

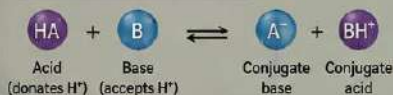
## CHAPTER 2

# IONIC EQUILIBRIUM

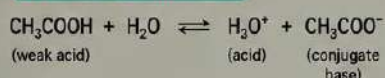
## The balance of ions in solution

In aqueous solutions, ions and molecules exist in dynamic equilibrium. This balance controls the acidity, solubility, and behavior of substances in a vast range of chemical systems.

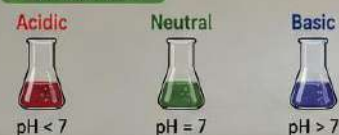
### 1. ACID-BASE CONCEPTS



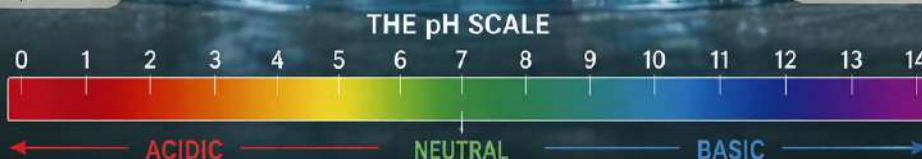
### 2. IONIC EQUILIBRIUM



### 3. pH AND pOH



Equilibrium is nature's way of maintaining balance in every drop.

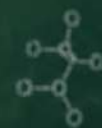


$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

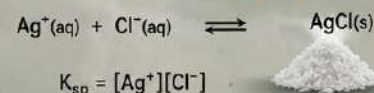
$$\text{pH} = -\log [\text{H}^+]$$

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

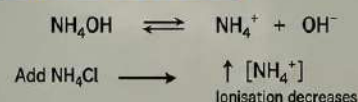
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$



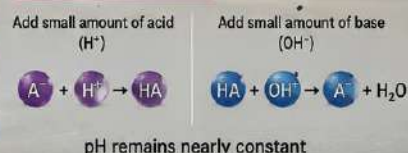
### 4. SOLUBILITY PRODUCT (K<sub>sp</sub>)



### 5. COMMON ION EFFECT



### 6. BUFFER SOLUTION



A small change can shift the equilibrium, but the system always adjusts.

## Learning outcomes

By the end of the chapter, students should be able to:

- ✓ State and explain different concepts of acids and bases (Arrhenius, Brønsted–Lowry, and Lewis).  
Explain the limitations of the Arrhenius concepts of acids and bases.  
Define conjugate acids and conjugate bases.  
Identify conjugate acid-base pairs of Brønsted acids and bases.
- ✓ Define and use the term degree of ionisation; apply Ostwald's Dilution Law.  
Use the extent of ionisation and dissociation constants of acids (K<sub>a</sub>) and bases (K<sub>b</sub>), and pK<sub>a</sub> and pK<sub>b</sub>.
- ✓ Explain autoionization of water, ionic product (K<sub>w</sub>), and calculate pH and pOH of aqueous solutions using K<sub>w</sub> values.
- ✓ Define and use the solubility product (K<sub>sp</sub>) and apply the solubility product principle.  
Calculate K<sub>sp</sub> from concentrations and vice versa
- ✓ Show understanding of the common ion effect.
- ✓ Explain the solubility product principle and common ion effect and its applications in qualitative analysis (precipitation reactions)
- ✓ Classify salts and explain the hydrolysis of salts with examples.
- ✓ Describe buffer solutions and show with equations how a Buffer system works and describe their significance/application.
- ✓ Explain the choice of appropriate indicators for acid-base titrations and interpret pH curves.

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- ✓ Define and differentiate different types of salts (simple salts, double salts, complex salts, acidic salts, basic salts and neutral salts).
- ✓ Explain hydrolysis of salts (salts of strong acid and strong base, salts of weak acid and strong base and salts of weak base and strong acid).
- ✓ Solve numerical problems related to the above topics.

**Ionic equilibrium** is the study of equilibrium in electrolyte solutions – the balance between ions and undissociated molecules.

### Ionic reactions:

When electrolytes dissolve in water, they dissociate into charged particles called **ions**. Reactions that occur between ions in solution are called **ionic reactions**. Ionic reactions form the basis of all acid-base chemistry, precipitation, and complexation phenomena.

When silver nitrate ( $\text{AgNO}_3$ ) and sodium chloride ( $\text{NaCl}$ ) solutions are mixed, a white precipitate of silver chloride ( $\text{AgCl}$ ) forms. We can write this in three ways:

| Equation Type         | Expression                                                                                                                                                                                            |
|-----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Molecular</b>      | $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s})\downarrow + \text{NaNO}_3(\text{aq})$                                                                            |
| <b>Complete Ionic</b> | $\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})\downarrow + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ |
| <b>Net Ionic</b>      | $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})\downarrow$ (spectator ions $\text{Na}^+$ and $\text{NO}_3^-$ cancelled)                                            |

Why are ionic equations important here?

