ ions to produce unionized $H_2S$. Thus, the dissociation of $H_2S$ is suppressed in the presence of HCl.*

***Q.103. Dissociation of HCN is suppressed by the addition of HCl. Explain. [2 Marks]**

**Ans:**

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 combines with $CN^-$ ions to produce unionized HCN. Thus, the dissociation of HCN is suppressed by the addition of HCl.

***Q.104. Solubility of a sparingly soluble salt get affected in presence of a soluble salt having one common ion. Explain. [2 Marks]**

**Ans:**

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.

***Q.105. Sulphides of cation of group II are precipitated in acidic solution ($H_2S$ + HCl) whereas sulphides of cations of group IIIB are precipitated in ammoniacal solution of $H_2S$.**
**Comment on the relative values of solubility product of sulphides of these. [3 Marks]**

**Ans:**

i. 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.

ii. Therefore, for the precipitation of cations of group II only small concentration of sulphide ion is required. This is achieved by passing $H_2S$ gas in presence of strong electrolyte HCl, which has a common ion ($H^+$) with $H_2S$. Due to 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 higher group remain in solution as they require higher concentration of $S^{2-}$ ions for precipitation.

iii. This higher concentration of $S^{2-}$ ions is achieved by using ammoniacal solution of $H_2S$, where the $H^+$ ions from $H_2S$ are removed by $OH^-$ ions in solution thereby increasing the dissociation of $H_2S$.

## Quick Review

➢ **Types of electrolytes:**

**Electrolytes**

- **Strong electrolytes** — **e.g.** HCl, NaOH
- **Weak electrolytes** — **e.g.** $CH_3COOH$

➢ **Various theories of acids and bases:**

| Theory | Acid | Base |
|---|---|---|
| **Arrhenius theory** | A substance that contains hydrogen and produces $H^+$ ions in aqueous solution. | A substance that contains OH group and produces $OH^-$ ions in aqueous solution. |
| **Bronsted-Lowry theory** | Any substance that can donate a proton ($H^+$) i.e., proton donor. | Any substance that can accept a proton i.e., proton acceptor. |
| **Lewis theory** | Any species that can accept a share in an electron pair. | Any species that can donate a share in an electron pair. |

➢ **Classification of acids and bases:**

**Acids and Bases**

Based on extent of dissociation

- **Strong acids** — **e.g.** $HNO_3$
- **Weak acids** — **e.g.** HF
- **Strong bases** — **e.g.** KOH
- **Weak bases** — **e.g.** $Cu(OH)_2$

➢ **pH of solutions:**

| | | |
|---|---|---|
| **Acidic solutions** | $[H^+] > 1.0 \times 10^{-7}$ M | pH < 7.00 |
| **Basic solutions** | $[H^+] < 1.0 \times 10^{-7}$ M | pH > 7.00 |
| **Neutral solutions** | $[H^+] = 1.0 \times 10^{-7}$ M | pH = 7.00 |

➢ **Types of salts:**

**Acidity and basicity of salts**

- **Salts of strong acid and strong base**
  - Solution will be neutral.
  - **e.g.** NaCl, $KNO_3$, $Na_2SO_4$
- **Salts of strong acid and weak base**
  - Solution will be acidic.
  - **e.g.** $NH_4Cl$, $NH_4NO_3$ $(NH_4)_2SO_4$
- **Salts of weak acid and strong base**
  - Solution will be basic.
  - **e.g.** $CH_3COONa$, KCN, $Na_2CO_3$
- **Salts of weak acid and weak base**
  - Solution may be acidic, basic or neutral depending on $K_a$ and $K_b$ values of weak acid and weak base respectively.
  - **e.g.** $CH_3COONH_4$, $NH_4CN$, $(NH_4)_2CO_3$
  - If $K_a > K_b$, solution is acidic. **e.g.** $NH_4F$
  - If $K_a < K_b$, solution is basic. **e.g.** $NH_4CN$
  - If $K_a = K_b$, solution is neutral. **e.g.** $CH_3COONH_4$

➢ **Buffer solutions:**

**Buffer solutions**

A buffer solution resists drastic changes in pH upon the addition of a small amount of either an acid or a base.

