Q.12 Why do the equilibrium constant value has its units for some of the reversible reactions but has no units for some other reactions?

Ans. i. If number of moles of reactants and products are equal, then K_c has no units.

$$\underset{1\ mol}{H_{2(g)}} + \underset{1\ mol}{I_{2(g)}} \rightleftharpoons \underset{2\ mol}{2HI}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(mol\ dm^{-3})^2}{(mol\ dm^{-3}.mol\ dm^{-3})} = \text{no units}$$

ii. If the number of moles of reactants and products are not equal.

$$N_{2(g)} + \underset{4\ mol}{3H_{2(g)}} \rightleftharpoons \underset{2\ mol}{2NH_{3(g)}}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}][mol\ dm^{-3}]^3} = mol^{-2}\ dm^{+6}$$

SELF-ASSESSMENT Chapter # 08

Total Mark: 3

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) Consider the equilibrium $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. If the concentration of $H_2O_{(g)}$ is increased, the concentrations of $H_{2(g)}$ and $O_{2(g)}$ will:

A. Increase. B. Decrease. C. Remain the same. D. Change irregularly

(ii) For which system, does the equilibrium constant, K_C has units of (concentration)^{1}?

A. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ B. $H_2 + I_2 \rightleftharpoons 2HI$
C. $2NO_2 \rightleftharpoons N_2O_4$ D. $2HF \rightleftharpoons H_2 + F_2$

(iii) The expression for Kc of the reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is:

A. $[NH_3]^2 / [N_2] + [H_2]^3$ B. $[N_2][H_2]^3 / [NH_3]^2$ C. $[NH_3] / [N_2][H_2]^3$ D. $[NH_3]^2 / [N_2][H_2]^3$

(iv) If the temperature of an exothermic reaction increases, then K_c:

A. Increases B. Decreases C. Remains same D. Becomes zero

(v) For a saturated solution of a salt in water, a dynamic equilibrium is between:

A. The dissolved ions and the undissolved solid salt
B. The solute and the solvent molecules
C. The solid salt and the water molecules
D. The hydrated ions and the water molecules in the bulk solvent

(vi) Which of the following condition will not change the equilibrium position?

A. Change in pressure B. Change in concentration
C. Adding catalyst D. Change in temperature

Q.2 Write short answers of the following questions. (2 × 8 = 1

(i) The dynamic equilibrium exists between water and its vapour at 100°C. Justify the statement.
(ii) Why ice at 0°C can be melted by applying pressure without supply of heat from outside?
(iii) Differentiate between macroscopic and microscopic changes with examples.
(iv) Mention the characteristics of chemical equilibrium.
(v) Derive the Kc expression for the reaction: $2SO_2 + O_2 \rightleftharpoons 2SO_3$.
(vi) Apply Le Chatelier's Principle when pressure is increased in a gaseous system.
(vii) If the reaction is endothermic, how does increase in temperature affect Kc?
(viii) Define dynamic equilibrium between two physical states with an example.

Q.3 Extensive Questions. (2 × 4 =

(a) By using Le Chatelier's Principle, explain how concentration, pressure, and temperature changes affect equilibrium
(b) Describe the industrial applications of equilibrium using Haber's process.

Chapter 09 ACID-BASE CHEMISTRY

Student Learning Outcomes

After studying this chapter, students will be able to:

- Define conjugate acid base pairs. **(Understanding)**
- Identify conjugate acid base pairs in reactions. **(Understanding)**
- Distinguish that Lewis acids accept lone pair, and Lewis bases donate lone pair to make a coordinate covalent bond. **(Understanding)**
- Define mathematically the terms K_w, pH, K_a and pK_a and use them in calculations. (K_b and the equation $K_w = K_a \times K_b$ will not be tested). **(Application)**
- Calculate $H^+_{(aq)}$ and pH values for: **(Application)**
- (a) strong acids (b) strong alkalis (c) weak acids (d) weak alkalies.
- Calculate the $[H_3O^+]$ given the K_a and molar concentration of weak acid. **(Application)**
- Apply the concept of the common ion effect to describe why the solubility of a substance changes when it is dissolved in a solution containing a common ion. **(Application)**
- Calculate the pH of buffer solutions in given appropriate data. **(Application)**
- Construct an expression for K_{sp}. **(Application)**
- Demonstrate the ability to comprehend and effectively apply the concept of solubility product K_{sp}. **(Application)**
- Perform calculations using K_{sp} values and concentration of a common ion. **(Application)**
- Calculate concentrations of ions of slightly soluble salts. **(Application)**
- Calculate K_{sp} from concentrations and vice versa. **(Application)**
- Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. **(Understanding)**
- Apply the concept of conjugate acid and conjugate base on salt hydrolysis. **(Application)**
- Select suitable indicators for acid-alkali titration, given appropriate data (pKa_a values will not be used). **(Understanding)**
- Perform acid-base titration to calculate molarity and strength of given sample solutions. **(Application)**

➲ Differences between Common Acids and Bases

Sr.No.	Acids	Bases
1.	Acids were first recognized as having sour taste.	Bases were first recognized as having bitter taste.
2.	Acids change the litmus from blue to red.	Bases change the litmus from red to blue.
3.	Acids change the indicator "Phenophthalein" from pink to colourless.	Bases change the indicator "Phenophthalein" from colourless to pink.
	Note: Acids and bases neutralize each other and during neutralization, acids and bases react with each other to produce ionic substances called salts.	

Interesting Information!

Acidity in our stomachs is due to excess HCL. It is treated by taking mild bases such as, baking soda.

BRONSTED-LOWRY CONCEPT

(Exercise L.Q.3)

Q. Describe the Bronsted-Lowry theory of acids and bases. Provide examples of conjugate acid-base pairs and explain clearly their relationship.

The Danish chemist J.N. Bronsted and the English chemist T.M. Lowry in 1923 independently expanded the Arrhenius theory of acid-base.

- **Bronsted-Lowry Acid:**
  According to the Bronsted-Lowry concept, **"an acid is the species donating a proton in a proton-transfer reaction".**
- **Bronsted-Lowry Base:**
  According to Bronsted-Lowry concept, **"a base is the species accepting the proton".**

Example:

When HCℓ dissolves in Water:

When HCℓ dissolves in water, an H^+ ion (a proton) is transferred from HCℓ to water, where it becomes attached to a lone pair of electrons on the O atom and forms H_3O^+. In fact, HCℓ (the acid) has donated the H^+ and H_2O (the base) has accepted it.

$$\underset{\text{Proton donor}}{HC\ell_{(g)}} + \underset{\text{Proton acceptor}}{H_2O_{(\ell)}} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+} + \underset{\text{Conjugate base}}{C\ell_{(aq)}}$$

The limitations of Arrhenius theory is that it describes the reaction of an acid and base only in the aqueous medium. There are many reactions that occur in solvents other than water or in the absence of any solvent. Bronsted-Lowry pointed out that acid-base reactions can be seen as proton transfer reactions and that acids and bases can be defined in terms of this proton (H^+) transfer.

Note:
- Chloride ion ($C\ell^-$) is indeed the conjugate base of hydrochloric acid (HCℓ) because it is the species that remains after the acid (HCℓ) has lost its proton.

- **Conjugate Acid:**
  "A species formed after a Bronsted base accepts a proton from the acid is called the conjugate acid". The hydronium ion (H_3O^+) is the conjugate acid of water.
- **Conjugate Base:**
  "A species formed when an acid donates a proton to a base is called the conjugate base". $HC\ell - C\ell^-$ and $H_2O - H_3O^+$ are conjugate acid-base pairs.

- A Bronsted-Lowry acid is a proton donor.
- A Bronsted-Lowry base is a proton acceptor.

Example:

When NH₃ dissolves in Water:

When ammonia dissolves in water, proton transfer also occurs. An H^+ from H_2O attaches to the N atom's lone pair and NH_4^+ and OH^- are formed. With fewer H^+, the water molecule becomes OH^- ion:

$$\underset{\text{Base}}{NH_{3(g)}} + \underset{\text{Acid}}{H_2O_{(\ell)}} \rightleftharpoons \underset{\text{Conjugate base}}{OH^-_{(aq)}} + \underset{\text{Conjugate base}}{NH^+_{4(aq)}}$$

In this case, H_2O (the acid) has donated the proton and NH_3 (the base) has accepted it. $NH_3 - NH_4^+$ and $H_2O - OH^-$ are conjugate acid-base pair.

Rock Your Mind!

1. In the reaction between HCℓ and water, which species acts as the conjugate base?
A) H_3O^+ B) $C\ell^-$
C) HCℓ D) H_2O

Rock Your Mind!

2. Conjugate acid-base pair differs by:
A) An electron pair B) A neutron
C) An electron D) A proton

Amphoteric Substance: An amphoteric substance is a species that can act as either an acid and a base (it can lose or gain a proton), depending on the other reactant.

H₂O is Amphoteric in Nature: H_2O is amphoteric in nature because it acts as a base in one case and as an acid in the other (as shown in the above examples).

$$\underset{}{\overset{\text{base}}{H_2O}} + \underset{\text{acid}}{H_2O} \longrightarrow \overset{\text{Conjugate acid}}{H_3O^+} + \underset{\text{Conjugate base}}{OH}$$

Application of Bronsted-Lowry Concept: The Bronsted-Lowry theory can be applied to acids in solvents other than water or even solventless reactions. The reaction between gaseous ammonia and HCℓ gives solid $NH_4C\ell$.

$$HC\ell_{(g)} + NH_{3(g)} \longrightarrow NH_4C\ell_{(s)}$$

HCℓ is an acid because in the reaction it donates a proton to the NH_3 molecule. The NH_3 acts as a base, even though hydroxide ion OH^- is not present, and accepts a proton from the HCℓ molecule. Similarly,

$$\overset{\text{acid}}{HC\ell} + \underset{\text{base}}{H_2O} \longrightarrow \overset{\text{conjugate base}}{H_3O^+} + \underset{\text{conjugate acid}}{C\ell}$$

Table: Conjugate Acid-Base Pairs of Common Species

Acid		Base		Conjugate Acid		Conjugate Base
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-

LEWIS CONCEPT OF ACIDS AND BASES

(Exercise L.Q.4)

Q. Define the Lewis theory of acids and bases. How does this theory differ from the Bronsted-Lowry theory? Give examples of Lewis acids and bases that do not involve proton transfer.

In 1923, G.N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

Rock Your Mind!

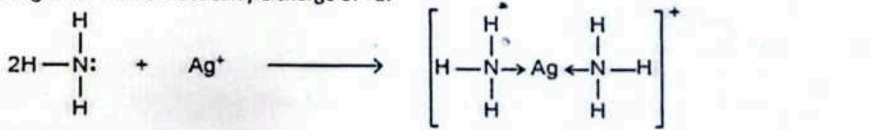
3. Why is BF₃ considered a Lewis acid?

- **Lewis Acid:**
  "A Lewis acid is any species (molecule or ion) that can accept a pair of electrons".
- **Lewis Base:**
  "A Lewis base is any species (molecule or ion) that can donate a pair of electrons".

A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid.

Example 1:

In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a positively charged silver ion, the Lewis acid. The sum of charges on the left side is +1, so the acid-base adduct on the right hand side must carry a charge of +1:



Lewis base **Lewis acid** **Acid base adduct**

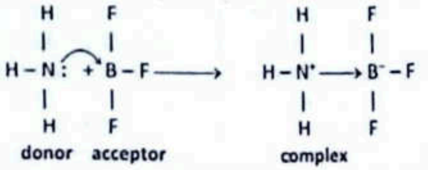
Example 2:

The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Boron atom has an incomplete octet. So it can behave as an electron pair acceptor. BF_3 is a very good Lewis acid and reacts with many Lewis bases e.g. a fluoride ion which is the Lewis base in this reaction, donates one of its lone pairs:

Lewis base **Lewis acid** **Acid base adduct**

The negative charge on the adduct is the sum of charges on the left hand side of the equation is −1, the sum of charges on the right hand side must also be −1.

Example 3: In the following reaction NH_3 has a lone pair on N-atom so it is a Lewis base (electron pair donor) and boron accepts the lone pair and is a Lewis acid.



$$H-N: + B-F \longrightarrow H-N^{+} \longrightarrow B^{-}-F$$

☑ QUICK CHECK 9.1

a) Identify the conjugate acid-base pairs in the following reactions:

i. $HCN_{(g)} + H_2O_{(\ell)} \rightleftharpoons H_3O^{+}_{(aq)} + CN^{-}_{(aq)}$

Also write down the balanced chemical equation for the reaction and explain.

Ans. The conjugate acid-base pairs are:

1. HCN (acid) and CN^- (its conjugate base)
   HCN donates a proton (H^+) to become CN^-.
2. H_2O (base) and H_3O^+ (its conjugate acid)
   H_2O accepts a proton (H^+) to become H_3O^+.

Summary of Pairs:

Bronsted Acid	Conjugate Base
HCN	CN^-
H_2O	H_3O^+

Important Note

- Acid → Conjugate base by losing H^+.
- Base → Conjugate acid by gaining H^+.

- **ii.** $CH_3COOH_{(\ell)} + H_2O_{(\ell)} \rightleftharpoons H_3O^{+}_{(aq)} + CH_3COO^{-}_{(aq)}$

Ans. Pair 1: CH_3COOH (Acid) and CH_3COO^- (Conjugate Base)

- **CH_3COOH** donates a proton (H^+) to become **CH_3COO^-**.
  - **Acid:** CH_3COOH (acetic acid).
  - **Conjugate Base:** CH_3COO^- (acetate ion).

Pair 2: H_2O (Base) and H_3O^+ (Conjugate Acid)

- **H_2O** accepts a proton (H^+) to become **H_3O^+**.
  - **Base:** H_2O (water).
  - **Conjugate Acid:** H_3O^+ (hydronium ion).

iii. $H_2S_{(g)} + H_2O_{(\ell)} \rightleftharpoons H_3O^{+}_{(aq)} + HS^{-}_{(aq)}$

Ans. Conjugate Acid-Base Pairs:

- **H_2S (acid) / HS^- (Conjugate base):** H_2S donates a proton (H^+) to become HS^-. (Acid: Proton (H^+) donor.)
- **H_2O (base) / H_3O^+ (Conjugate acid):** H_2O accepts a proton (H^+) to become H_3O^+. (Base: Proton (H^+) acceptor.)
- Pairs differ by **one proton (H^+)**.

Note: H_3O^+ is the strongest acid here; HS^- is the weakest base.

iv. $HC\ell_{(g)} + HCO^{-}_{3(aq)} \rightleftharpoons H_2CO_{3(aq)} + C\ell^{-}_{(aq)}$

Ans. Conjugate Acid-Base Pairs:

1. $HC\ell/C\ell^-$

- **$HC\ell$** (acid) donates a proton (H^+) to become **$C\ell^-$** (its conjugate base).

2. HCO_3^-/H_2CO_3

- **HCO_3^-** (base) accepts a proton (H^+) to become **H_2CO_3** (its conjugate acid).

Summary Table:

Acid	Conjugate Base
$HC\ell$	$C\ell^-$
H_2CO_3	HCO_3^-

b) Identify the Lewis acid and Lewis base in the reaction between:

i. **SO_3 and O^{2-}**

Ans. Balanced Chemical Equation:

$SO_3 + O^{2-} \longrightarrow SO_4^{2-}$

Lewis Acid-Base Identification:

1. **Lewis Acid: SO_3**
   - **Reason:** SO_3 **accepts an electron pair** from O^{2-} (its sulfur atom has an incomplete octet and is electron-deficient).
2. **Lewis Base: O^{2-}**
   - **Reason:** O^{2-} **donates an electron pair** to SO_3 (it has lone pairs available for bonding).

Mechanism Explanation:

1. **SO_3** (electron-deficient due to polar S=O bonds) acts as the **electron-pair acceptor (Lewis acid)**.
2. **O^{2-}** (a negatively charged ion with lone pairs) acts as the **electron-pair donor (Lewis base)**.
3. The O^{2-} attacks the sulphur in SO_3, forming a **coordinate covalent bond** and creating **SO_4^{2-}** (sulfate).

- **SO_3** is a classic Lewis acid (e.g., in sulfuric acid production: $SO_3 + H_2O \longrightarrow H_2SO_4$).
- **O^{2-}** is a strong Lewis base (common in oxide reactions).

ii. **$HC\ell$ and H_2O**

Ans. Balanced Equation:

$HC\ell_{(g)} + H_2O_{(\ell)} \longrightarrow H_3O^{+}_{(aq)} + C\ell^{-}_{(aq)}$

Lewis Acid-Base Identification:

1. **Lewis Acid: H^+ (from $HC\ell$)**
   - **Reason:** Accepts an electron pair from H_2O to form H_3O^+.
2. **Lewis Base: H_2O**
   - **Reason:** Donates an electron pair to H^+ to form a coordinate covalent bond in H_3O^+.

Explanation:

- $HC\ell$ dissociates into **H^+** (electron-pair acceptor, Lewis acid) and **$C\ell^-$**.
- H_2O (with lone pairs on oxygen) acts as the **electron-pair donor (Lewis base)**, forming hydronium (H_3O^+).

iii. **BF_3 and NH_3**

Ans. Balanced Chemical Equation:

$BF_3 + NH_3 \longrightarrow H_3N-BF_3$

Lewis Acid and Base Identification:

- **Lewis Acid: BF_3** (electron pair acceptor).
  - Boron in BF_3 has an **empty 2p orbital**, making it electron-deficient.
- **Lewis Base: NH_3** (electron pair donor).
  - Nitrogen in NH_3 has a **lone pair** it can donate.

Mechanism:

1. NH_3 donates its lone pair to the empty orbital of BF_3.
2. A **dative covalent bond** (coordinate bond) forms between N and B.

Key Points:

- **BF_3** is a classic Lewis acid (no protons involved!).
- **NH_3** is a Lewis base due to its lone pair.
- The product **(H_3N-BF_3)** is a stable adduct.

IONIC PRODUCT OF WATER

- Pure water is a poor conductor of electricity but its conductance is measurable.
- Water undergoes self-ionization reversibly as follows,

Rack Your Mind!

4. Why is the concentration of water considered constant in the K_w expression?

Net Reaction:

$$H_2O_{(\ell)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$H_2O_{(\ell)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for this reaction can be written as follows:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} = 1.8\times10^{-16}\ \text{mol dm}^{-3}$$

- The concentration of H_2O i.e. $[H_2O]$ in pure water may be calculated to be 1000 g dm^{-3} divided by 18 g mol^{-1} giving 55.5 moles dm^{-3} i.e. $\frac{1000\ \text{gdm}^{-3}}{18\ \text{gmol}^{-1}} = 55.5\ \text{mol dm}^{-3}$
- As water is present in very large excess and very few of its molecules undergo ionization, so its concentration remains effectively constant.
- Constant concentration of water is taken on L.H.S. and multiplied with K_c to get another constant called K_w.

$$K_c[H_2O] = [H^+][OH^-]$$

or

$$= 1.8\times10^{-16}\times55.5 = 1.01\times10^{-14} = [H^+][OH^-]$$

This 1.01×10^{-14} is called K_w of water at 25°C.

$$K_c[H_2O] = [H^+][OH^-]$$

As $K_c[H_2O] = K_w$ So, $K_w = [H^+][OH^-] = 10^{-14}$ at 25°C.

- K_w is called ionic product of water or dissociation constant of water.

Table: K_w at various temperature.

Temp. (°C)	Value of K_w
0	0.11×10^{-14}
10	0.30×10^{-14}
25	1.0×10^{-14}
40	3.00×10^{-14}
100	7.5×10^{-14}

➤ K_w of H_2O Increases with Increase of Temperature:

- The value of K_w increases almost 75 times when temperature is increased from 0°C to 100°C.

For neutral water

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

Or

$$[H^+][H^+] = 10^{-14}$$

$$[H^+]^2 = 10^{-14}\ (\text{at } 25^\circ C)$$

$$[H^+] = 10^{-7}\ \text{moldm}^{-3}$$

And

$$[OH^-] = 10^{-7}\ \text{moldm}^{-3}$$

The effect of temperature on K_w is shown in Table.

- Whenever some quantity of acid or base is added to water, then K_w remains the same, but $[H^+]$ and $[OH^-]$ are no more equal.

In case of addition of small amount of acid.

$$[H^+] > [OH^-]$$

While in the case of addition of few drops of a base.

$$[OH^-] > [H^+]$$

- During both of these additions, the values of K_w will remain the same, i.e. 10^{-14} at 25°C.

---

pH AND pOH

Rack Your Mind!

5. If the pH of a solution is 3, then its $[H^+]$ is:

A) 10^{-3} mol dm^{-3} B) 10^{-1} mol dm^{-3}
C) 10^{3} mol dm^{-3} D) 3 mol dm^{-3}

Interesting Information!

Solutions of negative pH and having values more than 14 are also known.

In all the aqueous solutions, the concentration of H^+ and OH^- are too low to be conveniently expressed and used in calculations.

In 1909, Sorenson, a Danish biochemist, introduced the term pH and pOH. So, the scales of pH and pOH were developed.

➤ **pH:**
"The negative logarithm of hydrogen ion concentration in the solution is called pH."

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

➤ **pOH:**
"The negative logarithm of hydroxide ion concentration in the solution is called pOH."

$$pOH = -\log[OH^-]$$

For neutral water, $pH = -\log[10^{-7}] = 7$

$$pOH = -\log[10^{-7}] = 7$$

Also, $pH + pOH = 14$

The value of pH normally varies between 0 → 14 at 25°C.

The pH values of some familiar aqueous solutions are shown in Figure. This table can help you to understand the acidic or basic nature of commonly used solutions.

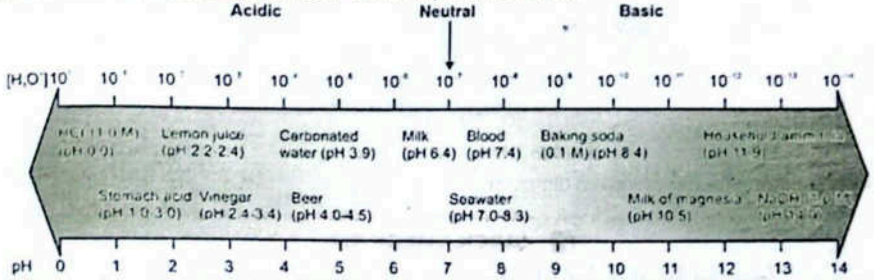


Figure: pH Values of some common substances

Sample Problem 9.1

In a solution, the pH is 9.2. Determine the ionic product of water K_w at 25°C.

Solution:

Calculate the pOH from the pH:

$$pOH = 14 - pH$$

$$pOH = 14 - 9.2$$

$$pOH = 4.8$$

Find the concentration of H^+ and OH^-,
Taking antilog of pH and pOH

$$\text{antilog } pH = \text{antilog}$$

$$[OH^-] = 10 - pH$$

$$[H^+] = 10^{-9.2}$$

$$[OH^-] \approx 6.3\times10^{-10}M$$

Similarly, antilog pOH = antilog (4.8)

$$[OH^-] = 10 - pOH$$

$$[OH^-] = 10^{-4.8}$$

$$[OH^-] \approx 1.6\times10^{-5}M$$

Sample Problem 9.2

The ionic product of water at a certain temperature is $K_w = 1.0\times10^{-14}$ at 25°C. If the concentration of H^+ ions in a solution is 1.0×10^{-7} M, calculate the concentration of OH^- ions, the pH and pOH of the solution.

Solution:

Use the expression for K_w:

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

Substitute the known values of K_w and the concentration of H^+:

$$1.0\times10^{-14} = (1.0\times10^{-7})[OH^-]$$

Solve for the concentration of OH^-

$$[OH^-] = \frac{1.0\times10^{-14}}{1.0\times10^{-7}} = 1.0\times10^{-14}$$

Calculate the pH:

$$\begin{aligned} pH &= -\log[H^+] \\ &= -\log(1.0\times10^{-7}) = 7 \end{aligned}$$

Calculate the pOH:

$$\begin{aligned} pOH &= -\log[H^-] \\ &= -\log(1.0\times10^{-7}) \\ & \boxed{pOH = 7} \end{aligned}$$

Calculate K_w

$$\begin{aligned} K_w &= [H^+][OH^-] \\ K_w &= (6.3\times10^{-10})(1.6\times10^{-5}) \\ K_w &= 1.008\times10^{-14} \end{aligned}$$

This is the ionic product of water at a given temperature

☑ QUICK CHECK 9.2

a) A solution is prepared by mixing equal volumes of two solutions: one with a pH of 4.0 and another with a pH of 10.0. Calculate the K_w for this mixture at 25°C.

Ans. Given:

- **Solution A:** pH = 4.0 → $[H^+] = 10^{-4}$ M
- **Solution B:** pH = 10.0 → $[OH^-] = 10^{-4}$ M (since pH 10 ⇒ pOH 4).

Step 1: Mix Equal Volumes

- $[H^+]$ from A and $[OH^-]$ from B neutralize each other:

$$H^+ + OH^- \longrightarrow H_2O$$

- **Result:** $[H^+] = [OH^-] = 10^{-4}$ M cancel out, leaving neutral water (pH 7).

Step 2: Final pH

- The mixture is neutral (pH = 7.0) because the H^+ and OH^- concentrations were equal and fully reacted.

Note on K_w:

- $K_w = [H^+][OH^-] = 1.0\times10^{-14}$ (constant at 25°C) for all aqueous solutions, including this mixture.

Final Answer:

The mixture has:

- pH = 7.0 (neutral).
- $K_w = 1.0\times10^{-14}$ (at 25°C).

b) At a specific temperature, the ionic product of water K_w is 1.0×10^{-14}. If the concentration of OH^- ions in a solution is 2.5×10^{-8} M. Calculate the concentration of H^+ ions and the pH of the solution.

Ans. Given:

$$\begin{aligned} K_w &= 1.0\times10^{-14} \\ [OH^-] &= 2.5\times10^{-8}\,M \\ K_w &= [H^+][OH^-] \\ [H^+] &= \frac{K_w}{[OH^-]} = \frac{1.0\times10^{-14}}{2.5\times10^{-8}} = 4.0\times10^{-7}\,M \end{aligned}$$

Calculation of pH

$$\begin{aligned} pH &= -\log[H^+] = -\log(4.0\times10^{-7}) \\ pH &= 6.40 \text{ (since } \log(4.0) \approx 0.60 \text{ and } \log(10^{-7}) = -7) \end{aligned}$$

Final Answer:

$$\begin{aligned} [H^+] &= 4.0\times10^{-7}\,M \\ pH &= 6.40 \end{aligned}$$

c) Copper-plate etching solutions is prepared by diluting concentrated HNO_3 to 0.30 M HNO_3. Calculate $[H^+]$, pH, $[OH^-]$ and pOH of this solutions at 25°C.

Ans. Given:

- **HNO_3 concentration:** 0.30 M (a strong acid, fully dissociates).
- **At 25°C:** $K_w = 1.0\times10^{-14}$.

Since HNO_3 is a strong acid:

$$\begin{aligned} [H^+] &= 0.30\,M \\ pH &= -\log[H^+] = -\log(0.30) \approx 0.52 \end{aligned}$$

As

$$\begin{aligned} pH + pOH &= 14 \\ pOH &= 14 - pH = 14 - 0.523 = 13.48 \end{aligned}$$

Final Results:

$$\begin{aligned} pOH &= -\log[OH^-] \\ [H^+] &= 0.30\,M \\ pH &= 0.52 \\ [OH^-] &= 3.3\times10^{-14}\,M \\ pOH &= 13.48 \\ pH + pOH &= 14 \end{aligned}$$

IONIZATION CONSTANTS OF ACIDS (K_a)

Acids and bases, when dissolved in water, may or may not be completely dissociated. Many acids are weak electrolytes and ionize to an extent which is much less than 100 %. The value of K_a called the dissociation constant of an acid, is the quantitative measure of the strength of the acid.

> **Mathematical Derivation of K_a**

Suppose we have an acid HA dissolved in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

K_c for the reversible reaction will be written as follows:

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Let $K_c[H_2O] = K_a$

Hence

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rock Your Mind!

6. What is K_a in acid-base chemistry?

This equation can be used to calculate K_a for any acidic solution if we know the pH or $[H^+]$ of that solution and the initial concentration of the dissolved acid [HA]. This can also be used to calculate the equilibrium concentration of H_3O^+ and A^- produced if we know the initial concentration of acid HA and its K_a value.

➢ K_a and Strength of Acids:

When $K_a < 10^{-3}$ acid is weak.

$K_a = 1$ to 10^{-3} acid is moderately strong.

$K_a > 1$ acid is strong.

The values of K_a for some acids are given in Table.

Table: The values of K_a for some acids

Acid	Dissociation	K_a	Relative strength
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	very large (10^9)	Very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	very large (10^3)	Very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large (10^2)	Very strong
HSO_4^-	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.3×10^{-2}	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-5}	Weak
CH_3COOH	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.85×10^{-5}	Weak
H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	4.4×10^{-7}	Weak
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	Weak
NH_4^+	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	Weak
HCO_3^-	$HCO_3 \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-11}	Weak
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-16}	Very weak

⮚ Calculating H_3O^+ ions from K_a

The weak acids do not completely dissociate in water. Therefore, the concentration of hydronium ions is not equal to the initial concentration of the acid. So, the equilibrium expression is used to calculate the H_3O^+ concentration.

For a weak acid HA, the dissociation in water can be represented as:

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

In water, H^+ combines with water to form H_3O^+:

$$H^+_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)}$$

So, the equilibrium equation in terms of $H_3O^+_{(aq)}$ is:

$$HA_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Let the initial concentration of the weak acid HA be C mol dm^{-3}.

At equilibrium:

$$[H_3O^+] = x; [A^-] = x \text{ and } [HA] = C - x$$

The expression for the acid dissociation constant (K_a) is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Substitute the equilibrium concentrations into this expression:

$$K_a = \frac{x.x}{C-x} = \frac{x^2}{C-x}$$

For weak acids, x is usually very small compared to C, so $C - x \approx C$. Therefore, the expression simplifies to:

$$K_a = \frac{x^2}{C}$$

Taking the square root of both sides:

$$x = \sqrt{K_a \times C}$$

Thus, the concentration of H_3O^+ is given by:

$$x = \sqrt{K_a \times C}$$

Sample Problem 9.3

Calculate the concentration of $[H_3O^+]$ in a 0.1 M (mol dm^{-3}) solution of acetic acid $[CH_3COOH]$, given that the acid dissociation constant K_a is 1.8×10^{-5}.

Solution:

$$[H_3O^+] = \sqrt{K_a \times C}$$

$$[H_3O^+] = \sqrt{1.8\times10^{-5}\times0.1}$$

$$[H_3O^+] = \sqrt{0.18\times10^{-4}}$$

$$[H_3O^+] = 1.34\times10^{-3} M(\text{mol dm}^{-3})$$

The concentration $[H_3O^+]$ in the solution is approximately **1.34×10^{-3} mol dm^{-3}**.

☑ QUICK CHECK 9.3

a) The pH of a 0.10 M solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

Ans. Given:

- Concentration of HCOOH ([HCOOH]): 0.10 M
- pH of the solution: 2.38
- Temperature: 25°C

Step 1: Calculate $[H^+]$ from pH

$$[H^+] = 10^{-pH} = 10^{-2.38} = 4.17\times10^{-3}\ M$$

Step 2: Set Up the Equilibrium Expression

Formic acid dissociates as:

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

At equilibrium:

- $[H^+] = [HCOO^-] = 4.17\times10^{-3}\ M$
- $[HCOOH] = 0.10 - 4.17\times10^{-3} = 0.0958\ M$

Step 3: Calculate Ka

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{(4.17\times10^{-3})^2}{0.0958} = 1.81\times10^{-4}$$

Final Answer:

$$K_a = 1.81\times10^{-4}$$

b) Calculate the concentration of $[H_3O^+]$ in a 0.1 M solution of nitrous acid $[HNO_2]$, given that the acid dissociation constant K_a is 4×10^{-4}.

Ans. **Step 1: Write the Dissociation Equation and K_a Expression**

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = 4\times10^{-4}$$

Step 2: Define Equilibrium Concentrations

Let $x = [H^+] = [NO_2^-]$ at equilibrium.

Since **HNO_2** is a weak acid, its dissociation is small, so:

$$[HNO_2] = 0.1 - x \approx 0.1\ M \text{ (assuming } x \ll 0.1)$$

Step 3: Substitute into K_a and Solve for x

$$K_a = \frac{x \cdot x}{0.1} = 4 \times 10^{-4}$$

$$x^2 = 4 \times 10^{-5}$$

$$x = \sqrt{4 \times 10^{-5}} = 2 \times 10^{-2.5} \approx 6.32 \times 10^{-3} M$$

$$[H_3O^+] = 6.32 \times 10^{-3} M$$

c) A vinegar sample is found to have 0.837 M CH_3COOH. Its hydronium ion concentration is found to be 3.86×10^{-3} mol dm^{-3}. Calculate K_a for acetic acid.

Ans. Given:

- **Initial concentration of CH_3COOH ([CH_3COOH]): 0.837 M**
- **Hydronium ion concentration ([H₃O+][H₃O+]): 3.86×10−3 M**

Write the Dissociation Equation

Acetic acid partially dissociates in water:

	$CH_3COOH_{(aq)}$	$\rightleftharpoons$	$H_3O^+_{(aq)}$	$CH_3COO^-_{(aq)}$
At t = 0	0.087 M		0	0
At t = equilibrium	0.087 − x		x	x

At equilibrium:

$$[CH_3COOH] = 0.837 - 3.86 \times 10^{-3}$$
$$= 0.833 \text{ mol dm}^{-3}$$
$$[H_3O^+] = 3.86 \times 10^{-3} \text{ mol dm}^{-3}$$
$$[CH_3COO^-] = 3.86 \times 10^{-3} \text{ mol dm}^{-3}$$

Calculate K_a

Using the equilibrium expression:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(3.86 \times 10^{-3})^2}{0.833}$$

$$K_a = \frac{1.49 \times 10^{-5}}{0.833} \approx 1.79 \times 10^{-5}$$

Final Answer:

$$K_a = 1.79 \times 10^{-5}$$

COMMON ION EFFECT

(Exercise LQ)

Q. Discuss applications and implications of the common ion effect in various fields.

Definition:

"The suppression of ionization of a weak electrolyte by adding a common ion to it is called common ion effect".

Applications of Common Ion Effect

Purification of NaCℓ:

NaCℓ is purified by passing hydrogen chloride gas through the saturated brine. Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

$$NaC\ell_{(s)} \rightleftharpoons Na^+_{(aq)} + C\ell^-_{(aq)}$$

$$K_c = \frac{[Na^+][C\ell^-]}{[NaC\ell]}$$

HCℓ also ionizes in solution.

- We can suppress the ionization of an electrolyte by common ion effect.

Q Give applications of common ion effect. (any two)

$$HC\ell \rightleftharpoons H^+_{(aq)} + C\ell^-_{(aq)}$$

On passing HCℓ gas, concentration of Cℓ⁻ ions is increased. Therefore, NaCℓ crystallizes out of the solution to maintain the constant value of equilibrium constant. This type of effect is called common ion effect.

The addition of a common ion to the solution of less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

$$Na^+_{(aq)} + C\ell^-_{(aq)} \rightleftharpoons NaC\ell_{(s)}$$

Precipitation of KCℓO₃ by KCℓ:

The solubility of a less soluble salt KCℓO₃ in water is suppressed by the addition of more soluble salt KCℓ by common ion effect. K⁺ is a common ion. The ionization of KCℓO₃ is suppressed and it settles down as precipitate.

$$KC\ell O_{3(s)} \rightleftharpoons K^+_{(aq)} + C\ell O^{-1}_{3(aq)}$$

$$KC\ell \rightleftharpoons K^+_{(aq)} + C\ell^-_{(aq)}$$

Precipitation of 2nd Group Basic Radicals of Salt Analysis:

The dissociation of a weak acid H₂S in water can be suppressed by the addition of stronger acid HCℓ. H⁺ is a common ion. H₂S becomes less dissociated in acidic solution. In this way, low concentration of S⁻² is developed.

$$H_2S \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

This low concentration of S²⁻ ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

$$HC\ell_{(aq)} \rightleftharpoons H^+_{(aq)} + C\ell^-_{(aq)}$$

- Common ion effect is an application of Le-Chatelier's principle.

- In common ion effect, the term electrolyte is used instead of acid, base or salt.

- In a solution of weak acid, hydrofluoric acid ($K_a = 7.2 \times 10^{-4}$), its salt sodium fluoride produces the common ion (F⁻).

$$HF_{(aq)} \xrightarrow{H_2O} H^+_{(aq)} + F^-_{(aq)}$$
$$NaF_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + F^-_{(aq)}$$

- Common ion effect is always in the reverse direction.

Rack Your Mind!

7. When ionization of a weak electrolyte is suppressed by a strong electrolyte having a common ion is called:
A) Hydrolysis
B) Buffering
C) Common ion effect
D) Precipitation reaction

Precipitation of 3rd Group Basic Radicals of Salt Analysis:

An addition of NH₄Cℓ in NH₄OH solution suppresses the concentration of $OH^-_{(aq)}$ due to the presence of a large excess of NH_4^+ from NH₄Cℓ. Actually, NH₄Cℓ is a strong electrolyte. The combination of these two substances is used as reagent in third group basic radicals.

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

$$NH_4C\ell_{(aq)} \rightleftharpoons Na^+_{4(aq)} + C\ell^-_{(aq)}$$

Uses in Qualitative Analysis and Preparation of Buffers:

Common ion effect has its extensive applications in the qualitative analysis and the preparation of buffers.

Note: In common ion effect, the term "Electrolyte" is used instead of acid, base or salt.

BUFFER SOLUTIONS

The solutions which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions.

- They have a specific constant value of pH. The pH values of buffer solutions do not change on dilution and on keeping for a long time.

Rack Your Mind!

8. What is a buffer solution?

Types of Buffer Solutions

Buffer solutions are mostly prepared by mixing two substances.

I. **Acidic Buffers:** By mixing a weak acid and its salt with a strong base. Such solutions give acidic buffers with pH less than 7. Mixture of acetic acid and sodium acetate is one of the best examples of acidic buffers.

II. **Basic Buffers:** By mixing a weak base and its salt with a strong acid. Such solutions will give basic buffers with pH more than 7. Mixture of NH₄OH and NH₄Cℓ is one of the best examples of basic buffers.

Example:

An acidic buffer consisting of CH_3COOH and CH_3COONa. CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH_3COONa, which is a strong electrolyte, is added to CH_3COOH solution, then the dissociation of CH_3COOH is suppressed, due to common ion effect of CH_3COO^-.

$$CH_3COOH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

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

If one goes on adding CH_3COONa in CH_3COOH solution, then the added concentrations of CH_3COO^- decrease the dissociation of CH_3COOH and the pH of solution increases. The Table tells us how the pH value of a mixture of two compounds is maintained. Greater the concentration of acetic acid as compared to CH_3COONa, lesser is the pH of solution.