**Types**

**Acidic buffer solution**

- A solution containing a weak acid and its salt with a strong base.
  **e.g.**
  $CH_3COOH$ and $CH_3COONa$ in water.
- Henderson-Hasselbalch equation is:

$$pH = pK_a + \log_{10}\frac{[salt]}{[acid]}$$

**Basic buffer solution**

- A solution containing a weak base and its salt with a strong acid.
  **e.g.**
  $NH_4OH$ and $NH_4Cl$ in water.
- Henderson-Hasselbalch equation is:

$$pOH = pK_b + \log_{10}\frac{[salt]}{[base]}$$

**Properties**

- 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.
- The dilution of a buffer solution will not change its pH.
- The pH of a buffer solution does not change with time.

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➢ **Different expressions for solubility product:**

| Type of electrolyte | Example | Equation | $K_{sp}$ expression | Molar solubility |
|---|---|---|---|---|
| AB (1 : 1 type salt) | AgCl | $AgCl \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{Cl^-}$ | $K_{sp} = [Ag^+][Cl^-]$<br>$\mathbf{K_{sp} = S^2}$ | $S = \sqrt{K_{sp}}$ |
| $AB_2$ (1 : 2 type salt) | $PbCl_2$ | $PbCl_2 \rightleftharpoons \underset{S}{Pb^{2+}} + \underset{2S}{2Cl^-}$ | $K_{sp} = [Pb^{2+}][Cl^-]^2$<br>$K_{sp} = [S][2S]^2$<br>$\mathbf{K_{sp} = 4S^3}$ | $S = \sqrt[3]{\frac{K_{sp}}{4}}$ |
| $A_2B$ (2 : 1 type salt) | $Ag_2CrO_4$ | $Ag_2CrO_4 \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{CrO_4^{2-}}$ | $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$<br>$K_{sp} = [2S]^2[S]$<br>$\mathbf{K_{sp} = 4S^3}$ | $S = \sqrt[3]{\frac{K_{sp}}{4}}$ |
| $AB_3$ (1 : 3 type salt) | $AlCl_3$ | $AlCl_3 \rightleftharpoons \underset{S}{Al^{3+}} + \underset{3S}{3Cl^-}$ | $K_{sp} = [Al^{3+}][3Cl^-]$<br>$K_{sp} = [S][3S]^3$<br>$\mathbf{K_{sp} = 27S^4}$ | $S = \sqrt[4]{\frac{K_{sp}}{27}}$ |
| $A_2B_3$ (2 : 3 type salt) | $As_2S_3$ | $As_2S_3 \rightleftharpoons \underset{2S}{2As^{3+}} + \underset{3S}{3S^{2-}}$ | $K_{sp} = [As^{3+}]^2[S^{2-}]^3$<br>$K_{sp} = [2S]^2[3S]^3$<br>$K_{sp} = 4S^2 \times 27S^3$<br>$\mathbf{K_{sp} = 108S^5}$ | $S = \sqrt[5]{\frac{K_{sp}}{108}}$ |

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➢ **Condition for the formation of a precipitate:**

| Condition | Type of solution | Result |
|---|---|---|
| Ionic product = $K_{sp}$ | Saturated solution | No precipitation |
| Ionic product > $K_{sp}$ | Supersaturated solution | Precipitation |
| Ionic product < $K_{sp}$ | Unsaturated solution | No precipitation |