Table: Effect of addition of acetate ions on the pH of acetic acid solution

$[CH_3COOH]$(mol dm^{-3})	$[CH_3COO^-]$(moldm^{-3})	% Dissociation	pH
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

Actually, a buffer mentioned above is a large reservoir of CH_3COOH and CH_3COO^- components. When an acid or H_3O^+ ions are added to this buffer, they will react with CH_3COO^- to give back acetic acid and hence the pH of the solution will almost remain unchanged. The reason is that CH_3COOH being a week acid will prefer to remain undissociated. Similarly, the buffer solution consisting of $NH_4C\ell$ and NH_4OH, can resist the change of pH and pOH, when acid or base is added from outside. When a base or OH^- ions are added in it, they will react with H_3O^+ to give back H_2O and the pH of the solution again will remain almost unchanged.

Acidic buffers	Basic buffers
• Those buffers which are formed by the mixing of a weak acid and a salt of it with a strong base are called acidic buffers.	• Those buffers which are formed by mixing of a weak base and a salt of it with a strong acid are called basic buffers.
• Their pH is usually less than 7.	• Their pH is more than 7.
• Henderson's equation for acidic buffers $pH = pK_a + \log\frac{[salt]}{[acid]}$	• Henderson's equation for basic buffers $pOH = pK_b + \log\frac{[salt]}{[base]}$
e.g. $\underset{\text{weak acid}}{CH_3COOH} + \underset{\text{salt of weak acid}}{CH_3COONa}$	e.g. $\underset{\text{weak base}}{NH_4OH} + \underset{\text{salt of weak base}}{NH_4C\ell}$

Calculating the pH of a Buffer

Let us discuss preparation of a buffer of definite pH.

Example:

Consider a weak acid HA and its salt with a strong base NaA (e.g. NaOH). The reversible reactions for dissociation of HA and NaA are as follows:

$$HA \rightleftharpoons H^+ + A^-$$

$$NaA \rightleftharpoons Na^+ + A^-$$

Calculation of pH of a buffer solution by using **Henderson equation:**

$$pH = pK_a - \log\frac{[Acid]}{[Salt]}$$

Interesting Information!

The body's blood buffering system, involving bicarbonates, helps maintain a

Interchanging the numerator and denominator, the sign of log changes.

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

This relationship is called **Henderson's equation.**

Factors Affecting pH of a Buffer:

Henderson's equation shows that **two factors** which govern the pH of a buffer solution are as follows:

(i) pK_a of the acid used.

(ii) The ratio of the concentrations of the salt and the acid.

- The best buffer is prepared by taking equal concentration of salt and acid.
- So, pH is controlled by pK_a of the acid.

Example: For acetic acid - sodium acetate buffer, if

$$[CH_3COOH] = [CH_3COONa]$$
$$pK_a = 4.74$$

Then $\quad pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$

$$pH = pK_a + \log(1)$$

$$pH = pK_a + 0 = pK_a$$

So, $\quad pH = 4.74$

It means that the pH of this buffer is just equal to the pK_a of the acid.

☑ QUICK CHECK 9.4

a) Explain the impact of common ion effect on solubility.

Ans. Effect of Common Ion on Solubility

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. Consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$$

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

Now add Na_2CrO_4 which is a soluble salt CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

b) To a saturated solution of $AgC\ell$, some of $NaC\ell$ solution was added.

i. State the effect of the concentration of Ag^+ on the equilibrium.

Ans. Effect on $[Ag^+]$:

The addition of $NaC\ell$ (which provides $C\ell^-$ ions) to a saturated $AgC\ell$ solution decreases the concentration of Ag^+ ions at equilibrium.

ii. Explain your answer with respect to the common ion effect.

Ans. Explanation (Common Ion Effect):

Equilibrium Shift:

- The dissolution equilibrium of $AgC\ell$ is:

$$AgC\ell_{(s)} \xrightleftharpoons{H_2O} Ag^+_{(aq)} + C\ell^-_{(aq)}$$

$$NaCl_{(s)} \xrightleftharpoons{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$$

- Adding $NaC\ell$ introduces excess $C\ell^-$(common ion), shifting the equilibrium left (Le-Chatelier's Principle) to reduce the added $C\ell^-$, causing more $AgC\ell$ to precipitate.

Mathematical Impact:

- The solubility product (K_{sp}) must remain constant:

$$K_{sp} = [Ag^+][C\ell^-]$$

If $[C\ell^-]$ increases, $[Ag^+]$ **must decrease** to maintain K_{sp}.

Result:

- Solubility of AgCℓ decreases, and the solution becomes less saturated with Ag^+ ions.

c) How does a buffer maintain pH stability?

Ans. A buffer maintains pH stability by resisting changes in pH when small amounts of acid (H^+) or base (OH^-) are added. Here's how it works concisely:

Mechanisms:

i. Composition:

- A buffer consists of a weak acid (HA) and its conjugate base (A^-) (e.g., CH_3COOH/CH_3COO^-) or a weak base (B) and its conjugate acid (BH^+) (e.g., NH_3/NH_4^+).

ii. Action Against Added Acid (H^+):

- The conjugate base (A^-) neutralizes H^+:

$$A^- + H^+ \longrightarrow HA$$

- **Example:** In CH_3COO^-/CH_3COOH buffer, CH_3COO^- consumes H^+ to form CH_3COOH.

iii. Action Against Added Base (OH^-):

- The weak acid (HA) neutralizes OH^-:

$$HA + OH^- \longrightarrow A^- + H_2O$$

- **Example:** CH_3COOH donates H^+ to OH^-, forming water and CH_3COO^-.

iv. pH Stability:

- The equilibrium between HA and A^- ensures $[H^+]$ (and thus pH) changes minimally.
- The Henderson-Hasselbalch equation predicts buffer pH:

$$pH = pK_a + \log([HA][A^-])$$

Conclusion:

Buffers stabilize pH by shifting equilibrium to consume added H^+ or OH^-, keeping the $[HA]/[A^-]$ ratio (and thus pH) nearly constant.

d) Calculate the pH of a buffer consisting of 0.50 M HF and 0.45 M of a fluoride (F^-) salt before and after addition of 0.40 g NaOH to 1.0 dm³ of the buffer (K_a of $HF = 6.8\times10^{-4}$).

Ans. Given Buffer Solution:

$$[HF] = 0.50\ M$$
$$[F^-] = 0.45\ M$$
$$\text{Volume} = 1.0\ dm^3$$
$$K_a \text{ of } HF = 6.8\times10^{-4}$$

- **Added NaOH** = 0.40 g (Molar mass = 40 g/mol → 0.01 mol NaOH in 1.0 dm³ → $[OH^-] = 0.01$ M)

Step 1: Calculate Initial pH (Before NaOH Addition)

Using the **Henderson-Hasselbalch equation**:

$$pH = pK_a + \log([F^-/[HF]])$$
$$pK_a = -\log(6.8\times10^{-4}) = 3.17$$
$$pK_a = -\log(6.8\times10^{-4}) = 3.17$$
$$pH = pKa + \log\frac{[F^-]}{[HF]}$$
$$pH = 3.17 + \log\left[\frac{0.45}{0.50}\right] = 3.17 + \log(0.9) \approx 3.17 - 0.046 = 3.12$$

Step 2: Calculate pH After Adding NaOH (0.01 M OH^-)

NaOH reacts with HF (weak acid) in the buffer:

$$HF + OH^- \rightarrow F^- + H_2O$$

- **[HF] consumed:** 0.50−0.01 = 0.49 M
- **[F^-] produced:** 0.45+0.01 = 0.46 M

New pH:

$$pH = 3.17 + \log(0.46/0.49) = 3.17 + \log(0.94) \approx 3.17 - 0.027 = 3.14$$

e) Calculate the pH of a buffer solution in which 0.11 molar CH_3COONa and 0.09 molar acetic acid solutions are present. K_a for CH_3COOH is 1.85×10^{-5}.

Given Data:

$$[CH_3COONa] = 0.11M$$
$$[CH_3COOH] = 0.09M$$
$$K_a \text{ of } CH_3COOH = 1.85\times10^{-5}$$

Required: pH of Buffer solution = ?

Solution:

$$pK_a = -\log K_a$$
$$= -\log 1.8\times10^{-5} = 4.74$$
$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$
$$pH = 4.74 + \log\frac{0.11}{0.09}$$
$$pH = 4.74 + 0.087$$
$$pH = 4.83$$

SOLUBILITY PRODUCT

(For slightly soluble ionic compounds)

(Exercise L.Q.6)

Q. What is the solubility product for sparingly soluble salts? Give its two applications.

Definition:

"The solubility product is the product of the concentrations of ions raised to an exponent equal to the coefficient of the balanced equation".

OR

"The product of the equilibrium concentration of ions raised to an exponent equal to the coefficient of the balanced equation at given temperature is called solubility product (K_{sp})".

When a soluble ionic compound is dissolved in water, like NaCℓ, it dissociates completely into ions. But for slightly soluble salts the dissociation is not complete at equilibrium stage.

➢ **Example 1, Lead Sulphate:**

When Lead Sulphate ($PbSO_4$) is shaken with water the solution contains Pb^{2+}, SO_4^{2-} and undissociated $PbSO_4$. It means that equilibrium exists between solid solute, $PbSO_4$ and the dissolved ions, SO_4^{2-} and SO_4^{2-}. Lead sulphate is a well-known sparingly soluble compound and it dissociates to a very small extent like $PbC\ell_2$.

$$PbSO_{4(s)} \xrightleftharpoons{H_2O} Pb^{2+}_{(aq)} + SO^{2-}_{4\,(aq)}$$

$$K_c = \frac{[Pb^{2+}][SO_4^{2-}]}{[PbSO_4]}$$

Being a sparingly soluble salt, the concentration of lead sulphate ($PbSO_4$) almost remains constant. Bring $[PbSO_4]$ on L.H.S. with K_c.

$$K_c[PbSO_4] = [Pb^{2+}][SO_4^{2-}]$$
$$\text{if} \quad K_c[PbSO_4] = K_{sp}$$
$$\text{then} \quad K_{sp} = [Pb^{2+}][SO_4^{2-}] = 1.6\times10^{-8} \text{ at } 25^\circ C$$

K_{sp} is called the solubility product of $PbSO_4$. It is the product of molar solubilities of two ions at equilibrium stage.

Rock Your Mind!

9. What is the effect of temperature on the K_{sp} value?

A) It always remains constant
B) It decreases with temperature
C) It changes with temperature
D) It increases with pressure

➢ **Example 2, Lead Chloride:**

Consider a sparingly soluble salt, $PbC\ell_2$. $K_{sp} = [Pb^{2+}][C\ell^-]^2$

K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent. The value of K_{sp} is a measure of the dissociation of sparingly soluble salt.

The following Table shows the K_{sp} values of some slightly soluble ionic compounds.

Table: K_{sp} values for some ionic compounds

Salt	Ion Product	K_{sp}	Salt	Ion Product	K_{sp}
AgBr	$[Ag^+][Br^-]$	5.0×10^{-13}	CuS	$[Cu^{2+}][S^{2-}]$	8×10^{-34}
AgCl	$[Ag^+][Cl^-]$	1.8×10^{-10}	Fe_2S_3	$[Fe^{3+}]^2[S^{2-}]^3$	1.4×10^{-85}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	3×10^{-34}	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	3.5×10^{-8}
$BaCO_3$	$[Ba][CO_3^{2-}]$	1.1×10^{-10}	MnS	$[Mn^{2+}][S^{2-}]$	3×10^{-11}
$CaCO_3$	$[Ca^{2+}][Ca_3^{2-}]$	3.3×10^{-9}	$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}]$	2.3×10^{-13}
CaF_2	$[Ca^{2+}][F^-]^2$	3.2×10^{-11}	$PbSO_4$	$[Pb^{2+}][SO_4^{2-}]$	1.6×10^{-8}

➲ Applications of Solubility Product

a) Determination of Solubility from K_{sp}

For this purpose, we need the formula of the compound and K_{sp} value. Then the unknown molar solubility S is calculated and the concentration of the ions is determined. Table shows the relationship between the K_{sp} values and the solubility of some sparingly soluble compounds.

Table: The relation between solubility and solubility products of some salts

Formula	No. of Ions	K_{sp}	Solubility g dm^{-3}
$PbSO_4$	2	1.69×10^{-4}	1.3×10^{-4}
$Ca(OH)_2$	3	6.5×10^{-6}	1.175×10^{-2}
CaF_2	3	3.2×10^{-11}	2.0×10^{-4}
Ag_2CrO_4	3	2.6×10^{-12}	8.7×10^{-5}

Smart Thinking

Relationship Between K_{sp} and Molar Solubility (s)

Compound	Cation	Anion	Ksp Expression	Relation Between Ksp and s
AgCl	s	s	$[Ag^+][Cl^-]$	$K_{sp} = s^2 \Rightarrow s = (K_{sp})^{\frac{1}{2}}$
$BaSO_4$	s	s	$[Ba^{2+}][SO_4^-]$	$K_{sp} = s^2 \Rightarrow s = (K_{sp})^{\frac{1}{2}}$
PbF_2	s	2s	$[Pb^{2+}][F^-]^2$	$K_{sp} = 4s^3 \Rightarrow s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
Ag_2CO_3	2s	s	$[Ag^+]^2[CO_3^{2-}]$	$K_{sp} = 4s^3 \Rightarrow s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	s	3s	$[Al^{3+}][OH^-]^3$	$K_{sp} = 27s^4 \Rightarrow s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	3s	2s	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$K_{sp} = 108s^5 \Rightarrow s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

Sample Problem 9.4

$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6}. Calculate the solubility of $Ca(OH)_2$.

Solution:

Let the solubility be represented by S in terms of mol dm^{-3}..

The balanced equation is:

$$Ca(OH)_{2(aq)} \rightleftharpoons Ca_{(aq)} + 2OH^-_{(aq)}$$

$$Ca(OH)_{2(aq)} \rightleftharpoons 0+0 \qquad \text{Initial Stage}$$

$$Ca(OH)_2 \rightleftharpoons S+S \qquad \text{Equilibrium Stage}$$

The concentration of OH^- is double than the concentration of Ca^{2+}, so

$$K_{sp} = [Ca^{2+}][OH^-]^2 = S\times(2S)^2$$

$$4S^3 = 6.5\times10^{-6}$$

$$S^3 = \frac{6.5\times10^{-6}}{4}$$

$$S = (1.625)^{1/3}\times10^{-2}$$

$$S = 1.18\times110^{-2}\ \text{mol dm}^{-3}$$

Hence, at equilibrium stage 1.18×10^{-2}moldm^{-3}moldm^{-3} of Ca^{2+} and $2\times1.18\times10^{-2}$mol dm $=2.36\times10^{-2}$ mol dm^{-3}. OH^- are present in the solution. In this way, we have calculated the individual concentrations of Ca^{2+} and OH^- ions from the solubility product of $Ca(OH)_2$.

b) Common Ion Effect

$$\boxed{\text{Solubility} \propto \frac{1}{\text{concentration (no.) of common ions}}}$$

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}{}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

Now add Na_2CrO_4 which is a soluble salt.

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^+ + CrO_4^{2-}$$

CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

c) Predicting Precipitation

Ionic Product	Type of Solution	Precipitation
$>K_{sp}$	Supersaturated	Yes
$=K_{sp}$	Saturated	No
$<K_{sp}$	Unsaturated	No

The solubility product (K_{sp}) helps in predicting whether the precipitation of a salt will occur or not. For example, the solubility product of $CaSO_4$ is 2×10^{-5}. If we add 10^{-2} moldm^{-3} solution Ca^{2+} to 10^{-2} mol dm^{-3} solution of SO_4^{2-} ions at 25°C, the concentrations of each ionic species can be calculated as:

$$[Ca^{2+}] = [SO_4^{2-}] = \frac{10^{-2}}{2} = 5.0\times10^{-3}\ \text{mol dm}^{-3}$$

$$[Ca^{2+}][SO_4^{2-}] = 5.0\times10^{-3}\,\text{moldm}^{-3}\times5.0\times10^{-3}\,\text{moldm}^{-3}$$

$$= 2.5\times10^{-5}\ \text{mol}^2\text{dm}^{-6}$$

$$= 2.5\times10^{-5}\ \text{mol}^2\text{dm}^{-6} > K_{sp}\ \text{of}\ CaSO_4$$

As the product of concentrations is greater than K_{sp}, therefore $CaSO_4$ will precipitate out.

QUICK CHECK 9.5

a) The solubility product constant (K_{sp}) of silver chloride ($AgC\ell$) is 1.77×10^{-10} at 25°C. A solution already contains 0.10 M of Sodium chloride ($NaC\ell$). Find the solubility of $AgC\ell$ in a solution that contains 0.10 $NaC\ell$.

Ans. Given Data:

- Ksp of $AgC\ell = 1.77 \times 10^{-10}$
- $[C\ell^-]$ from $NaC\ell$ = 0.10 M (this is the common ion).

Let S = molar solubility of $AgC\ell$ (mol/dm^3) in the presence of $NaC\ell$.

- **Dissolution equation:**

$$AgC\ell_{(s)} \rightleftharpoons Ag^+_{(aq)} + C\ell^-_{(aq)}$$

- **At equilibrium:**

$$\begin{aligned}[Ag^+] &= S(\text{from } AgC\ell)\\ [C\ell^-] &= 0.10\,M\,(\text{from } NaC\ell) + S \approx 0.10\,M\,(\text{since } S \ll 0.10)\\ K_{sp} &= [Ag^+][C\ell^-]\\ 1.77 \times 10^{-10} &= S \times 0.10\\ S &= 1.77 \times 10^{-10}/0.10 = 1.77 \times 10^{-9}\,M\end{aligned}$$

b) Predict whether $CaSO_4$ will be precipitated or not when 10^{-3} moldm^{-3} of each of Ca^{2+} and SO_4^{2-} is mixed together.

Ans. Given:

$$\begin{aligned}[Ca^{2+}] &= 10^{-3}\,mol\,dm^{-3}\\ [SO_4^{2-}] &= 10^{-3}\,mol\,dm^{-3}\\ K_{sp}\text{ of } CaSO_4 &= 2.4 \times 10^{-5}\ (\text{at } 25^\circ C, \text{ literature value}).\end{aligned}$$

Calculation of the ionic Product (Q)

$$Q = [Ca^{2+}][SO_4^{2-}] = (10^{-3})(10^{-3}) = 10^{-6}$$

Comparison of Q to K_{sp}

- **If $Q > K_{sp}$:** Precipitation occurs.
- **If $Q < K_{sp}$:** No precipitation.

Here: $Q = 10^{-6}$ vs. $K_{sp} = 2.4 \times 10^{-5}$

Since $10^{-6} < 2.4 \times 10^{-5}$ i.e., **$Q < K_{sp}$**.

Conclusion:

$CaSO_4$ will NOT precipitate under these conditions because the ion product (Q) is less than K_{sp}.

c) Solution of potassium carbonate is basic.

i. Explain why the solution is alkaline.

Ans. Solution is Alkaline:

Potassium carbonate (K_2CO_3) dissolves in water to produce CO_3^{2-}, which hydrolyzes to form OH^- ions, making the solution basic:

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

- CO_3^{2-} (a strong base) reacts with water, accepting protons (H^+) and releasing **OH^-**.
- K^+ (from K_2CO_3) is a spectator ion and does not hydrolyze.

ii. Also give the equation for the hydrolysis of the above salt.

Ans. Hydrolysis Equation:

$$K_2CO_3 \rightarrow 2K^+ + CO_3^{2-} \qquad \text{(Dissociation)}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad \text{(Hydrolysis)}$$

The OH^- generated during hydrolysis raises the pH (>7), making the solution alkaline.

Interesting Information!

The shell of this nautilus is composed mainly of calcium carbonate. The nautilus adjusts conditions so shell material is formed when the concentration of calcium ions and carbonate ions in seawater are high enough to precipitate calcium carbonate.

SALT HYDROLYSIS

When a salt dissolves in water, it dissociates into its constituent ions. These ions can interact with water, affecting the solution's pH depending on the nature of the acid and base from which the salt is derived.

➢ **Hydrolysis:**

"The interaction between salts and water are called hydrolytic reactions and this phenomenon is called hydrolysis".

Salts of Strong Acids and Strong Bases

For salts derived from strong acids and strong bases (e.g., sodium chloride, $NaC\ell$), the conjugate base of a strong acid (e.g., $C\ell^-$ from $HC\ell$) is very weak and does not significantly react with water. The conjugate acid of a strong base (e.g., Na^+ from NaOH) is also very weak and does not significantly react with water.

$$NaC\ell_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + C\ell^-_{(aq)}$$

Na^+ is the conjugate acid of NaOH (a strong base) and does not affect the pH.

$C\ell^-$ is the conjugate base of $HC\ell$ (a strong acid) and does not affect the pH.

The solution remains neutral.

Examples are $KC\ell$ ($HC\ell$ + KOH), KNO_3(HNO_3 + KOH), Na_2SO_4(H_2SO_4 + NaOH) etc.

Salts of Strong Acids and Weak Bases

For salts derived from strong acids and weak bases (e.g., ammonium chloride, $NH_4C\ell$), The conjugate base of the strong acid (e.g., $C\ell^-$) does not react with water. The conjugate acid of the weak base (e.g., NH_4^+ from NH_3) reacts with water to produce H_3O^+ ions, making the solution acidic.

$$NH_4C\ell_{(s)} \rightleftharpoons NH^+_{4(aq)} + C\ell^-_{(aq)}$$

NH_4^+ is the conjugate acid of NH_3 (a weak base) and reacts with water:

$$NH^+_{4(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_{3(g)} + H_3O^+_{(aq)}$$

$C\ell^-$ is the conjugate base of $HC\ell$ (a strong acid) and does not affect the pH.

The solution is acidic due to the NH_4^+ ion.

Examples: $A\ell C\ell_3$, $CuSO_4$, NH_4NO_3 etc.

Salts of Weak Acids and Strong Bases

The example of salt of weak acid and strong base is sodium acetate.

$$CH_3COONa_{(s)} + H_2O_{(\ell)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

CH_3COO^- is the conjugate base of CH_3COOH (a weak acid) and reacts with water:

$$CH_3COO^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

Na^+ Is the conjugate acid of NaOH (a strong base) and does not affect the pH . The solution is basic due to the CH_3COO^- ion.

Examples: Na_2CO_3(H_2CO_3 + NaOH), Na_3PO_4(H_3PO_4 + NaOH)

Salts of Weak Acids and Weak Bases

For salts derived from weak acids and weak bases (e.g., ammonium acetate, NH_4CH_3COO): The conjugate acid (NH_4^+) and the conjugate base (CH_3COO^-) both affect the pH.

$$NH_4CH_3COO_{(aq)} \rightleftharpoons NH_{4(aq)}^+ + CH_3COO_{(aq)}^-$$

NH_4^+ hydrolyzes to produce H_3O^+.

$$NH_{4(aq)}^+ + H_2O_{(\ell)} \rightleftharpoons NH_{3(aq)} + H_3O_{(aq)}^+$$

CH_3COO^- hydrolyzes to produce OH^-.

$$CH_3COO_{(aq)}^- + H_2O_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + OH_{(aq)}^-$$

The resultant pH of the solution depends on the relative strengths of the conjugate acid and conjugate base. The solution may be acidic, basic, or nearly neutral, depending on which reaction is more dominant.
Examples: $NH_4CN(NH_4OH + HCN)$, $(NH_4)_2CO_3(H_2CO_3 + NH_3)$

ACID-BASE INDICATORS

An indicator is a substance that changes color to mark a titration's endpoint. Acid-base indicators exhibit one color in acid and another in base. Most indicators used in acid-base titration are weak organic acids or weak organic bases. In solution, a weak-acid indicator (HIn) can be represented by the equation below.

$$HIn \rightleftharpoons H^+ + In^-$$

Here In^- is the symbol of the anion part of the indicator. Because the reaction is reversible, both HIn and In^- are present. The colors displayed result from the fact that HIn and In^- have different colors.

In acidic solutions, any In^- ions that are present act as Bronsted bases and accept protons from the acid. The indicator is then present in largely unionized form, HIn. In basic solutions, the OH^- ions from the base combine with the H^+ ions produced by the indicator. The indicator molecules further ionize to equalize the loss of H^+ions. The indicator is thus present largely in the form of its anion, In^-. The solution now shows the base-indicating color, which for litmus is blue.

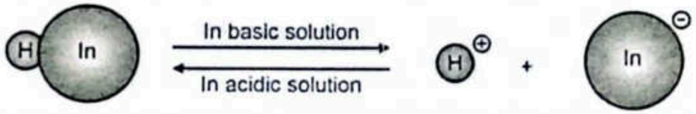


Figure: Unionized acid-base indicators and their ionised forms exist in an equilibrium

Different indicators change color at different pH values. The color depends on the relative amounts of HIn and In^- at a given pH. For example, methyl red changes from red to yellow between pH 4.4 and 6.2. At pH 4.4, the indicator exists mostly as HIn molecules, which appear red in the solution. The indicator ranges are given below for some of the indicators commonly used.

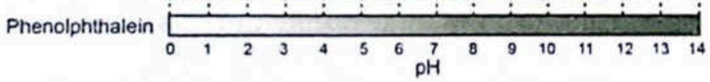


Figure: Range and color changes of some common Acid-Base Indicators

Selecting a Suitable Indicator

The two general criteria for an indicator to be used in a titration are:

- The pH at the end of the titration should be close to the indicator's neutral point.
- The indicator should indicate a sharp color change near the equivalence point of the titration.

Each pH indicator changes color over a defined range of pH, known as the indicator range. An indicator changes colour over a range of about 2 pH units.

(Exercise L.Q.7)

Q. Describe the general shape of a titration curve for a strong acid titrated with a strong base. How can you identify the equivalence point on this titration curve?

Titration Curve and Equivalence Point

- **pH Curve:** A pH curve is a graph of the pH of the solution verses the volume of titrant added.
- **Equivalence Point:** The equivalence point is the point at which the amount of titrant added is just enough to neutralize the analyte solution completely.
- **Titration curves:** Titration curves show how the pH of an acidic or basic solution changes as a basic or acidic solution is added to it. We can use the titration curve to choose an indicator that will show when the titration is complete and we reach the equivalence point.
- **End Point:** The end point of the titration occurs when the indicator changes color. We choose an indicator with an end point close to the equivalence point.

1. **Strong Acid-Strong Base Titration Curve:**

Consider the titration of HCℓ with NaOH. Initially, the solution contains only the strong acid. Since the acid is strong, it completely dissociates, leading to a high concentration of H^+ ions and the pH is very low.

As NaOH is added, OH^- ions from NaOH begin to neutralize the H^+ ions from HCℓ and pH of the solution rises.

The equivalence point is reached when the amount of OH^- added is stoichiometrically equal to the amount of H^+ originally present in the acid. **The pH at the equivalence point in a strong acid-strong base titration is 7.0.**

The titration curve at this stage shows a steep rise in pH, changing quickly from acidic to neutral. The pH value at the endpoint changes about from 4.0 to 10.0. These titrations have a pH of 7.0 at equivalence, so, such phenolphthalein as indicator can be used as they show different colours in this range.

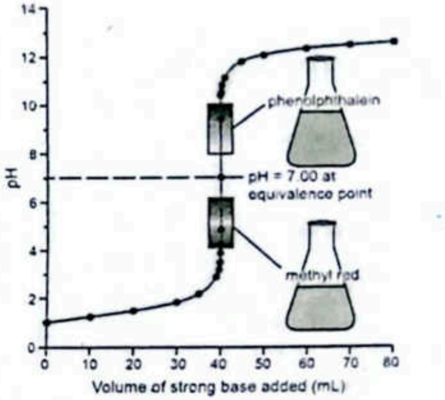


Figure: Strong acid-strong base titration curve

2. **Strong Acid-Weak Base Titration Curve**

Consider the titration of aqueous NH_3 with HCℓ. Initially, the solution contains only the weak base and it only partially dissociates, with a lower concentration of OH^- ions compared to a strong base. The initial pH will be greater than 7 but lower than the pH of a strong base. As HCℓ is added, the concentration of OH^-decreases, causing a further decrease in pH.

Before reaching the equivalence point, the solution is in a buffer-like region where the pH changes more gradually. The presence of the weak base and its conjugate acid (from the salt formed) creates a buffering effect, which helps to moderate the pH change as the base is added.

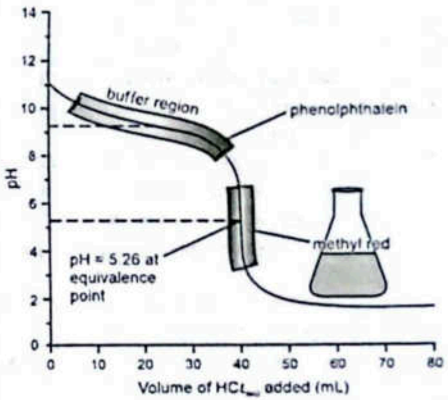


Figure: strong acid-weak base titration curve

The pH at the equivalence point will be less than 7(pH=5.27) because the conjugate acid slightly dissociates, releasing H^+ ions making the solution acidic ($NH_4^+ \rightarrow NH_3 + H^+$).

After the equivalence point, the pH of the solution decreases rapidly. This is because the strong acid dissociates completely in water, providing a high concentration of hydrogen ions H^+, which significantly lowers the pH. Methyl orange has its colour change in this range, therefore, it can be used as an indicator for strong acid-weak base titrations.

Rack Your Mind!

10. What is the equivalence point in a titration?

Table: pH ranges of common indicators

Indicators	Acid color	Base color	pH Range	Type of Titration
Methyl orange	orange	yellow	3.2 – 4.5	strong acid-strong base strong acid-weak base
Phenolpthalein	colorless	red	8.2 – 10.0	strong acid-strong base

☑ QUICK CHECK 9.6

a) Differentiate end point and equivalent point.

Ans. The differences between Endpoint and Equivalence:

Feature	Equivalence Point	Endpoint
Definition	The point where stoichiometrically equivalent amounts of analyte and titrant react.	The point where the indicator changes color, signaling completion of titration.
Theoretical vs. Experimental	Theoretical (calculated from stoichiometry).	Experimental (observed visually or instrumentally).
Dependence on Indicator	Independent of indicator.	Depends on the choice of indicator.
pH (Acid-Base Titration)	pH is determined by the salt formed (e.g., pH = 7 for strong acid-strong base).	pH may slightly differ due to indicator range (e.g., phenolphthalein changes at pH 8.2–10).
Precision	Exact (based on reaction stoichiometry).	Approximate (may not perfectly match equivalence point).

b) Explain how an indicator changes its colour in acidic and basic solution.

Ans. An Indicator Changes Color in Acidic vs. Basic Solutions:

1. **Chemical Structure:**
   - Indicators are **weak acids (HIn)** or **weak bases (InOH)** with **different colors** in protonated (acidic) and deprotonated (basic) forms.
2. **Acidic Solution (pH < pK$_a$):**
   - Excess **H^+ ions** shift the equilibrium to the left:

     $$HIn \rightleftharpoons H^+ + In^-$$

   - **The protonated form (HIn)** dominates (e.g., **red** for methyl orange).
3. **Basic Solution (pH > pK$_a$):**
   - **OH^- ions** remove H^+, shifting equilibrium **right**:

     $$HIn \longrightarrow In^- + H^+$$

   - **The deprotonated form (In^-)** dominates (e.g., **yellow** for methyl orange).
4. **Transition Range (pH ≈ pK$_a$ ± 1):**
   - Color change occurs (e.g., phenolphthalein turns pink at pH 8.2–10).

Example:

- **Methyl Orange:**

  Acidic (red, HIn) → Basic (yellow, In^-).

- **Phenolphthalein:**

  Acidic (colorless, HIn) → Basic (pink, In^-).

Key Idea: The indicator's color reflects the dominant form (HIn or In^-) based on pH.

c) Suggest a suitable indicator for weak acid and strong base titration.

Ans. For the titration of a weak acid (e.g., CH_3COOH) with a strong base (e.g., NaOH), the best indicator is: **Phenolphthalein**

- **pH Range: 8.2–10.0** (colorless → pink).
- **Reason:** The equivalence point pH is >7 (due to hydrolysis of the conjugate base, e.g., CH_3COO^-). Phenolphthalein's range matches this alkaline pH.

d) Suggest a suitable indicator for weak acid and weak base titration.

Ans. For weak acid-weak base titrations, no indicator is ideal due to the gradual pH change near the equivalence point. However, if required:

Suggested Indicator: Bromothymol Blue

- **pH Range:** 6.0 (yellow) to 7.6 (blue).
- **Reason:** Covers the neutral pH (≈7) typical for weak acid-weak base titrations (e.g., acetic acid + ammonia).

Limitation:

Weak acid-weak base titrations often lack a sharp pH jump, making pH meters more reliable than visual indicators.

Solution File Rack Your Brain!

Sr. #	Option	Explanation
1.	B	HCl (acid) → $H^+ + Cl^-$ (conjugate base) HCl donates a proton, making Cl^- its conjugate base.
2.	D	When an acid donates a proton, it forms its conjugate base, and when a base accepts a proton, it forms its conjugate acid.
3.	S.Q	BF_3 is a Lewis acid because the boron atom has only six electrons in its valence shell, which is less than an octet. This incomplete octet makes BF_3 electron-deficient and able to accept a lone pair from a Lewis base like fluoride ion.
4.	S.Q	Water concentration remains effectively constant (about 55.5 mol dm^{-3}) because water is present in large excess and only a tiny fraction ionizes, so its concentration does not change significantly.
5.	A	$H^+ = 10^{(-pH)}$ $= 10^{(-3)}$ $= 0.001$ M or $1 \times 10^{(-3)}$M pH is defined as the negative logarithm of the hydrogen ion concentration.
6.	S.Q	K_a is the acid dissociation constant. It represents the extent to which an acid donates protons in water. A higher K_a value means a stronger acid.
7.	C	Presence of a common ion from a strong electrolyte reduces the ionization of a weak electrolyte, shifting the equilibrium towards the reactants.

8.	S.Q	• A buffer solution resists a change in pH when a small amount of acid or base is added. • It maintains a constant pH and is stable over time and on dilution. • Buffers are made from a weak acid/base and its salt.
9.	C	Based on "Le Chatelier's Principle" the system shifts to oppose the temperature change. So "temperature can increase or decrease Ksp" depending on the heat change of the dissolution reaction.
10.	S.Q	• The equivalence point is when the amount of acid equals the amount of base. • It is where complete neutralization occurs. • It is not always at pH 7, depending on acid and base strength.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. Given the following reaction:

$$NH_{3(g)} + H_2O_{(\ell)} \longrightarrow NH^+_{4(aq)} + OH^-_{(aq)}$$

a) NH_3 is the acid, H_2O is the base b) NH_3 is the base, H_2O is the acid
c) NH_4^+ is the base, OH^- is the acid d) H_2O is the base, OH^- is the acid

II. The pH of 10^{-3} mol dm^{-3} of an aqueous solution of H_2SO_4 is:

a) 3.0 b) 2.7 c) 2.0 d) 1.5

III. The solubility product of AgCℓ is 2.0×10^{-10} moldm^{-6}. The maximum concentration of Ag^+ ions in the solution is:

a) 2.0×10^{-10} moldm^{-3} b) 1.41×10^{-5} moldm^{-3} c) 1.0×10^{-10} moldm^{-3} d) 4.0×10^{-20} moldm^{-3}

IV. Which indicator is typically used for titrations involving strong acids and strong bases?

a) Methyl red b) Phenolphthalein c) Bromothymol blue d) Litmus solution

V. Which of the following is the conjugate base of water?

a) $OH^-_{(aq)}$ b) $OH^+_{(aq)}$ c) $H_2O_{(\ell)}$ d) $H_3O^+_{(aq)}$

VI. Which of the following is a Lewis acid but not a Bronsted-Lowry acid?

a) HCℓ b) NH_3 c) $A\ell C\ell_3$ d) H_2O

VII. In an acid-base titration, the equivalence point is reached when:

a) pH of the solution is 7.0. b) The indicator changes color.
c) Equal volumes of acid and base have been added. d) The reaction stops.

VIII. If the concentration of $C\ell^-$ ion in a solution is increased, the solubility of silver chloride (AgCℓ) will:

a) Decrease b) Increase c) Remain unchanged d) Become zero

IX. Which of the following pairs of substances can act as a conjugate acid-base pair according to the Bronsted-Lowry theory?

a) HCℓ and NaOH b) NH_3 and NH_4^+ c) H_2O and H_2SO_4 d) H_2O and CH_4

X. If the pH of a solution is 11, what is the $[OH^-]$ concentration in the solution?

a) 1×10^{-3} M b) 1×10^{-11} M c) 1×10^{-2} M d) 1×10^{-14} M

XI. Which of the following pairs forms a buffer solution?

a) HCℓ and NaCℓ b) CH_3COONa and CH_3COOH
c) NaOH and HCℓ d) NH_3 and Na_2SO_4

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	b	NH_3 is the base, H_2O is the acid	• NH_3 accepts H^+, making it a base; H_2O donates H^+, making it an acid.
II.	b	2.7	• $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$ $[H^+] = 2\times10^{-3}$ pH = −log [H⁺] $pH = -\log 2\times10^{-3} = -(\log 2 - 3\log 10) = -(0.301-3)$ pH = 2.67 Or 2.7
III.	b	1.41×10^{-5} moldm^{-3}	• $AgC\ell \rightleftharpoons Ag^{+1} + C\ell^-$ $K_{sp} = [Ag^{+1}][C\ell^{-1}]$ $2.0\times10^{-10} = [Ag^{+1}][C\ell^{-1}]$ Since $[Ag^{+1}] = [C\ell^{-1}]$ $2.0\times10^{-10} = [Ag^{+1}]^2$ $\sqrt{2.0\times10^{-10}} = \sqrt{[Ag^{+1}]^2}$ $[Ag^{+1}] = 1.414\times10^{-5}$ mol dm^{-3}
IV.	b	Phenolphthalein	• Changes color near pH 7–9, ideal for strong acid-strong base titrations.
V.	a	$OH^-_{(aq)}$	• H_2O loses H^+ to form OH^- so OH^- is its conjugate base.
VI.	c	$A\ell C\ell_3$	• Accepts an electron pair but does not donate H^+.
VII.	c	Equal volumes of acid and base have been added.	• Equivalence point is stoichiometric, not necessarily pH 7.
VIII.	a	Decrease	• Common ion effect reduces solubility.
IX.	b	NH_3 and NH_4^+	• NH_3 gains H^+ to form NH_4^+
X.	a	1×10^{-3} M	• pH = 11 → pOH = 3 → $[OH^-] = 10^{-3}$ M.
XI.	b	Sodium acetate (CH_3COONa) and acetic acid (CH_3COOH)	• Weak acid (CH_3COOH) + its conjugate base (CH_3COO^-) forms buffer.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Define the following with an example for each:
i) Ionization constant **ii) Solubility product**
iii) Common ion effect **iv) Acid-base Indicator**

Ans.

(i) Ionization Constant: The quantitative measure of the strength of the acid and base is called ionization constant.
Example: we have an acid HA dissolved in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

(ii) Solubility Product: The solubility product is the product of the concentrations of ions raised to an exponent equal to the co-efficient of the balanced equation.
Example: For AgCℓ

$$AgC\ell \rightleftharpoons Ag^+ + C\ell^-, \quad K_{sp} = [Ag^+][C\ell^-]$$

(iii) Common Ion Effect: The suppression of ionization of a weak electrolyte by adding a common ion to it is called common ion effect.

$$NaC\ell_{(s)} \rightleftharpoons Na^+_{(aq)} + C\ell^-_{(aq)}$$

$$HC\ell_{(g)} \rightleftharpoons H^+_{(aq)} + C\ell^-_{(aq)}$$

(iv) Acid-base Indicator: An indicator is a substance that changes colour to mark a titration's endpoint. Acid-base indicators exhibit one colour in acid and another in base. Most indicators used in acid-base titration are weak organic acids or weak organic bases.