## Important Formulae

1. **Degree of dissociation (α):**

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Total number of moles}}$$

2. **Ostwald's dilution law:**

$$\alpha \propto \frac{1}{\sqrt{C}}$$

**OR**

$$\alpha \propto \sqrt{V}$$

**3. Acid dissociation constant ($K_a$):**

For weak acid HA, $K_a = \frac{[H^+][A^-]}{[HA]}$

$K_a = \alpha^2/V$ and $K_a = \alpha^2 c$

**4. Base dissociation constant ($K_b$):**

For weak base BOH, $K_b = \frac{[B^+][OH^-]}{[BOH]}$

$K_b = \alpha^2/V$ and $K_b = \alpha^2 c$

**5. Ionic product of water ($K_w$):**

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

**6. pH of solution:**

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

**7. pOH of solution:**

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

**8. Relation between pH and pOH:**

pH + pOH = 14

**9. Henderson-Hasselbalch equation:**

Acidic buffer:

$$pH = pK_a + \log_{10}\frac{[salt]}{[acid]}$$

Basic buffer:

$$pOH = pK_b + \log_{10}\frac{[salt]}{[base]}$$

**10. Solubility product ($K_{sp}$):**

$K_{sp} = [B^{y+}]^x [A^{x-}]^y$

**11. Molar solubility, S (mol/L)**

$$= \frac{\text{Solubility in g/L}}{\text{Molar mass in g/mol}}$$

**12. Relation between $K_{sp}$ and S:**

$K_{sp} = x^x y^y S^{x+y}$

## Exercise

### 3.1 Introduction

1. What is ionic equilibrium? **[1 Mark]**

**Ans:** *Refer Q.1. (Definition).*

### 3.2 Types of electrolyte

2. Define strong electrolytes. **[1 Mark]**

**Ans:** *Refer Q.4. (i)*

3. What is degree of dissociation? Give its formula. **[2 Marks]**

**Ans:** *Refer Q.7 and Q.8. (ii)*

### 3.3 Acids and bases

4. Define acids and bases according to the Arrhenius theory. Give suitable examples. **[2 Marks]**

**Ans:** *Refer Q.9.*

5. What are acids and bases according to Bronsted-Lowry theory? Give an example. **[2 Marks]**

**Ans:** *Refer Q.11.*

6. Explain conjugate acid-base pair with a suitable example. **[2 Marks]**

**Ans:** *Refer Q.14.*

7. What are acids and bases according to Lewis theory? Give an example. **[2 Marks]**

**Ans:** *Refer Q.17. (Definitions and any one example)*

8. $AlCl_3$ is a Lewis acid. Explain. **[2 Marks]**

**Ans:** *Refer Q.19. (i)*

### 3.4 Ionization of acids and bases

9. Give two examples of weak bases. **[1 Mark]**

**Ans:** *Refer Q.23. (v)*

10. Give two examples of strong acids. **[1 Mark]**

**Ans:** *Refer Q.24. (i)*

11. Define dissociation constant of a weak acid or weak base. **[1 Mark]**

**Ans:** *Refer Q.26. (v)*

12. The dissociation constant of $NH_4OH$ is $1.8 \times 10^{-5}$. Calculate its degree of dissociation in 0.05 M solution. **[2 Marks]**

**Ans:** 0.01897

13. The dissociation constant of weak monobasic acid is $3.2 \times 10^{-4}$. Calculate its degree of dissociation in 0.02 M solution. **[2 Marks]**

**Ans:** 0.1265

14. A weak monobasic acid is 12% dissociated in 0.05 M solution. What is percent dissociation in 0.1 M solution? **[2 Marks]**

**Ans:** 8.485%

15. Calculate $[H_3O^+]$ in 0.3 mol $dm^{-3}$ solution of acetic acid.
[Given: $K_a$ ($CH_3COOH$) = $1.8 \times 10^{-5}$] **[2 Marks]**

**Ans:** $2.324 \times 10^{-3}$ mol $dm^{-3}$

### 3.5 Autoionization of water

16. Define ionic product of water. **[1 Mark]**

**Ans:** *Refer Q.38. (v)*

17. Derive the expression: $K_w = [H_3O^+][OH^-]$. **[2 Marks]**

**Ans:** *Refer Q.38.*

### 3.6 pH scale

18. Define pH and pOH. **[2 Marks]**
**Ans:** *Refer Q.41. (i) and (ii)*

19. Calculate pH of 0.02 M sulphuric acid. **[2 Marks]**
**Ans:** 1.3979

20. The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3}$ M. What is its pH? **[2 Marks]**
**Ans:** 2.42

21. pH of a solution is 5.68. Calculate the concentration of $H_3O^+$ ion. **[2 Marks]**
**Ans:** $2.089 \times 10^{-6}$ M