Example:

Phenolphthalein: Colorless ($pH < 8.3$) to Pink ($pH > 10.0$)

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b. Differentiate between:

i) Hydrolysis and dissolution **ii) Acidic and basic buffer solutions**

Ans. i) Hydrolysis and Dissolution

Feature	**Hydrolysis**	**Dissolution**
Definition	A chemical reaction where water breaks bonds in a compound.	A physical process where a solute dissolves in a solvent.
Nature	Chemical process (forms new substances).	Physical process (no new substances formed).
Involves	Reaction with water molecules (H^+ and OH^- may participate).	Mixing of solute and solvent (e.g., salt in water).
Energy Change	May release or absorb energy (exo/endothermic).	Often absorbs energy (endothermic, but not always).
Result	Forms new products (e.g., acids, bases, or ions).	Forms a homogeneous mixture (solution).
Example	$A\ell C\ell_3 + 3H_2O \rightleftharpoons A\ell(OH)_3 + 3H^+ + 3C\ell^-$	$NaC\ell_{(s)} \longrightarrow Na^+_{(aq)} + C\ell^-_{(aq)}$

(ii) Acidic and Basic Buffer Solutions

Acidic buffers	**Basic buffers**
• Those buffers which are formed by the mixing of a weak acid and a salt of it with a strong base are called acidic buffers.	• Those buffers which are formed by mixing of a weak base and a salt of it with a strong acid are called basic buffers.
• Their pH is less than 7.	• Their pH is more than 7.
• Henderson's equation for acidic buffers $pH = pK_a + \log\frac{[salt]}{[acid]}$	• Henderson's equation for basic buffers $pOH = pK_b + \log\frac{[salt]}{[base]}$
e.g. $\underset{\text{weak acid}}{CH_3COOH} + \underset{\text{salt of weak acid}}{CH_3COONa}$	e.g. $\underset{\text{weak base}}{NH_4OH} + \underset{\text{salt of weak base}}{NH_4C\ell}$

---

c. Explain the concept of conjugate acid-base pairs. How are they related in terms of proton transfer?

Ans. Conjugate Acid:

"A species formed after a Bronsted base accepts a proton from the acid is called the conjugate acid". The hydronium ion (H_3O^+) is the conjugate acid of water.

Example:

When NH_3 dissolves in Water:

When ammonia dissolves in water, proton transfer also occurs. H^+ from H_2O attaches to the N atom's lone pair and NH_4^+ and OH^- are formed. With fewer H^+, the water molecule becomes OH^- ion:

$$\underset{\text{Base}}{NH_{3(g)}} + \underset{\text{Acid}}{H_2O_{(\ell)}} \rightleftharpoons \underset{\text{Conjugate base}}{OH^-_{(aq)}} + \underset{\text{Conjugate acid}}{NH^+_{4(aq)}}$$

In this case, H_2O (the acid) has donated the proton and NH_3 (the base) has accepted it. $NH_3 - NH_4^+$ and $H_2O - OH^-$ are conjugate acid-base pair.

Conjugate Base:

"A species formed after a Bronsted base accepts a proton from the acid is called the conjugate acid."

Example: The hydronium ion (H_3O^+) is the conjugate acid of water. A species formed when an acid donates a proton to a base is called the conjugate base. $HC\ell + C\ell^-$ and $H_2O \rightarrow H_3O^+$ are conjugate acid-base pairs.

$$\overset{\text{acid}}{HC\ell} + \underset{\text{base}}{H_2O} \longrightarrow \underset{\text{conjugate acid}}{H_3O^+} + \overset{\text{conjugate base}}{C\ell^-}$$

---

d. What is the relationship between the strength of an acid and the strength of its conjugate base?

Ans. A strong acid has a weak conjugate base because it donates protons easily. A weak acid has a stronger conjugate base as it holds onto protons.

Example: $HC\ell$ (strong acid) forms $C\ell^-$ (very weak base).

- Strong Acid ($HC\ell$): Weak conjugate base ($C\ell^-$).
- Weak Acid (CH_3COOH): Strong conjugate base (CH_3COO^-).

---

e. For the following three reactions, identify the reactants that are Arrhenius bases, Bronsted-Lowry bases, and/or Lewis bases. State which type(s) of bases each reactant is. Explain your answers.

i) $NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$ ii) $HF_{(aq)} + H_2O_{(\ell)} \longrightarrow F^-_{(aq)} + H_3O^+_{(aq)}$ iii) $H^+_{(aq)} + NH_{3(aq)} \longrightarrow NH^+_{4(aq)}$

Ans. (i) OH^- is an Arrhenius and Bronsted-Lowry base (accepts H^+).

(ii) H_2O is a Bronsted-Lowry base (accepts H^+) and Lewis base (donates lone pair).

(iii) NH_3 is a Bronsted-Lowry and Lewis base (accepts H^+ and donates lone pair).

---

f. An amphoteric substance can behave as either an acid or a base. Identify whether water behaves as an acid or a base in each of the following reactions.

i) $H_2O + HC\ell \longrightarrow H_3O^+ + C\ell^-$ ii) $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

iii) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$ iv) $CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$

Ans.

	Reaction	**H_2O Role**	**Reason**
i)	$H_2O + HC\ell^- \longrightarrow H_3O^+ + C\ell^-$	Base	Accepts H^+ from $HC\ell$.
ii)	$NH_3 + H_2O^- \longrightarrow NH_4^+ + OH^-$	Acid	Donates H^+ to NH_3.
iii)	$HNO_3 + H_2O^- \longrightarrow H_3O^+ + NO_3^-$	Base	Accepts H^+ from HNO_3.
iv)	$CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$	Base	Accepts H^+ from CH_3COOH.

---

g. Which salt would you expect to dissolve more readily in acidic solution: Barium sulfate or Barium fluoride? Explain. $K_{sp(BaCO_3)} = 1.1\times10^{-10}, K_{sp(CuS\ 8\times10^{-36})}$

Ans. Barium fluoride (BaF_2) dissolves more in acid.

Reason: F^- reacts with H^+ to form HF:

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^- \qquad F^- + H^+ \longrightarrow HF$$

$BaSO_4$ is unaffected because SO_4^{2-} doesn't react with H^+.

---

h. Why does common ion effect decrease solubility of a less soluble salt?

Ans. The solubility of a less soluble salts $KC\ell O_3$ in water is suppressed by the addition of a more soluble salt $KC\ell$ by common ion effect. K^+ is a common ion. The ionization of $KC\ell O_3$ is suppressed and it settles down as precipitate.

$$KC\ell O_{3(s)} \rightleftharpoons K^+_{(aq)} + C\ell O^-_{3(aq)}$$

$$KC\ell_{(s)} \rightleftharpoons K^+_{(aq)} + C\ell^-_{(aq)}$$

i. State the basic principle of solubility product. Mention factors affecting solubility product.

Ans. It is the product of molar solubilities of two ions at equilibrium stage.

For example: sparingly soluble salt, $PbCl_2$. $K_{sp} = [Pb^{2+}][Cl^-]^2$

K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent.

Factors Affecting K_{sp}:

- Temperature
- Presence of common ions
- pH (if salt has basic/acidic ions)

j. Prove by equations what happens when Na_2CrO_4p is added to saturated solution of $PbCrO_4$.

Ans. When Na_2CrO_4 is added to a saturated $PbCrO_4$ solution, it increases the concentration of CrO_4^{2-} ions. According to Le Chatelier's Principle, the equilibrium shifts left to reduce the added CrO_4^{2-} ions:

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$$

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^+ + CrO_4^{2-}$$

- **Result:** More $PbCrO_4$ precipitates out, decreasing its solubility.
- **Reason:** The common ion (CrO_4^{2-}) suppresses the dissociation of $PbCrO_4$.

This is an example of the common ion effect reducing solubility.

k. According to the Lewis acid-base concept, Boron trifluoride (BF_3) can act as an acid. Is this statement correct?

Ans. Correct, BF_3 is a Lewis acid.

Reason: Boron in BF_3 has an empty p-orbital and can accept an electron pair (Lewis acid).

Example: When BF_3 reacts with NH_3 (a Lewis base), it forms a coordinate covalent bond:

$$BF_3 + NH_3 \longrightarrow H_3N \longrightarrow BF_3$$

Here, BF_3 accepts the lone pair from NH_3.

l. If the concentration of hydrogen ions in a solution is 1×10^{-5} M, what is the pH of the solution?

Given Data:

Concentration of hydrogen ions, $[H^+] = 1 \times 10^{-5}$ M

To Find:

pH of the solution = ?

Solution:

Step 1: pH formula:

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

Step 2: Substitute the given $[H^+]$ into the formula:

$pH = -\log(1\times10^{-5})$

Step 3: Simplify the logarithm:

$pH = -(-5) = 5$

Answer: The pH of the solution is 5.

DESCRIPTIVE QUESTIONS

Q.3 Describe the Bronsted-Lowry theory of acids and bases. Provide examples of conjugate acid-base pairs and explain clearly their relationship.

Ans. See Page No. (294)

Q.4 Define the Lewis theory of acids and bases. How does this theory differ from the Bronsted-Lowry theory? Give examples of Lewis acids and bases that do not involve proton transfer.

Ans. See Page No. (295)

Q.5 Discuss applications and implications of the common ion effect in various fields.

Ans. See Page No. (305)

Q.6 What is the solubility product for sparingly soluble salts? Give its two applications.

Ans. See Page No. (309)

Q.7 Describe the general shape of a titration curve for a strong acid titrated with a strong base. How can you identify the equivalence point on this titration curve?

Ans. See Page No. (315)

NUMERICAL PROBLEMS

Q.8 A buffer solution has a pH of 5.0. It is made from a weak acid HA with a pK_a of 4.8. What is the ratio of the concentration of the conjugate base $[A^-]$ to the concentration of the weak acid [HA] in this buffer?

Given Data:

$pH = 5.0$

$pK_a = 4.8$

Formula: $pH = pK_a + \log\frac{[salt]}{[acid]}$

Putting the values: $5.0 = 4.8 + \log\left(\frac{[A^-]}{[HA]}\right)$

Solve for the log term: $\log\left(\frac{[A^-]}{[HA]}\right) = 5.0 - 4.8 = 0.2$

Convert log to ratio (antilog):

$$\frac{[A^-]}{[HA]} = 10^{0.2} \approx 1.58$$

Final Result: $\frac{[A^-]}{[HA]} = \boxed{1.58}$

The buffer contains 1.58 times more conjugate base (A^-) than weak acid (HA) to maintain pH 5.0.

Q.9 Calculate the solubility of a sparingly soluble salt lead (II) iodide (PbI_2) in water. It has $K_{sp} = 1.4\times10^{-8}$.

Given Data: $K_{sp} = 1.4 \times 10^{-8}$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^-_{(aq)}$$

Define Solubility (s):

Let s = molar solubility of PbI_2 (mol/dm^3).

At equilibrium: $[Pb^{2+}] = s$

$[I^-] = 2s$ (2 moles of I^- are produced per mole of PbI_2).

K_{sp} Expression: $K_{sp} = [Pb^{2+}][I^-]^2$

$= (s)(2s)^2 = 4s^3$

Solve for s: $4s^3 = 1.4 \times 10^{-8}$

$$s^3 = \frac{1.4\times10^{-8}}{4} = 3.5 \times 10^{-9}$$

$$s = \sqrt[3]{3.5\times10^{-9}} \approx \boxed{1.52 \times 10^{-3}\ mol/dm^3}$$

Final Answer: The solubility of PbI_2 is $1.52 \times 10^{-3}\ mol/dm^3$.

Q.10 The molar solubility of silver chromate (Ag_2CrO_4) in pure water at 298 K is $6.5\times10^{-5}\ mol\ dm^{-3}$. Calculate the K_{sp} of silver chromate at this temperature.

Given Data:

Molar solubility (s) of Ag_2CrO_4 = $6.5 \times 10^{-5}\ mol\ dm^{-3}$

$$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + CrO^{2-}_{4(aq)}$$

Ion Concentrations in Terms of s

$[Ag^+] = 2s$ (2 moles of Ag^+ per mole of Ag_2CrO_4).

$[CrO_4^{2-}] = s$ (1 mole of CrO_4^{2-} per mole of Ag_2CrO_4).

K_{sp} Expression: $K_{sp} = [Ag^+]_2[CrO_4^{2-}]$

$= (2s)^2(s) = 4s^3$

Substitute s and Solve for K_{sp}: $K_{sp} = 4 \times (6.5 \times 10^{-5})^3$

$K_{sp} = 4 \times (2.746 \times 10^{-13})$

$K_{sp} = 1.10 \times 10^{-12}\ mol^3\ dm^{-9}$

Final Answer: $K_{sp} = \boxed{1.1 \times 10^{-12}}$

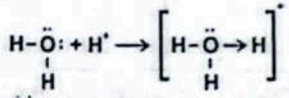
ADDITIONAL SLOs BASED MCQs

1. **Water cannot act as:**
   A. Lewis acid B. Lewis base C. Bronsted acid D. Bronsted base
2. **pH of 0.01 M HCl solution is:**
   A. 10^{-2} B. 10^{+2} C. 2.0 D. 1.0
3. **An aqueous solution of ammonium chloride is:**
   A. Basic B. Acidic C. Neutral D. Amphoteric
4. **An aqueous solution of which compound is basic.**
   A. Ammonium nitrate B. Calcium chloride C. Ammonium acetate D. Potassium carbonate
5. **If a liquid has a pH of 7 then:**
   A. It must be colourless B. It has boiling point of 100°C
   C. It must be a solution D. It must be neutral
6. **When air is bubbled through pure water, the pH is lowered from 7.0 to 5.6, which gas in the air is responsible for this change.**
   A. Argon B. Carbon dioxide C. Nitrogen D. Oxygen
7. **Which of the following oxides is classified incorrectly?**
   A. Zinc oxide (ZnO) amphoteric B. Carbon dioxide (CO_2) acidic
   C. Carbon monoxide (CO) neutral D. Lead oxide (PbO) basic
8. **If 25cm³ of 1 mole. dm⁻³ nitric acid is added to 50 cm³ of 0.5 potassium hydroxide solution, what would be the pH of the resulting solution?**
   A. 5 B. 7 C. 9 D. 14
9. **A base is a substance which will neutralize an acid. Which of these substances is not a base?**
   A. Aqueous ammonia B. Copper oxide C. Potassium chloride D. Sodium carbonate
10. **A strong acid:**
    A. Is always partially ionized when in solution B. Is always fully ionized when in solution
    C. Always decomposes carbonates D. Always contains oxygen
11. **Which one of the following oxides dissolves in water to form acidic solution?**
    A. MgO B. Na_2O C. SO_2 D. SiO_2
12. **When crystals of copper sulphate are heated, the colour changes from blue to white. This is caused by:**
    A. Loss of water only B. Loss of water and SO_2
    C. Reaction with CO_2 in the air D. Loss of water, sulphur dioxide and oxygen
13. **The oxide of a metal was found to react with HCl and aqueous NaOH solution. Which of the following is the best description of the oxide?**
    A. Acidic B. Amphoteric C. Basic D. Neutral

Answer Key with Explanations

<table>
<tr><th>Q. No</th><th>Ans.</th><th>Explanation</th></tr>
<tr><td>1.</td><td>A</td><td>

- Water can donate and accept proton (H^+). So it can act as Bronsted acid as well as base.
  $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
- Similarly, in water, oxygen has electron pairs which it can donate to other species, so water acts as Lewis base.



But water cannot act as Lewis acid.</td></tr>
<tr><td>2.</td><td>C</td><td>$HCl \rightleftharpoons H^+O + Cl^-$
0.01M 0.01M
Since HCl is a strong acid, it ionized completely giving $[H^+] = 0.01M = 10^{-2}M$
$pH = -\log[H^+]$
$pH = -\log 10^{-2}$
$pH = 2 \log 10$ $\log 10 = 1$
$pH = 2$</td></tr>
<tr><td>3.</td><td>B</td><td>$HCl + NH_3 \rightleftharpoons NH_4Cl$
Strong acid weak base Acidic salt
When NH_4Cl is added, the solution becomes acidic.</td></tr>
<tr><td>4.</td><td>D</td><td>
<table>
<tr><th>Salt</th><th>Type</th><th>Nature of Solution</th></tr>
<tr><td>NH_4NO_3
Ammonium Nitrate</td><td>Acidic Salt</td><td>Acidic solution</td></tr>
<tr><td>$CaCl_2$
Calcium chloride</td><td>Neutral salt</td><td>Somewhat neutral solution</td></tr>
<tr><td>K_2CO_3
Potassium carbonate</td><td>Basic salt</td><td>Basic solution</td></tr>
</table>
</td></tr>
<tr><td>5.</td><td>D</td><td>Solution
pH = 7 (Neutral)
pH > 7 (Basic)
pH < 7 (Acidic)</td></tr>
<tr><td>6.</td><td>B</td><td>When air is bubbled through pure water, CO_2 combines with water and forms carbonic acid.
$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)}$
As a result, pH of the solution decreases</td></tr>
<tr><td>7.</td><td>D</td><td>Lead oxide (PbO) is an amphoteric oxide.
$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$
(base) (acid)
$PbO + 2NaOH + H_2O \longrightarrow Na_2[Pb(OH)_4]$
(acid) (base)</td></tr>
<tr><td>8.</td><td>B</td><td>Concentration = Molarity × Volume of H^+ or OH^-
Since $[H^+] = [OH^-]$ in both cases, so a neutral solution having pH = 7 is formed.</td></tr>
<tr><td>9.</td><td>C</td><td>$KOH + HCl \longrightarrow KCl + H_2O$
Strong base Strong acid Neutral salt
KCl will not hydrolyse, so solution remains neutral.</td></tr>
<tr><td>10.</td><td>B</td><td>The strength of an acid depends upon its extent of ionization. A strong acid fully ionizes in solution.</td></tr>
<tr><td>11.</td><td>C</td><td>Generally – Metals form basic oxides
Non-metals form acidic oxides</td></tr>
</table>

		$SO_2 + H_2O \longrightarrow H_2SO_3$ (sulphurous acid) Acidic oxide
12.	A	When deep blue coloured solid copper (II) sulphate pentahydrate is heated to dry off water vapours, it forms white solid copper (II) sulphate.
13.	B	Aluminum oxide (Al_2O_3) is amphoteric and it reacts with both acidic and basic solution. $Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$ (basic) $Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)}$ (acidic)

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Why do the equilibrium constant value has its units for some of the reversible reactions but has no units for some other reactions?

Ans. i. If number of moles of reactants and products are equal, then K_c has no units.

$$\underset{1\ mol}{H_{2(g)}} + \underset{1\ mol}{I_{2(g)}} \rightleftharpoons \underset{2\ mol}{2HI}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(mol\ dm^{-3})^2}{(mol\ dm^{-3}.mol\ dm^{-3})} = \text{no units}$$

ii. If the number of moles of reactants and products are not equal.

$$\underset{4\ mol}{N_{2(g)} + 3H_{2(g)}} \rightleftharpoons \underset{2\ mol}{2NH_{3(g)}}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}][mol\ dm^{-3}]^3} = mol^{-2}\ dm^{+6}$$

Q.2 Define pH and pOH with mathematical expressions. What is the sum of pH and pOH?

Ans. pH: "The negative log of hydrogen ion concentration is called pH."

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

pOH: "The negative log of concentration of hydroxide ion is called pOH."

$$pOH = -\log[OH^-]$$

Relationship between pH and pOH:

$$pH + pOH = 14 \text{ at } 25°C$$

The sum of pH and pOH for a solution must be equal to 14 at 25°C.

Q.3 Write the relationship of pH and pOH with pK_w.

Ans. Relation of pH and pOH with pK_w:

From the concept of ionic product of water we have

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

Taking log: $\log K_w = \log[H^+]\ \log[OH^-]$

Now multiply with (–1)

$$-\log K_w = -\log[H^+] + (-\log[OH^-])$$

$$pK_w = pH + pOH$$

$$pH + pOH = 14 \text{ at } 25°C \qquad (\text{Since, } pK_w = 14 \text{ at } 25°C)$$

Thus, the sum of pH and pOH is equal to pK_w i.e., 14 at 25°C.

Q.4 What is ionization constant of acids.

Ans. Ionization Constant of Acids:

The ionization constants of the acids is the quantitative measure of the strength of the acid. Acids and bases when dissolved in water may or may not be completely dissociated. Many acids are weak electrolytes and they ionize to an extent which is less than 100%.

Q.5 Define Lowry Bronsted concept of acids and bases.

Ans. Bronsted Acid:

"Those species (ions or molecules) which donate or have a tendency to donate proton $[H^+]$ are called acids."

Example: $$\overset{H^+}{\curvearrowright}$$
$$\underset{Acid}{HCl} + \underset{Base}{H_2O} \rightleftharpoons H_3O^+ + Cl^-$$

Bronsted Base:

"These species (ions or molecules) which accept or have a tendency to accept proton (H^+) are called bases."

Q.6 What are conjugate acids and bases?

Ans. Conjugate Acid:

A conjugate acid is the specie (molecule or ion) formed when a proton is added to a base. **e.g.,**
When a weak acid or a weak base is dissolved in water, the conjugate acid base pair is produced.

e.g., $$\underset{acid}{CH_3COOH} + \underset{base}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{CH_3COO^-} + \underset{\text{conjugate acid}}{H_3O^+}$$

Conjugate base: The species (ions or molecules) formed when acid loses its H^+ ions and resulting species become its conjugate base.

Example:

$$\overset{H^+}{\curvearrowleft}$$
$$\underset{Base}{NH_3} + \underset{Acid}{H_2O} \rightleftharpoons NH_4^+ + OH^-$$

Conjugate acid-base Pair

When a weak acid or a weak base is dissolved in water, the conjugate acid base pair is produced.

Example:

$$\underset{acid}{CH_3COOH} + \underset{base}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{CH_3COO^-} + \underset{\text{conjugate acid}}{H_3O^+}$$

Q.7 What is the formula to calculate the percentage ionization of weak acid? (LHR 2018 GII)

Ans. Percentage of Ionization of Weak Acids:

We can calculate the percentage of ionization of weak acid and the formula is as follows:

$$\%\ \text{ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100$$

Q.8 Define pK_a and pK_b. Give its significance.

Ans. pK_a:

"The negative log of dissociation constant of acid (K_a) is called pK_a".

$$pK_a = -\log K_a$$

$$pK_a \propto \frac{1}{k_a}$$

pK_b:

"The negative log of K_b is called pK_b".

$$pK_b = -\log K_b$$

Significance:

- pK_a and pK_b gives us the quantitative strength of acids and bases respectively.
- Larger the value of pK_a, weaker will be the acid and vice versa.
- Larger the value of pK_b, weaker will be the base and vice versa.

Q.9 Prove that $pK_a + pK_b = 14$ at 25°C.

Ans. Let us take the log of equation:

$$\log(K_a \times K_b) = \log(K_w)$$

$$\log K_a + (\log K_b) = \log K_w$$

Multiply both sides by '−1'

$$-\log K_a - \log K_b = -\log K_w$$

Since, $pK_a = -\log K_a$ and $pK_b = -\log K_b$

So, $pK_a + pK_b = pK_w = 14$

Hence pK_a and pK_b of conjugate acid base pair has a very simple relation with each other.

$$pK_a + pK_b = 14 \text{ at } 25°C$$

Q.10 What is ionic product of water? Write its value at 25°C.

Ans. Ionic Product of Water:

The product of molar concentration of H^+ and OH^- in pure water is called ionic product of water. It is represented by K_w and its value is 10^{-14} at 25°C.

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

$$K_w = 10^{-14} \text{ at } 25°C$$

Q.11 What is buffer solution? Give types of buffer solution with one example each.

Ans. Buffer Solutions:

"These solutions which resist the change in their pH when a small amount of an acid or a base is added to them are called Buffer solution."

The buffer solutions have a specific constant value of pH.

The pH values of buffer solutions do not change on dilution and on keeping for a long time.

Types of Buffer Solutions: Buffer solutions are mostly prepared by mixing two substances.

Acidic Buffers	Basic Buffers
• These buffers which are formed by the mixing of a weak acid and a salt of it with a strong base are called acidic buffers.	• These buffers which are formed by mixing of a weak base and a salt of it with a strong acid are called basic buffers.
• Their pH is usually less than 7.	• Their pH is more than 7.
• Henderson's equation for acidic buffers $pH = pK_a + \log\frac{[salt]}{[acid]}$	• Henderson's equation for basic buffers $pOH = pK_b + \log\frac{[salt]}{[base]}$
e.g., CH_3COOH + CH_3COONa weak acid salt of weak acid	e.g., NH_4OH + NH_4Cl weak base salt of weak base

Q.12 Define buffer capacity. Write down the Henderson's equation for acidic buffers.

Ans. Buffer Capacity:

"The capability of a buffer solution to resist the change in its pH when a small amount of acid or a base is added in it is called buffer capacity."

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

Q.13 Define common ion effect. How can NaCl be purified by common ion effect?

Ans. Common Ion Effect:

"The suppression of ionization of a weak electrolyte by adding a common ion from outside is called common ion effect."

Example: Purification of NaCl:

NaCl is purified by passing hydrogen chloride gas through the saturated brine. Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$K_c = \frac{[Ha^+][Cl^-]}{[NaCl]}$$

HCl also ionizes in solution.

$$HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

On passing HCl gas, concentration of Cl^- ions is increased. Therefore, NaCl crystallizes out of the solution to maintain the constant value of equilibrium constant. This type of effect is called common ion effect.

$$Na^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons NaCl_{(s)}$$

The addition of a common ion to the solution of less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

Q.14 Give applications of common ion effect (any two).

Ans. Applications of Common Ion Effect:

- **Precipitation of 2nd Group Basic Radicals of Salt Analysis:**
  The dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion. H_2S becomes less dissociated in acidic solution. In this way, low concentration of S^{-2} is developed.
  $$H_2S \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$
  This low concentration of S^{2-} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.
  $$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$
- **Precipitation of 3rd Group Basic Radicals of Salt Analysis:**
  An addition of NH_4Cl in NH_4OH solution suppresses the concentration of $OH^-_{(aq)}$ due to the presence [illegible] large excess of NH_4^+ from NH_4Cl. Actually, NH_4Cl is a strong electrolyte. The combination of these two substances is used as reagent in third group basic radicals.
  $$NH_4Cl_{(aq)} \rightleftharpoons Na^+_{4(aq)} + Cl^-_{(aq)}$$
  $$NH_4OH_{(aq)} \rightleftharpoons Na^+_{4(aq)} + OH^-_{(aq)}$$

Q.15 Write the effect of common ion on solubility. Prove by equations that what happens when Na_2CrO_4 is added to saturated solution of $PbCrO_4$?

Ans. Effect of Common Ion on Solubility:

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$$

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^+_{(aq)} + CrO_4^{2-}$$

Now add Na_2CrO_4, which is a soluble salt. CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

Q.16 Define Solubility Product Constant (K_{sp}). Give two examples.

Ans. Solubility Product:

"The product of the equilibrium concentration of ions raised to an exponent equal to the coefficient of the balanced equation at given temperature is called solubility product (K_{sp})."

Mathematical Form:

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

$$K_c = \frac{[A^{+y}]^x[B^{-x}]^y}{[A_xB_y]}$$

$$K_c\,[A_xB_y] = [A^{+y}]^x[B^{-x}]^y$$

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

- K_{sp} is the product of molar solubilities of two ions at equilibrium.

Examples:

1. When Lead Chloride ($PbC\ell_2$) is shaken with water, the solution contains Pb^{+2}, $C\ell^-$ and un-dissociated $PbC\ell_2$. It means an equilibrium exists between $PbC\ell_2$ (solid solute) and the dissolved ions, Pb^{+2} and $C\ell^-$.

$$PbC\ell_{2(s)} \rightleftharpoons PbC\ell_{2(aq)} \rightleftharpoons Pb^{+2}_{(aq)} + 2C\ell^-_{(aq)}$$

According to law of mass action:

$$K_c = \frac{[Pb^{+2}][C\ell^-]^2}{[PbC\ell_2]}$$

$$K_c\,[PbC\ell_2] = [Pb^{+2}][C\ell^-]^2$$

$$K_{sp} = [Pb^{+2}][C\ell^-]^2 = 1.6 \times 10^{-5} \text{ at } 25°C$$

2. **Solubility Product Expression for Ag_2CrO_4:**

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{-2}$$

$$K_c = \frac{[Ag^+]\,[CrO_4^{-2}]}{[Ag_2CrO_4]}$$

$$K_c\,[Ag_2CrO_4] = [Ag^+][CrO_4^{-2}]$$

$$K_{sp} = [Ag^+]^2\,[CrO_4]^{-2} = 2.6 \times 10^{-12} \text{ at } 25°C$$

◆ ◆ ◆ ◆ ◆

SELF-ASSESSMENT Chapter # 09

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) Given the following reaction:

$$NH_{3(g)} + H_2O_{(l)} \longrightarrow NH^+_{4(aq)} + OH^-_{(aq)}$$

A. NH_3 is the acid, H_2O is the base
B. NH_3 is the base, H_2O is the acid
C. NH_4^+ is the base, OH^- is the acid
D. H_2O is the base, OH^- is the acid

(ii) In the given reaction, the conjugate base is:

$$NH_3 + HC\ell \longrightarrow NH_4^+ + C\ell^-$$

A. NH_3
B. $C\ell^-$
C. NH_4^+
D. $HC\ell$

(iii) Which statement correctly describes a Lewis acid?

A. Accepts a lone pair of electrons
B. Donates a lone pair of electrons
C. Always donates protons
D. Has a negative charge

(iv) If the pH of a solution is 11, what is the $[OH^-]$ concentration in the solution?

A. 1×10^{-3} M
B. 1×10^{-11} M
C. 1×10^{-2} M
D. 1×10^{-14} M

(v) The solubility product of $AgC\ell$ is 2.0×10^{-10} mol dm^{-6}. The maximum concentration of Ag^+ ions in the solution is:

A. 2.0×10^{-10} mol dm^{-3}
B. 1.41×10^{-5} mol dm^{-3}
C. 1×10^{-10} mol dm^{-3}
D. 4.0×10^{-20} mol dm^{-3}

(vi) Which indicator is typically used for titrations involving strong acids and strong bases?

A. Methyl red
B. Phenolphthalein
C. Bromothymol blue
D. Litmus solution

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) Identify the Lewis acid and Lewis base in the reaction between:
(a) SO_3 and O^{2-} (b) $HC\ell$ and H_2O
Also write down the balanced chemical equation for the reaction and explain
(ii) Calculate the pH of a 0.01 M NaOH solution.
(iii) Determine $[H_3O^+]$ in a 0.01 M HA solution given $K_a = 1.0 \times 10^{-6}$.
(iv) Define common ion effect. Give a suitable example.
(v) Differentiate end point and equivalent point.
(vi) A solution is prepared by mixing equal volumes of two solutions: one with a pH of 4.0 and another with a pH of 10.0. Calculate the K_W for this mixture at 25°C.
(vii) How does a buffer maintain pH stability?
(viii) Why is aqueous solution of $NH_4C\ell$ slightly acidic?

Q.3 Extensive Questions. **(2 × 4 = 8)**

(a) Describe the Bronsted-Lowry theory of acids and bases. Provide examples of conjugate acid-base pairs and explain clearly their relationship.
(b) The molar solubility of silver chromate (Ag_2CrO_4) in pure water at 298 K is 6.5×10^{-5} mol dm^{-3}. Calculate the K_{sp} of silver chromate at this temperature.

◆

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Chapter 10

ELECTROCHEMISTRY

Student Learning Outcomes

After studying this chapter, students will be able to:

- Define the terms redox, oxidation, reduction, and disproportionation (in terms of electron transfer and changes in oxidation number). **(Knowledge)**
- Apply the concept of oxidation numbers in identifying oxidation and reduction reactions. **(Application)**
- Identify the oxidizing and reducing agents in a redox reaction. **(Knowledge)**
- Describe the role of oxidizing and reducing agents in the redox reaction. **(Understanding)**
- Apply the concept of changes in oxidation numbers to balance chemical equations. **(Application)**
- Explain how electrolytic cells convert electrical energy to chemical energy, with oxidation at the anode and reduction at the cathode. **(Understanding)**
- Predict the identities of substances liberated during electrolysis based on the state of the electrolyte, position in the redox series, and concentration. **(Knowledge)**
- Apply the relationship between the Faraday constant, Avogadro constant, and the charge on the electron to solve problems. **(Application)**
- Calculate the quantity of charge passed during electrolysis and the mass or volume of substance liberated during electrolysis. **(Application)**
- Deduce the Avogadro constant by an electrolytic method. **(Application)**
- Define the terms standard electrode potential and standard cell potential. **(Knowledge)**
- Describe the standard hydrogen electrode (SHE) and methods used to measure standard electrode potentials. **(Understanding)**
- Calculate the standard cell potentials by combining the potentials of two standard electrodes and then use these to predict the feasibility of a reaction and the direction of electron flow in a simple cell. **(Application)**
- Deduce the relative reactivity of elements compounds, and ions as oxidizing agents or reducing agents from their electrode potential values. **(Application)**
- Construct redox equations using relevant half-equations. **(Application)**
- Explain how voltaic (galvanic) cells convert energy from spontaneous, exothermic chemical processes to electrical energy, with oxidation at the anode and reduction at the cathode. **(Understanding)**
- Explain how voltaic cells convert chemical energy from redox reactions to electrical energy using $Cu-Zn$ galvanic cell as an example. **(Understanding)**
- Explain how electrode potentials vary with the concentrations of aqueous ions and use the Nernst equation to predict this quantitatively. **(Understanding)**
- Explain the concept of the activity series of metals and how it relates to the ease of oxidation. **(Understanding)**
- Deduce the feasibility of redox reactions from activity series or reaction data. **(Understanding)**
- Explain the merits of photovoltaic cells as sustainable ways of meeting energy demands by making reference to the photovoltaic principle. **(Understanding)**
- Explain the use of the Winkler Method to measure biochemical oxygen demand (BOD) and its use as a measure of water pollution. **(Understanding)**

The branch of chemistry which deals with inter conversion of electrical and chemical energy i.e., electrical energy into chemical energy and chemical energy into electrical energy is called **electrochemistry.**

OXIDATION, REDUCTION, AND REDOX REACTIONS

Interesting Information!

Photosynthesis is a redox reaction which provides food for the entire planet, and another one is respiration that keeps you alive, both are redox reactions.

Rack Your Mind!

1. **Calculate the oxidation number of Cr in K_2CrO_4.**

Oxidation is a process involving loss of electron or electrons.

$$Fe^{+2} \longrightarrow Fe^{+3} + e^-$$
$$Zn^{\circ} \longrightarrow Zn^{+2} + e^-$$

Here Fe^{+2} and Zn^0 have lost electrons, therefore they are oxidized.

Reduction is a process involving gain of electron or electrons.

$$C\ell^{\circ} + e^- \longrightarrow C\ell^{-1}$$
$$Cu^{+2} + 2e^- \longrightarrow Cu^{\circ}$$

In these examples, $C\ell^{\circ}$ and Cu^{+2} have gained electrons; therefore, they are reduced.

Differences between Oxidation and Reduction:

Sr. No.	Oxidation	Reduction
1.	The addition of oxygen in a specie is called oxidation. e.g., $S + O_2 \longrightarrow SO_2$ $C + O_2 \longrightarrow CO_2$ $2CO + O_2 \longrightarrow 2CO_2$ In these examples, oxygen is added to S, C and CO.	The removal of oxygen or an electronegativity element from a specie is called reduction. e.g., $ZnO + C \longrightarrow Zn + CO$ $CuO + C \longrightarrow Cu + CO$ $2FeC\ell_3 + H_2 \longrightarrow 2FeC\ell_2 + 2HC\ell$
2.	The removal of hydrogen is also called oxidation. e.g., $H_2S + C\ell_2 \longrightarrow 2HC\ell + S$ $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ So, H_2S and CH_4 are oxidized.	The addition of hydrogen to a specie is called reduction. e.g., $H_2S + Br_2 \longrightarrow 2HBr + S$ Here bromine gets reduced as it gains hydrogen to form HBr. $H_2C = CH_2 + H_2 \longrightarrow H_3C - CH_3$
3.	Loss of electron/s and hence decrease in oxidation number is called oxidation. e.g., $Zn \longrightarrow Zn^{2+} + 2e^-$ Here Zn is oxidized to form Zn^{2+} ions.	Gain of electrons and hence decrease in oxidation number is called reduction. e.g., $Zn^{2+} + 2e^- \longrightarrow Zn$ Here Zn^{2+} is reduced to form Zn.
4.	In electrochemical cells, oxidation takes place at anode.	In electrochemical cells, reduction takes place at cathode.

➢ **Redox Reactions**

"Those reactions in which one species (atom, ion or molecule) is **oxidized** while other is **reduced** are called redox reactions".

There are two ways of finding out whether or not a substance has been oxidized or reduced during a chemical reaction:

- Electron transfer
- Changes in oxidation number

Oxidation Number rules can be applied to any compound, whether ionic or covalent species.

OXIDATION NUMBER AND ITS SIGNIFICANCE

Definition

"An oxidation number is a number given to each atom or ion in a compound that shows us its degree of oxidation."

Or

"It is the apparent charge on an atom (per atom) of an element in a molecule or an ion."

- The oxidation numbers are also called oxidation states.
- Oxidation numbers can be positive, negative or zero. The + or − sign must always be included.
- Higher positive oxidation numbers mean that an atom or ion is more oxidized.
- Higher negative oxidation numbers mean that an atom or ion is more reduced.

Oxidation Number Rules

Rack Your Mind!

2. **In all oxidation reactions, atoms of an element in a chemical species lose electrons and increase their:**
   - (a) Oxidation state
   - (b) Electrode
   - (c) Reductions
   - (d) Negative charges

The oxidation number of any atom or ion can be deduced by using oxidation number rules. It is important to note that an oxidation number refers to a single atom in a compound.

i. The oxidation number of any uncombined element is zero. For example, the oxidation number of each atom in $S_8, H_2, C\ell_2$, Na, Mg and Zn is zero.

ii. In either a compound or an ion, the more electronegative element is given the negative oxidation number. In HF, fluorine has −1 oxidation number.

iii. In compounds, many atoms or ions have fixed oxidation numbers, group 1 alkali metals are always +1, group 2 alkaline earth elements are always +2, group 17 halogens in binary compounds are always −1, hydrogen is +1 (except in metal hydrides, such as NaH, where it is −1), oxygen is −2 (except in peroxides, where it is −1, and in F_2O, where it is +2).

iv. The oxidation number of an element in a mono-atomic ion is always the same as the charge on the ion, for example, $C\ell^-$ is −1, $A\ell^{3+}$ is +3.

v. The sum of the oxidation numbers in a compound is **zero**. In neutral molecules, the algebraic sum of the oxidation numbers of all the elements is zero. e.g., In HCℓ (+1 − 1 = 0), NaCℓ (+1 − 1 = 0).

vi. In polyatomic ions, the algebraic sum of oxidation number equals the charge on the ion. e.g., NH_4^+, CO_3^{-2} and SO_4^{-2}.

vii. For transition metals and many non-metals, Ox. No. cannot be fixed as they show variable Ox states. Therefore, there Ox. Nos. are always determined by calculations.