22. A weak monobasic acid is 0.05 % dissociated in 0.2 M solution. Calculate the pH of the solution. **[2 Marks]**
**Ans:** 4

23. pH of a weak monobasic acid is 2.52 in its 0.02 M solution. Calculate its dissociation constant. **[3 Marks]**
**Ans:** $4.56 \times 10^{-4}$

### 3.7 Hydrolysis of salts

24. Give four examples of salts derived from strong acid and strong base. **[2 Marks]**
**Ans:** *Refer Q.57. (i)*

25. Explain hydrolysis of a salt of strong acid and strong base. **[2 Marks]**
**Ans:** *Refer Q.59.*

26. Why does aq. $CuSO_4$ solution turn blue litmus red? **[2 Marks] [July 22]**
**Ans:** *Refer Q.61.*

27. To get clear solution of $CuSO_4$, the addition of $H_2SO_4$ would be required. Give reason. **[2 Marks]**
**Ans:** *Refer Q.62.*

### 3.8 Buffer solutions

28. Define acidic buffer solution. **[1 Mark]**
**Ans:** *Refer Q.74. (i)*

29. Give two properties of buffer solution. **[2 Marks]**
**Ans:** *Refer Q.79.*

30. Give two applications of buffer solution. **[2 Marks]**
**Ans:** *Refer Q.82.*

31. Find the pH of buffer solution if it contains 0.06 mol NaF per litre and 0.02 mol HF per litre. [$K_a = 7.2 \times 10^{-4}$ for HF] **[3 Marks]**
**Ans:** 3.62

### 3.9 Solubility product

32. Define solubility product. **[1 Mark]**
**Ans:** *Refer Q.86. (x)*

33. Define molar solubility. **[1 Mark]**
**Ans:** *Refer Q.90. (i)*

34. What is the relationship between molar solubility and solubility product for $Ca_3(PO_4)_2$? **[1 Mark]**
**Ans:** *Refer Q.94. (ii)*

35. A solution is prepared by mixing equal volumes of 0.2 M $MgCl_2$ and 0.5 M $Na_2C_2O_4$ at 293 K. Would $MgC_2O_4$ precipitate out? $K_{sp}$ of $MgC_2O_4$ at 293 K is $8.56 \times 10^{-5}$. **[3 Marks]**
**Ans:** Yes, $MgC_2O_4$ **will precipitate** out from the solution.

36. Solubility product of $BaF_2$ is $1.7 \times 10^{-6}$. Estimate its molar solubility. **[2 Marks]**
**Ans:** $7.518 \times 10^{-3}$ mol dm$^{-3}$

### 3.10 Common ion effect

37. Write a short note on common ion effect. **[2 Marks]**
**Ans:** *Refer Q.100.*

38. Solubility of AgCl decreases by the addition of $AgNO_3$. Explain. **[2 Marks]**
**Ans:** *Refer Q.104.*

## Multiple Choice Questions

**[1 Mark Each]**

*1. The conjugate base of $[Zn(H_2O)_4]^{2+}$ is _____
(A) $[Zn(H_2O)_4]^{2-}$ $NH_3$ (B) $[Zn(H_2O)_3]^{2-}$
(C) $[Zn(H_2O)_3OH]^+$ (D) $[Zn(H_2O)H]^{3+}$

2. Which of the following fluoro compounds is most likely to behave as a Lewis base?
(A) $SiF_4$ (B) $BF_3$
(C) $PF_3$ (D) $CF_4$