While applying the oxidation number rules in the following examples, 'Ox. No.' as an abbreviation for oxidation number is used.

KEEP IN MIND

- Hydrogen shows −1 oxidation state with all metals.
- Hydrogen shows +1 oxidation state with all non-metals.
- Oxygen shows negative oxidation state with all metals.
- Oxygen shows negative oxidation state with all non-metals except fluorine.
- Oxygen shows −2, −1 and −1/2 in H_2O, Na_2O_2, and KO_2 respectively.

Finding Oxidation Number of an Element in a Compound or a Radical

The oxidation number or state of any atom of an element present in a compound or a radical can be determined by making use of the above-mentioned rules.

➢ **Compounds of a Metal with a Non-metal**

A metal always has the positive Ox. No. and nonmetals have the negative Ox. State. For example, in sodium sulfide, $Na_2\underline{S}$:

$$2(+1) + S = 0$$
$$+2 + S = 0$$
$$S = -2$$

- **Compounds of a Non-metal with a Non-metal**

  In compounds containing two different non-metals, the sign of the Ox. No. depends on the electronegativity of each atom. The most electronegative element is given the negative sign.

Sample Problem 10.1

Find the oxidation No. of S in Sulfur dioxide, SO_2.

Ox. No. of each O atom = −2

For two oxygen atoms = 2 × (−2) = −4

SO_2 has no charge, so the total Ox. No. is zero. So,

$$S + 2(-2) = 0$$
$$S - 4 = 0$$
$$S = +4$$

Ox. No. of S = +4

Compound Ions

Compound ions are ions with two or more different atoms. **Examples** are the sulfate ion, SO_4^{2-}, and the nitrate ion, NO_3^-.

Sample Problem 10.2

Calculate the oxidation number (Ox. No.) of Sulphur in SO_4^{2-}.

Solution:

$$[\text{Ox. No. of S}] + 4[\text{Ox. No. of O}] = -2$$
$$S + 4(-2) = -2$$
$$S = +6$$

Thus, the oxidation number of sulphur in SO_4^{2-} is +6.

Rock Your Mind!

3. In NaOCl the oxidation number of Cl is:

(a) −8 (b) +8

(c) −6 (d) +1

☑ QUICK CHECK 10.1

a) Define oxidation and reduction in terms of electron transfer with examples.

Ans. Oxidation: The loss of electrons by a substance.

Example:

$$Na \longrightarrow Na^+ + e^-$$

Sodium loses one electron — **oxidation**.

Reduction: The gain of electrons by a substance.

Example:

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

Chlorine gains electrons — **reduction**.

b) Define oxidation and reduction in terms of change in oxidation number with examples.

Ans. Oxidation: The process involving increase in oxidation number is called Oxidation.

Example:

$$Fe_2^+ \longrightarrow Fe_3^+ + e^-$$

Oxidation number increases from +2 to +3 — **oxidation**.

Reduction: The process to decrease in oxidation number is called reduction.

Example:

$$Cl_2 \longrightarrow 2Cl^-$$

Oxidation number decreases from 0 to −1 — reduction.

c) Determine Ox. No. of:

i) Oxygen (N) in Na_2O

Ans. Oxygen (O) in Na_2O

Let oxidation number of oxygen = x

Na = +1

2(+1)+x = 0 ⇒ 2 + x = 0 ⇒ x = −2 Oxidation no. of O in Na_2O = −2

ii) Iodine (I) in ICl_3

Ans. Iodine (I) in ICl_3

Let Iodine = x, Chlorine = −1

x+3(−1) = 0 ⇒ x−3 = 0 ⇒ x = +3 Oxidation no. of I in ICl_3 = + 3

iii) Nitrogen (N) in NO_3^{1-}

Ans. Nitrogen (N) in NO_3^-

Let N = x, O = −2

x+3(−2) = −1 ⇒ x−6 = −1 ⇒ x = +5 Oxidation no. of N in NO_3^- = +5

iv) Chromium (Cr) in $K_2Cr_2O_7$

Ans. Chromium (Cr) in $K_2Cr_2O_7$

K = +1, O = −2, Cr = x

2(+1)+2(x)+7(−2) = 0

⇒ 2 + 2x − 14 = 0 ⇒ 2x = 12 ⇒ x = +6 Oxidation no. of Cr in K_2CrO_7 = +6

v) Manganese (Mn) in $KMnO_4$.

Solution:

(Ox. No. of K) + (Ox. No. of Mn) + 4(Ox. No. of O) = 0

$$+1 + Mn + 4(-2) = 0$$
$$(+1) + Mn - 8 = 0$$

or $Mn = +7$ Oxidation no. of Mn in $KMnO_4$ = +7

DISPROPORTIONATION REACTION

Disproportionation Reaction

A chemical reaction where a single substance (a species i.e. molecule, atom or ion) acts as both the oxidizing and reducing agent, resulting in two different products with different oxidation states.

This type of reaction involves the simultaneous oxidation and reduction of the same element.

- **Example 1:**

The decomposition of hydrogen peroxide (H_2O_2) to form water (H_2O) and oxygen (O_2) is a disproportionation reaction:

$$2H_2O_2 \longrightarrow H_2O_2^{-1} + O_2^0$$

Oxidation number of oxygen in H_2O_2 = −1

Oxidation number of oxygen in H_2O = −2 (Oxygen is reduced from −1 to −2)

Oxidation number of oxygen in O_2 = 0 (Oxygen is oxidized from −1 to 0)

Rock Your Mind!

4. What are redox reactions? Give an example.

- **Example 2:**

$$6NaOH_{(aq)} + 3Cl^0_{2(g)} \rightarrow 5NaCl^{-1}_{(aq)} + NaCl^{+5}O_{3(aq)} + 3H_2O$$

Oxidation number of chlorine atoms in Cl_2 = 0

Oxidation number of chlorine in NaCl = −1 (Cl is reduced from 0 to −1)

Oxidation number of chlorine in $NaClO_3$ = +5 Cl is (oxidized from 0 to +5)

Important: Disproportionation reactions can occur where ions or molecules can exist in multiple oxidation states in a reaction.

OXIDIZING AGENT (OXIDANT) AND REDUCING AGENT (REDUCTANT)

Oxidizing Agent	Reducing Agent
An oxidizing agent (atom, ion or molecule) is that substance which oxidizes some other substance, and is itself reduced to a lower oxidation state by gaining one or more electrons.	A reducing agent (atom, ion or molecule) is that substance which reduces some other substance, and is itself oxidized to a higher oxidation state by losing one or more electrons.
If an element M gains one or more electrons and is converted into M^- anion, the element M is said to be acting as an oxidizing agent, since it withdraws an electron from the other atom, in this process oxidation number of M has decreased that is: **For oxidizing agent** $X + e^- \longrightarrow X^-$ [Ox. No. = 0] [Ox. No. = −1] (Higher Oxidation State) (Lower Oxidation State) **For example,** $C\ell + e^- \longrightarrow C\ell^-$	If an element M loses one electron and is converted to M^+ cation, the element M is said to be acting as a reducing agent, since it is providing electrons, it gets higher oxidation state. Thus, **For reducing agent** $M \longrightarrow M^+ + e^-$ [Ox. No. = 0] [Ox. No. = −1] (Lower Oxidation State) (Higher Oxidation State) **For example,** $Na \longrightarrow Na^+ + e^-$

☑ QUICK CHECK 10.2

a) **Identify the oxidized species and reduced species in the following equation. Also identify the oxidizing and reducing agents on the reactant side.**

i. $Fe_2O_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$

Ans.

1. **Assign Oxidation Numbers (O.N.):**
   - **Fe_2O_3:** O is −2. So, 2(O.N. of Fe) + 3(−2) = 0 ⇒ 2(O.N. of Fe) = +6 ⇒ O.N. of Fe = **+3**.
   - **CO:** O is −2. So, O.N. of C + (−2) = 0 ⇒ O.N. of C = **+2**.
   - **Fe:** O.N. of Fe = **0** (elemental form).
   - **CO_2:** O is −2. So, O.N. of C + 2(−2) = 0 ⇒ O.N. of C = **+4**.
2. **Identify Changes in O.N.:**
   - **Fe:** O.N. changes from +3 in Fe_2O_3 to 0 in Fe. (Decrease in O.N.)
   - **C:** O.N. changes from +2 in CO to +4 in CO_2. (Increase in O.N.)
   - **O:** O.N. remains -2 throughout.
3. **Identify Oxidized and Reduced Species:**
   - **Reduced Species:** Fe in Fe_2O_3 is reduced (its O.N. decreases from +3 to 0). So, Fe_2O_3 is the species containing the element that is reduced.
   - **Oxidized Species:** C in CO is oxidized (its O.N. increases from +2 to +4). So, **CO** is the species containing the element that is oxidized.
4. **Identify Oxidizing and Reducing Agents (on reactant side):**
   - **Oxidizing Agent:** The species that causes oxidation and gets reduced itself. Fe_2O_3 gets reduced. So, Fe_2O_3 is the oxidizing agent.
   - **Reducing Agent:** The species that causes reduction and gets oxidized itself. CO gets oxidized. So, CO is the reducing agent.

ii. $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

Ans.

1. **Assign Oxidation Numbers (O.N.):**
   - **CH_4:** H is +1. So, O.N. of C + 4(+1) = 0 ⇒ O.N. of C = **−4**.
   - **O_2:** O.N. of O = **0** (elemental form).

   - **CO_2:** O is −2. So, O.N. of C + 2(−2) = 0 ⇒ O.N. of C = **+4**.
   - **H_2O:** H is +1, O is −2. O.N. of O = **−2**.
2. **Identify Changes in O.N.:**
   - **C:** O.N. changes from −4 in CH_4 to +4 in CO_2. (Increase in O.N.)
   - **O:** O.N. changes from 0 in O_2 to −2 in CO_2 and H_2O. (Decrease in O.N.)
   - **H:** O.N. remains +1 throughout.
3. **Identify Oxidized and Reduced Species:**
   - **Oxidized Species:** C in CH_4 is oxidized (its O.N. increases from −4 to +4). So, CH_4 is the species containing the element that is oxidized.
   - **Reduced Species:** O in O_2 is reduced (its O.N. decreases from 0 to −2). So, O_2 is the species that is reduced.
4. **Identify Oxidizing and Reducing Agents (on reactant side):**
   - **Oxidizing Agent:** The species that causes oxidation and gets reduced itself. O_2 gets reduced. So, O_2 is the oxidizing agent.
   - **Reducing Agent:** The species that causes reduction and gets oxidized itself. CH_4 gets oxidized. So, CH_4 is the reducing agent.

b) **Identify the species in the following reaction which undergoes both oxidation and reduction.**

i. $2NaO_{2(s)} + 2H_2O_{(l)} \rightarrow 4NaOH_{(aq)} + O_{2(g)}$

Ans.

1. Identify oxidation states:
- In NaO_2 (Sodium superoxide)
- Na is always + 1
- Let the oxidation state of O be x
- So: $+1 + 2x = 0 \Rightarrow 2x = -1 \Rightarrow x = -\frac{1}{2}$

Each oxygen in O_2^-
- In NaOH:
  O is −2
- In O_2 (oxygen gas)
  O is 0

2. What happening to oxygen
- In NaO_2:
  Oxygen starts at −1/2

Products:
- Some oxygen atoms become −2 in NaOH → reduction
- Some become 0 in O_2 gas → oxidation

The species that undergoes both oxidation and reduction is:
The superoxide ion (O_2^-) in NaO_2
It disproportionate:
- Part of it is oxidaized to O_2 (0)
- Part of it is reduced to OH^- (via NaOH, where O is −2)

ii. $P_{4(s)} + 3OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow PH_{3(g)} + 3H_2PO^-_{2(aq)}$

Ans.

1. **Assign Oxidation Numbers (O.N.) of Phosphorus in each species:**
   - **P_4 (White phosphorus):** O.N. of P = **0** (elemental form).
   - **PH_3 (Phosphine):** H is +1. So, O.N. of P + 3(+1) = 0 ⇒ O.N. of P = **−3**.
   - **H_2PO_2 (Hypophosphite ion):** H is +1, O is −2. So, 2(+1) + O.N. of P + 2(−2) = −1 (charge of the ion)
     ⇒ +2 + O.N. of P − 4 = −1 ⇒ O.N. of P − 2 = −1 ⇒ O.N. of P = **+1**.
   - (O and H in OH^- and H_2O do not change their usual oxidation states).

2. **Analyze the changes for Phosphorus:**
   - In the reactant P_4, P has an O.N. of 0.
   - In the product PH_3, P has an O.N. of −3 (Reduction: 0 → −3, decrease).
   - In the product H_2PO_2, P has an O.N. of +1 (Oxidation: 0 → +1, increase).
3. **Conclusion:**
   The species that undergoes both oxidation and reduction is Phosphorus in P_4. (Or you can say the species is P_4 itself).

BALANCING OF REDOX EQUATIONS BY OXIDATION NUMBER METHOD

The following steps are carried out for balancing of redox equations by oxidation number method:

i. Write down the skeleton equation of the redox reaction under consideration.

ii. Identify the elements, which undergo a change in their oxidation number during the reaction.

iii. Record the oxidation number above the symbols of the element, which have undergone a change in the oxidation number.

iv. Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation. It shows number of electrons gained or lost.

v. Equate the increase or decrease in the oxidation number, i.e., electrons gained or lost by multiplying with a suitable digit.

vi. Balance the rest of the equation by inspection (hit and trial) method.

Did You Know?

Sequence of the balancing the chemical equation using inspection (hit and trial) method.

- Firstly, balance atoms of all elements except nitrogen, oxygen and hydrogen.
- Secondly, balance atoms of nitrogen (if in the equation).
- Thirdly, balance atoms of oxygen (if in the equation).
- Lastly, balance atoms of hydrogen (if in the equation).

KEEP IN MIND

a) If an element in a species undergoes only increase in oxidation number or decrease in oxidation number in a reaction. The specie containing such element is written once on the RHS of the equation.

$$Zn_{(s)} + HC\ell_{(aq)} \longrightarrow ZnC\ell_{2(aq)} + H_{2(g)}$$

b) If an element in a species undergoes both increase in oxidation number or decrease in oxidation number simultaneously in a reaction (as in case of self-redox or disproportionation reaction). The specie containing such element is written twice on the RHS of the equation. First for increase in oxidation number while second is written for decrease in oxidation number.

$$C\ell_2 + NaOH + C\ell_2 \longrightarrow NaC\ell + H_2O + NaOC\ell$$

c) If an element in a species undergoes increase or decrease in oxidation number as well as no change in oxidation number in a reaction. The specie containing such element is also written twice. First, for change in oxidation number while second is for no change in oxidation number.

$$HNO_3 + Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O + NO_2$$

$$HC\ell + K_2Cr_2O_7 + HC\ell \longrightarrow C\ell_2 + KC\ell + CrC\ell_3 + H_2O$$

Sample Problem 10.4

Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + HC\ell \rightarrow KC\ell + CrC\ell_3 + C\ell_2 + H_2O$$

Solution:

1. Write down the skeleton of chemical equation.

$$K_2Cr_2O_7 + HC\ell \longrightarrow C\ell_2 + KC\ell + CrC\ell_3 + H_2O$$

2. Write down the oxidation number of each element.

$$K_2^{1+}Cr_2^{6+}O_7^{2-} + H^{1+}C\ell^{1-} \longrightarrow C\ell_2^{0} + K^{1+}C\ell^{1-} + Cr^{3+}C\ell_3^{1-} + H_2^{1+}O^{2-}$$

3. Identify the elements that show change in oxidation number on both sides.

$$\overbrace{K_2^{1+}Cr_2^{6+}O_7^{2-} + H^{1+}C\ell^{1-} \rightarrow C\ell_2^{0} + K^{1+}C\ell^{1-} + Cr^{3+}}^{6e}C\ell_3^{1-} + H_2^{1+}O^{2-}$$

$$\underbrace{C\ell^{1-} \rightarrow C\ell_2^{0}}_{2e}$$

Here, Cr undergoes a change in oxidation state from +6 to +3 and it is reduced (acts as an oxidizing agent) while Cℓ undergoes a change in oxidation state from −1 to 0 and it is oxidized (acts as a reducing agent).

4. Write two half reactions separately i.e., reduction and oxidation reactions

$$K_2Cr_2^{6+}O_7 \longrightarrow 2Cr^{3+}C\ell_3 \text{ Half reduction reaction } \underline{\qquad\qquad} \text{(ii)}$$

$$2HC\ell^{1-} \longrightarrow C\ell_2^{0} \text{ Half oxidation reaction } \underline{\qquad\qquad} \text{(iii)}$$

Decrease in Ox. No. of Cr is 6 units for one molecule of $K_2Cr_2O_7$.

Increase in Ox. No. of Cℓ is 2 units for 2 molecules of HCℓ.

Eq. (iii) is multiplied by 3 in order to equalize the loss of electrons and the gain of electrons i.e., 6 electrons in this equation.

$$3 \times 2HC\ell \longrightarrow 3C\ell_2$$

$$6HC\ell \longrightarrow 3C\ell_2 \underline{\qquad\qquad} \text{(iv)}$$

Now eq. (i) becomes:

$$K_2Cr_2O_7 + 6HC\ell \longrightarrow 3C\ell_2 + KC\ell + 2CrC\ell_3 + H_2O$$

5. Rest of the following equation is balanced by inspection method:

$$K_2Cr_2O_7 + 6HC\ell \longrightarrow 3C\ell_2 + 2KC\ell + 2CrC\ell_3 + H_2O$$

To balance Cℓ and K, 14 molecules of HCℓ and 2 KCℓ molecules are required, therefore, we add 8 HCℓ to left hand side

$$8HC\ell + K_2Cr_2O_7 + 6HC\ell \longrightarrow 2CrC\ell_3 + 3C\ell_2 + 2KC\ell + H_2O$$

To balance hydrogen and oxygen, $6H_2O$ are added to RHS.

Hence, the balanced equation is,

$$K_2Cr_2O_7 + 14HC\ell \longrightarrow 2KC\ell + 2CrC\ell_3 + 3C\ell_2 + 7H_2O$$

☑ QUICK CHECK 10.3

Balance the given equations by oxidation number method.