3. The value of $[H_3O^+]$ in mol lit$^{-1}$ of 0.001 M acetic acid solution ($K_a = 1.8 \times 10^{-5}$) is _____. **[Mar 22]**
(A) $1.34 \times 10^{-1}$ (B) $1.34 \times 10^{-2}$
(C) $1.34 \times 10^{-3}$ (D) $1.34 \times 10^{-4}$

*4. For pH > 7, the hydronium ion concentration would be _____.
(A) $10^{-7}$ M (B) $< 10^{-7}$ M
(C) $> 10^{-7}$ M (D) $\geq 10^{-7}$ M

5. The pH of $10^{-4}$ M KOH solution will be _____.
(A) 4 (B) 11
(C) 10.5 (D) 10

*6. The pH of $10^{-8}$ M of HCl is _____.
(A) 8 (B) 7
(C) less than 7 (D) greater than 7

7. What is the pH of millimolar solution of ammonium hydroxide which is 20% dissociated?
(A) 3.699 (B) 10.301
(C) 4.691 (D) 9.301

8. Aqueous solution of which of the following will be basic?
(A) $NH_4Cl$ (B) $FeCl_3$
(C) $CuSO_4$ (D) $CH_3COONa$

9. Which of the following salts will give highest pH in water?
(A) KCl (B) NaCl
(C) $Na_2CO_3$ (D) $CuSO_4$

*10. Which of the following solution will have pH value equal to 1.0?
(A) 50 mL of 0.1 M HCl + 50 mL of 0.1 M NaOH
(B) 60 mL of 0.1 M HCl + 40 mL of 0.1 M NaOH
(C) 20 mL of 0.1 M HCl + 80 mL of 0.1 M NaOH
(D) 75 mL of 0.2 M HCl + 25 mL of 0.2 M NaOH

*11. Which of the following is a buffer solution?
(A) $CH_3COONa$ + NaCl in water
(B) $CH_3COOH$ + HCl in water
(C) $CH_3COOH$ + $CH_3COONa$ in water
(D) HCl + $NH_4Cl$ in water

*12. Blood in human body is highly buffered at pH of _____.
(A) 7.4 (B) 7.0
(C) 6.9 (D) 8.1

13. Penicillin preparation are stabilized by addition of _____ as buffer.
(A) sodium citrate
(B) sodium carbonate
(C) sodium benzoate
(D) sodium acetate

14. A buffer solution contains 0.1 M of acetic acid and 0.1 M of sodium acetate. What will be its pH, if $pK_a$ of acetic acid is 4.75?
(A) 4.00 (B) 4.75
(C) 5.00 (D) 5.25

15. What is the solubility product ($K_{sp}$) of $BaSO_4$ in pure water?
[S = molar solubility]
(A) $4\ S^3$ (B) $S^2$
(C) $27\ S^4$ (D) $108\ S^5$

16. What is the solubility product ($K_{sp}$) of calcium phosphate in pure water?
[S = molar solubility]
(A) $108\ S^5$ (B) $72\ S^3$
(C) $6\ S^5$ (D) $121\ S^2$

*17. The solubility product of a sparingly soluble salt AX is $5.2 \times 10^{-13}$. Its solubility in mol $dm^{-3}$ is _____.
(A) $7.2 \times 10^{-7}$ (B) $1.35 \times 10^{-4}$
(C) $7.2 \times 10^{-8}$ (D) $13.5 \times 10^{-8}$

18. Concentration of the $Ag^+$ ions in a saturated solution of $Ag_2C_2O_4$ is $2.2 \times 10^{-4}$ mol $L^{-1}$. Solubility product of $Ag_2C_2O_4$ is _____.
(A) $2.42 \times 10^{-8}$ (B) $2.66 \times 10^{-12}$
(C) $4.25 \times 10^{-11}$ (D) $5.3 \times 10^{-12}$

19. Solubility of AgCl is least in _____.
(A) 0.1 M $BaCl_2$ (B) 0.1 M $AlCl_3$
(C) 0.1 M NaCl (D) pure water

## Answers to Multiple Choice Questions

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. | (C) | 2. | (C) | 3. | (D) | 4. | (B) |
| 5. | (D) | 6. | (C) | 7. | (B) | 8. | (D) |
| 9. | (C) | 10. | (D) | 11. | (C) | 12. | (A) |
| 13. | (A) | 14. | (B) | 15. | (B) | 16. | (A) |
| 17. | (A) | 18. | (D) | 19. | (B) | | |

## Hints to Multiple Choice Questions

3. $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
$(1-\alpha)c$ $\alpha c$ $\alpha c$

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.001}} = 0.134$$

$[H_3O^+] = \alpha \times c = 0.134 \times 0.001$
$= 1.34 \times 10^{-4}$ mol $L^{-1}$

6. $10^{-8}$ M indicates a very dilute solution.
Thus, $H^+$ of water cannot be ignored.
But dissociation of water is suppressed due to common ion effect.
$\therefore$ $[H^+] \neq 10^{-7}$ but less than $10^{-7}$.

$H_2O \rightleftharpoons H^+ + OH^-$
$(10^{-8} + \alpha)$ $\alpha$

$K_w = (10^{-8} + \alpha)\ \alpha$
$\therefore$ $\alpha^2 + \alpha \times 10^{-8} - 10^{-14} = 0$
Solving above quadratic equation, we get
$\alpha = 0.95 \times 10^{-7}$
$\therefore$ $[H^+] = 10^{-8} + 0.95 \times 10^{-7} = 1.05 \times 10^{-7}$ M
$\therefore$ pH = 6.9788
i.e., pH is less than 7.

7. $c = 1\ mM = 10^{-3}\ M$
For a weak base,
$[OH^-] = c \times \alpha$
$[OH^-] = 10^{-3} \times \frac{20}{100}$
$[OH^-] = 2 \times 10^{-4}\ M$
$pOH = -\log_{10}[OH^-] = -\log_{10}(2 \times 10^{-4})$
$pOH = 3.699$
$pH + pOH = 14$
$\therefore$ $pH = 14 - pOH = 14 - 3.699$
$pH = 10.301$

10. (A) $[H^+] = [OH^-] \Rightarrow$ Neutral solution (pH = **7**)
(B) $H^+ = 6 \times 10^{-3}$ mol, $OH^- = 4 \times 10^{-3}$ mol
Excess $H^+ = 2 \times 10^{-3}$ mol
Total volume = 0.06 + 0.04 = 0.1 L
$\therefore$ $[H^+] = \frac{2 \times 10^{-3}}{0.1} = 2 \times 10^{-2}\ M$
$\therefore$ $pH = -\log_{10}[H^+] = -\log_{10}(2 \times 10^{-2})$
$= \mathbf{1.7}$
(C) $H^+ = 2 \times 10^{-3}$ mol, $OH^- = 8 \times 10^{-3}$ mol
Excess $OH^- = 4 \times 10^{-3}$ mol
$\therefore$ pH **> 7**
(D) $H^+ = 0.015$ mol, $OH^- = 0.005$ mol
Excess $H^+ = 0.01$ mol
Total volume = 0.075 + 0.025 = 0.1 L
$\therefore$ $[H^+] = \frac{0.01}{0.1} = 0.1\ M$
$\therefore$ $pH = -\log_{10}[H^+] = -\log_{10}(0.1)$
$= -\log_{10}(10^{-1}) = \mathbf{1.0}$

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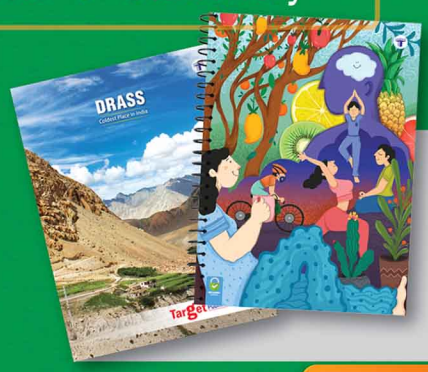


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