I. $Fe_2O_{3(s)} + CO_{(g)} \longrightarrow Fe_{(s)} + CO_{2(g)}$

Ans. Step 1: Oxidation numbers

- **Fe in Fe_2O_3: +3 → Fe: 0 (reduced)**
- **C in CO: +2 → C in CO_2: +4 (oxidized)**

Step 2: Determine changes

- **Fe: +3 → 0 (gain of 3 electrons per Fe, 2 Fe atoms = 6 e^- gain)**
- **C: +2 → +4 (loss of 2 electrons per C atom)**

Step 3: Equalize e^- transfer

- **Multiply CO by 3 and Fe_2O_3 by 1**

Balanced equation:

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

ii. $MnO_2 + HC\ell \rightarrow MnC\ell_2 + H_2O + C\ell_2$

Ans. Step 1: Oxidation numbers

- Mn in MnO_2: +4 → Mn in $MnC\ell_2$: +2 (reduced)
- $C\ell$ in $HC\ell$: −1 → $C\ell_2$: 0 (oxidized)

Step 2: Determine changes

- Mn: +4 → +2 (gain of 2 electrons)
- $C\ell$: −1 → 0 (loss of 1 electron per $C\ell$ atom; $C\ell_2$ = 2 $C\ell$ atoms = $2e^-$ lost)

Step 3: Equalize e^- transfer

- $2C\ell^-$ oxidized = $2e^-$ loss
- 1 Mn^{4+} reduced = $2e^-$ gain → already equal

Balanced equation:

$$MnO_2 + 4HC\ell \longrightarrow MnC\ell_2 + 2H_2O + C\ell_2$$

iii. $Fe^{2+}_{(aq)} + MnO^{4}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)}$

Ans. Step 1: Oxidation numbers

- $Fe^{2+} \rightarrow Fe^{3+}$ (oxidation, loss of 1 e^-)
- Mn^{7+} in $MnO_4^- \rightarrow Mn^{2+}$ (reduction, gain of 5 e^-)

Step 2: Equalize electrons

- Multiply $Fe^{2+} \rightarrow Fe^{3+}$ by 5

Step 3: Balance rest (acidic medium)

- $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Balanced equation:

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

iv. $K_2Cr_2O_{7(aq)} + FeSO_{4(aq)} + H_2SO_{4(aq)} \longrightarrow Cr_2(SO_4)_{3(aq)} + Fe_2(SO_4)_{3(aq)} + K_2SO_{4(aq)} + H_2O_{(\ell)}$

Ans. Step 1: Oxidation numbers

- Cr in $Cr_2O_7^{2-}$: +6 → Cr^{3+}: +3 (reduction, gain of $3e^-$ per Cr)
- $Fe^{2+} \rightarrow Fe^{3+}$: oxidation (loss of $1e^-$)

Step 2: $Cr_2O_7^{2-}$ contains 2 Cr → $6e^-$ gained

- Therefore, 6 Fe^{2+} needed (each loses $1e^-$)

Balanced half reactions:

- $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
- $6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

Combine:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Include sulphates and potassium:

- $Cr_2O_7^{2-} \rightarrow Cr_2(SO_4)_3$
- $Fe^{2+} \rightarrow Fe_2(SO_4)_3$ (needs 6 $Fe^{2+} \rightarrow$ 3 $Fe_2(SO_4)_3$)
- K^+ and SO_4^{2-} balance with K_2SO_4

Full Balanced equation:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

ELECTROLYTIC CELL

An electrolytic cell is a device that converts electrical energy into chemical energy through a process called electrolysis.

- **Construction:**

  It consists of two electrodes, typically made of metal or another conductive material, which are immersed in an electrolyte-a substance containing free ions that carry electric current.

- **Process:**

  When a direct electric current is applied, one electrode becomes negatively charged (the cathode) and the other positively charged (the anode).

  In an electrolytic cell, positive ions in the electrolyte migrate towards the cathode, where they gain electrons (a reduction process), while negative ions move towards the anode, where they lose electrons (an oxidation process). This movement of ions and transfer of electrons results in chemical changes at the electrodes, effectively converting electrical energy into chemical energy.

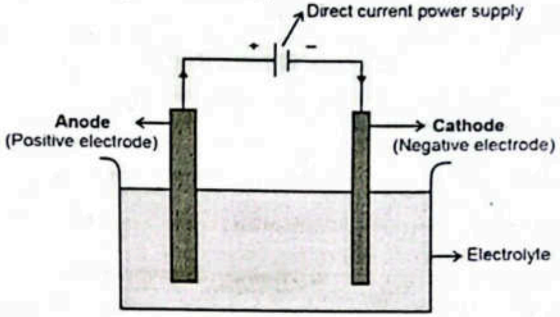

Figure: Main parts of an electrolytic cell

- **Applications of Electrolytic Cells:**

  Electrolytic cells are used in the electrolysis of sodium chloride to produce sodium metal and chlorine gas, the refining and plating of metals, and the production of chemicals like caustic soda. Electrolysis is also used to produce non-metals such as chlorine and to purify metals. Electrolysis is generally carried out in an electrolysis cell as shown in Figure.

  In the electrolysis cell:

  - **Electrolyte:** The electrolyte is the compound that is decomposed; it is either a molten ionic compound or a concentrated aqueous solution of ions
  - **Electrodes:** The electrodes are, made from either carbon (graphite) or metal, which conduct electricity to and from the electrolyte - the anode is the positive electrode - the cathode is the negative electrode
  - **DC:** The power supply must be direct current.

  (**Note:** The actual structure of the cell will vary according to the element extracted).

REDOX REACTIONS IN ELECTROLYSIS

During electrolysis, the positive ions (cations) move to the cathode. When they reach the cathode, they gain electrons from the cathode.

For example:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$
$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

Gain of electrons is reduction and it always occurs at the cathode. If metal atoms are formed, they may be deposited as a layer of metal on the cathode. Alternatively, they may form a molten layer in the cell. If hydrogen gas is formed, it bubbles off.

The negative ions **(anions)** move to the anode. When they reach the anode, they lose electrons to the anode. Loss of electrons is oxidation. Oxidation always occurs at the anode.

For example:

$$2C\ell^-_{(aq)} \longrightarrow C\ell_{2(g)} + 2e^-$$
$$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(\ell)} + 4e^-$$

Electrolysis is a redox reaction. For example, when molten zinc chloride ($ZnC\ell_2$) is electrolyzed, the electrode reactions are:

- **Cathode:** $Zn^{2+}_{(\ell)} + 2e^- \longrightarrow Zn_{(s)}$ (Reduction)
- **Anode:** $2C\ell^-_{(\ell)} \longrightarrow C\ell_{2(s)} + 2e^-$ (Oxidation)

The electron loss at the anode balances the electron gain at the cathode. The overall reaction is

$$ZnC\ell_{2(\ell)} \longrightarrow Zn_{(s)} + C\ell_{2(g)}$$

☑ QUICK CHECK 10.4

Molten copper (II) bromide ($CuBr_2$) is electrolyzed using inert electrodes.

i. Which ions are present in this solution?

Ans. The ions present are Cu^{2+} and Br^-.

ii. Name the electrode on which the formation of copper metal occurs?

Ans. Copper metal forms on the cathode.

iii. Give the half-equation that represents the formation of copper metal.

Ans. $Cu^{2+} + 2e^- \longrightarrow Cu$

iv. Write the half-equation for the formation of bromine on the other electrode.

Ans. $2Br^- \longrightarrow Br_2 + 2e^-$ (occurs at the anode)

MASS OF A SUBSTANCE DEPOSITED DURING ELECTROLYSIS

The mass of a substance produced at an electrode during electrolysis is proportional to the time over which a constant electric current pass and the strength of the electric current.

Combining current and time, we get the relationship:

$$Q = I \times t$$

Where
Q = Charge (in coulombs, C)
I = Current (in amperes, A)
t = Time (in seconds, s)

The mass of a substance produced at (or removed from) an electrode during electrolysis is proportional to the quantity of electricity (in coulombs) which passes through the electrolyte.

➢ **Faraday:**

The quantity of electricity is often expressed in terms of a unit called the **Faraday** (symbol F). 1 Faraday is the quantity of electric charge carried by 1 mole of electrons or 1 mole of singly charged ions. Its value is 96500 C mol^{-1}.

➢ **Electrolysis of Silver Nitrate Solution:**

During the electrolysis of silver nitrate solution, silver is deposited at the cathode.

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$$

1 mol 1 mol 1 mol

1 Faraday of electricity (96500 C) is required to deposit 1 mole of silver.

➢ **Electrolysis of Copper(II) Sulphate:**

During the electrolysis of copper (II) sulphate solution, copper is deposited at the cathode.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

1 mol 2 mol 1 mol

The equation shows that 2 moles of electrons are needed to produce 1 mole of copper from Cu^{2+} ions. So, it requires 2 Faradays of electricity (2×96500 C) to deposit 1 mole of copper.

No. of Faraday = No. of moles of electrons gained or lost

AMOUNT OF SUBSTANCE PRODUCED DURING ELECTROLYSIS

The value of F can be used to calculate the mass of substance deposited at an electrode and the volume of gas produced at an electrode.

Sample Problems 10.5

Calculate the mass of lead (Pb) deposited at the cathode during electrolysis when a current of 1.50 A flows through molten lead (II) bromide ($PbBr_2$) for 20.0 min. (relative atomic mass, Ar value: (Pb) = 207; F = 96500 C mol^{-1})

Solution:

Step 1: Write the half-equation for the reaction.

$$Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$$

Step 2: Find the number of coulombs required to deposit 1 mole of product at the electrode.

2 moles of electrons are required per mole of Pb formed = 2F

$$= 2 \times 96500$$
$$= 193000 \text{ C mol}^{-1}$$

Step 3: Calculate the charge transferred during the electrolysis.

$$Q = I \times t$$
$$= 1.50 \times 20 \times 60$$
$$= 1800 \text{ C}$$

Step 4: Calculate the mass by simple proportion using the relative atomic mass.

193000 C deposits 1 mole Pb, = 207 g Pb

$$1 \text{ C deposits} = \frac{207}{193000} \text{g}$$

$$1800 \text{ C deposits} = \frac{207}{193000} \times 1800 = 1.93 \text{ g Pb}$$

AVOGADRO'S CONSTANT BY THE ELECTROLYTIC METHOD

(Exercise L.Q.4)

Q. How Avogadro's number can be derived using an electrolytic cell?

➢ **Avogadro's Constant:**

- The Avogadro's constant, L, is the number of specified particles (atoms, molecules, or ions) in 1 mole. An electrolytic method can be used to find a value for the Avogadro's constant by calculating the charge associated with 1 mole of electrons.

$$N_A = \frac{\text{Charge on1 mole of electrons}}{\text{Charge on1 electron}}$$

- The charge on the electron can be calculated by experiment. The results show us that the charge on the electron is approximately 1.60×10^{-19} C.

➲ Finding the Charge on 1 Mole of Electrons

- The charge on 1 mole of electrons can be found from a simple electrolytic experiment. The apparatus for this is shown in Figure.

Procedure:

- The procedure is to weigh the pure copper anode and pure copper cathode separately arrange the apparatus during the electrolysis of aqueous copper(II) sulfate as shown in Figure.

- The variable resistor is used to keep the current constant pass about 0.2 amperes.
- Pass a constant electric current for a measured time interval, e.g., 40 min.
- Remove the cathode and anode and wash and dry them with distilled water and then with propanone.
- Reweigh the cathode and anode.

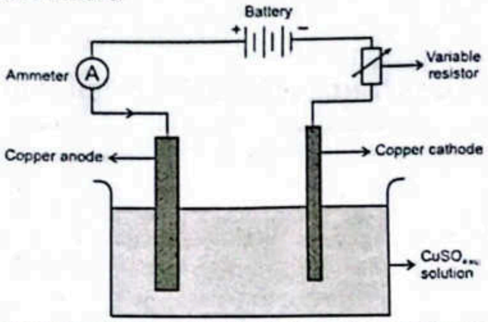

Figure: Apparatus for calculating the mass of copper deposited

- The cathode increases in mass because copper is deposited.
- The anode decreases in mass because the copper goes into solution as copper ions. The decrease in the mass of the anode is measured. This is preferred because the copper does not always stick to the cathode very well.

Calculating Charge on An Electron

A sample calculation is shown below, using a current of 0.20 A for 34 min.

mass of anode at start of the experiment = 56.53 g
mass of anode at end of experiment = 56.40 g
mass of copper removed from anode = 0.13 g
quantity of charge passed Q $= I \times t$
$= 0.20 \times 34 \times 60$
$= 408$ C

As the amount of copper removed is 0.13 g
So, 0.13 g of copper requires = 408 C

$$1\text{ g of copper requires} = \frac{408}{0.13}$$

$$63.5\text{ g of copper requires} = \frac{408}{0.13} \times 63.5 = 99646\text{ C}$$

But the equation for the electrolysis shows that 2 moles of electrons are needed to produce 1 mole of copper:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$$\text{The charge on 1 mole of electrons} = \frac{190500}{2} = 95,250\text{ C}$$

If the charge on one electron is 1.60×10^{-19} C,

$$\text{Charge on an electron} = \frac{95250}{6.02 \times 10^{23}} = 1.58 \times 10^{-19}\text{ C}$$

☑ QUICK CHECK 10.5

a) An aqueous solution of silver nitrate is electrolysed. Calculate the mass of silver deposited at the cathode when the electrolysis is carried out for exactly 35 min using a current of 0.18 A. ($Ar[Ag] = 108; F = 96500\,C\,mol^{-1}$)

Ans. Electrolysis of Silver Nitrate ($AgNO_3$)

According to Faraday's First Law of Electrolysis:

Mass (m) = Q × Mn × F

Where:

$Q = I \times t$
times t = charge in coulombs
M = molar mass of Ag = 108 g/mol
N = number of electrons per ion ($Ag^+ \rightarrow Ag = 1\,e^-$)
F = Faraday's constant = 96,500 C/mol

Step 1: Calculate Q

$I = 0.18$ A
$t = 35\text{ min} = 35 \times 60 = 2100$ s
$Q = I \times t = 0.18 \times 2100 = 378$ C

Step 2: Calculate Mass of Ag

$$m = \frac{Q \times M}{n \times F} = \frac{378 \times 108}{1 \times 96500} = \frac{40824}{96500} = 0.423\text{g}$$

b) An electric current of 1.04 A was passed through a solution of dilute sulfuric acid for 6.00 min. The volume of hydrogen produced at STP was 41.5 cm³.

i. How many coulombs of charge were passed during the experiment?

Ans. Calculate total charge passed

$I = 1.04$ A
$t = 6.00\text{ min} = 6 \times 60 = 360$ s
$Q = I \times t = 1.04 \times 360 = 374.4$ C

ii. How many coulombs of charge are required to liberate 1 mole of hydrogen gas? ($F = 96\,500\,C\,mol^{-1}$)

Ans. Charge required to liberate 1 mole of H_2 gas

Reaction at Cathode:

$$2H^+ + 2e^- \longrightarrow H_2$$

So, 2 moles of electrons are required for 1 mole of H_2.

Charge = $2 \times F = 2 \times 96500 = 193000$ C

ELECTRODE POTENTIALS
(Ease of oxidation and reduction)

During the redox processes, a redox equilibrium exists between two chemically related species that are in different oxidation states.

Definition:

"When a metal is put into a solution of its ions, an electric potential (voltage) is established between the metal and the metal ions in solution. This is called electrode potential".

It indicates the ease of oxidation or reduction of a substance.

Example: When a copper rod is placed in contact with an aqueous solution of its ions, the following equilibrium exists:

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

- **Explanation:**

There are two opposing reactions in this equilibrium.

a) Metal atoms from the rod entering the solution as metal ions. This leaves electrons behind on the surface of the electrode.

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$

b) Ions in solution accepting electrons from the metal rod and get deposited as metal atoms on the surface of the electrode.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The redox equilibrium is established when the rate of electron gain equals the rate of electron loss.

For unreactive metals such as copper, if this equilibrium is compared with the equilibrium set up by other metals, the equilibrium set up by copper lies further over to the right.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$Cu^{2+}_{(aq)}$ ions are therefore relatively easy to reduce. They gain electrons readily to form copper metal.

For reactive metals such as vanadium, the equilibrium lies further over to the left.

$$V^{2+}_{(aq)} + 2e^- \longrightarrow V_{(s)}$$

$V^{2+}_{(aq)}$ ions are therefore relatively difficult to reduce. They gain electrons much less readily by comparison.

The position of equilibrium differs for different combinations of metals placed in solutions of their ions.

➲ Electrical Double Layer

It is thought that the **absolute electrode potentials** cannot be measured due to the formation of an electrical double layer, when an element is placed in a solution of its ions.

Example:

A strip of Zinc in a solution containing Zn ions:

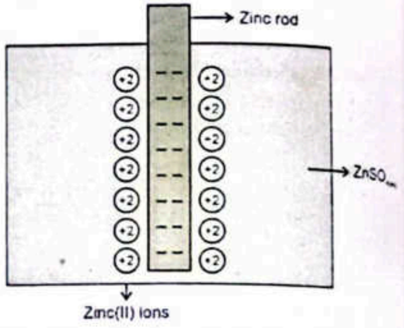

Figure: Formation of electrical double layer

- When zinc is placed in a solution containing zinc ions, a tiny number of zinc atoms on the surface of the metal is converted to zinc ions, which go into solution. This leaves an excess of electrons on the surface of the zinc.
- The solution around the metal now has excess Zn^{2+} ions. Some of these cations near the surface of the zinc are attracted to its surface. So, an electrical double layer is formed.
- This buildup of charge causes an electric potential (voltage) between the metal and the metal ions in solution as shown in Figure 10.3.
- Due to the formation an electrical double layer, the potential cannot directly be measured.
- The difference in potential between the metal/metal ion system and another system can be measured. We call this value the **electrode potential**, E. Electrode potential is measured in volts. The system we use for comparison is the **standard hydrogen electrode (SHE).**

STANDARD HYDROGEN ELECTRODE (SHE)

(Exercise LQ.5

Q. What is meant by Standard Hydrogen Electrode (SHE)? How it is used to measure the electrode potential of another electrode?

The **Standard Hydrogen Electrode (SHE)** is one of several types of half-cell that can be used as reference electrode.

➢ Construction:

Figure shows a standard hydrogen electrode.

SHE is a reversible electrode.

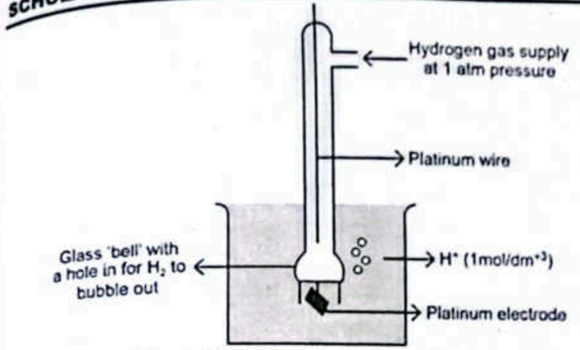

Figure: Standard hydrogen electrode (SHE)

S/Q. Why platinum black is a preferred catalyst?

Ans. Platinum black is a highly preferred catalyst due to its exceptionally high surface area, which significantly enhances its catalytic activity. This high surface area, achieved through a fine powder form, provides numerous active sites for chemical reactions to occur. It boosts reaction rates and overall efficiency.

Standard Hydrogen Electrode consists of:

- Hydrogen gas at 101 kPa pressure, in equilibrium with H^+ ions of concentration 1.00 mol dm^{-3}
- A platinum electrode covered with platinum black in contact with the hydrogen gas and the H^+ ions.

The **platinum black** is finely divided platinum, which allows close contact of hydrogen gas and H^+ ions in solution so that equilibrium between H_2 gas and H^+ ions is established quickly. The platinum electrode is inert so it does not take part in the reaction. Standard electrode potential E° values for all half-cells are measured relative to this electrode.

When connected to another half-cell, the value read on the voltmeter gives the standard electrode potential for that half-cell. The half-equation for the hydrogen electrode can be written:

Reduction (Acts as cathode): $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ $E^\circ = 0.00\ V$

Oxidation (Acts as anode): $H_2 \longrightarrow 2H^+ + 2e$ $E^\circ = 0.00\ V$

The way that the half-equation is balanced makes no difference to the value of E°. The equation does not affect the tendency for the element to gain electrons.

Electrode Potential: Its voltage is arbitrarily fixed at 0.00 V.

STANDARD ELECTRODE POTENTIAL (E°)

The voltage of an electrochemical cell will also depend on concentration, temperature, and pressure of the gas. Therefore, we should use standard conditions when comparing electrode potentials.

Conditions:

- Concentration of ions at 1.00 mol dm^{-3}
- A temperature of 25°C(298 K)
- Any gases should be at a pressure of 1 atmosphere (101 kPa)
- The value of the electrode potential of the half-cell is measured relative to the standard hydrogen electrode.

Under these conditions, the electrode potential we measure is called the standard electrode potential. This has the symbol, E°. It is spoken of as ' E standard'.

"The standard electrode potential for a half-cell is the voltage measured under standard conditions with a standard hydrogen electrode (SHE) as the other half-cell".