Many reactions in ionic equilibrium involve ions in solution. For example, acid-base reactions, precipitation reactions and salt hydrolysis can all be understood by looking at the ions involved.

## Acid-Base Concepts

The three important acid-base concepts developed in this order:

1. Arrhenius concept
2. Bronsted-Lowry concept &
3. Lewis's concept

### 1. Arrhenius Concept

An **acid** is a substance that **gives hydrogen ions** ( $\text{H}^+$ ) when dissolved **in water**. *e.g.*,  $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$

A **base** is a substance that **gives hydroxyl ions** ( $\text{OH}^-$ ) when dissolved **in water**. *e.g.*,  $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$

A **salt** is an ionic compound formed from the positive ion of a base and the negative ion of an acid.

*e.g.*,  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

**Neutralisation** according to Arrhenius: An acid and a base react to form water and a salt:

$\text{H}^+$  (from acid) +  $\text{OH}^-$  (from base)  $\rightarrow \text{H}_2\text{O}$

### Limitations of Arrhenius's Concept

The main limitation is that Arrhenius cannot adequately describe substances that can behave as acids and bases **outside the narrow  $\text{H}^+/\text{OH}^-$  aqueous framework** (cannot explain acidic/basic behaviour in non-aqueous media).

For example;

- a. Cannot explain the basicity of  **$\text{NH}_3$**  and its organic derivatives, as they do not contain  $\text{OH}^-$ .
- b. **Metal oxides** ( $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ) act as bases but do not contain  $\text{OH}^-$ .
- c. Certain compounds ( $\text{AlCl}_3$ ,  $\text{BF}_3$ ) show acidic nature without having  $\text{H}^+$  ions.
- d. Fails to account for the **amphoteric nature** of substances (*e.g.*,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$ )

**Conclusion:** The Arrhenius concept is too narrow to explain many acid-base behaviours

## 2. Bronsted-Lowry Concept (Proton Transfer Theory)

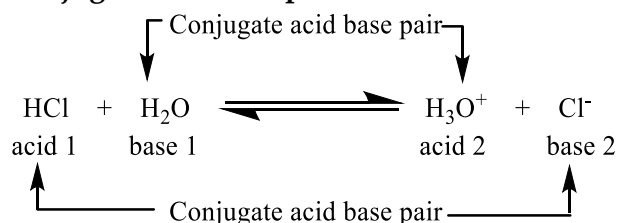
- **Acid:** A species that donates one or more protons ( $H^+$ ) – *proton donor*.
- **Base:** A species that accepts one or more protons ( $H^+$ ) – *proton acceptor*.
- **Forward reaction:**
  - $HCl$  donates a proton  $\rightarrow HCl$  is the **acid**.
  - $H_2O$  accepts a proton  $\rightarrow H_2O$  is the **base**.
- **Reverse reaction:**
  - $H_3O^+$  donates a proton  $\rightarrow H_3O^+$  is the **acid**.
  - $Cl^-$  accepts a proton  $\rightarrow Cl^-$  is the **base**.

Species that tend to give as well as accept a proton are termed amphoteric species or substances. Example:  $H_2O$ ,  $HCO_3^-$ , and  $HSO_4^-$  are amphoteric or amphiprotic substances.

**Amphoteric** is a general term for a substance showing the dual nature of acid and base.

While the **amphiprotic** term is used when acid-base behaviour is restricted to proton transfer.

### Conjugate acid-base pairs



When an acid donates a proton, the remaining species is its **conjugate base**.  
When a base accepts a proton, the new species is its **conjugate acid**.

From the above reaction:

- $HCl$  (**acid**) and  $Cl^-$  (**conjugate base**) form one pair.
- $H_2O$  (**base**) and  $H_3O^+$  (**conjugate acid**) form the other pair.

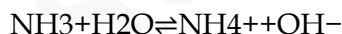
### ★ Easy rule

Acid loses  $H^+ \rightarrow$  conjugate base

Base gains  $H^+ \rightarrow$  conjugate acid

### 🧠 QUICK CHECK

In the reaction below, identify the acid, base, conjugate acid and conjugate base.



### The relative strength of acids and bases

If an acid is strong, its conjugate base will be weak and vice versa.

| RELATIVE STRENGTH OF ACIDS AND CONJUGATE BASES   |                                                                                                         |                                  |
|--------------------------------------------------|---------------------------------------------------------------------------------------------------------|----------------------------------|
| ACID                                             |                                                                                                         | CONJUGATE BASE                   |
| Perchloric acid (HClO <sub>4</sub> )             | Strong Acids<br>       | ClO <sub>4</sub> <sup>-</sup>    |
| Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> ) |                                                                                                         | HSO <sub>4</sub> <sup>-</sup>    |
| Hydroiodic acid (HI)                             |                                                                                                         | I <sup>-</sup>                   |
| Hydrobromic acid (HBr)                           |                                                                                                         | Br <sup>-</sup>                  |
| Hydrochloric acid (HCl)                          |                                                                                                         | Cl <sup>-</sup>                  |
| Nitric acid (HNO <sub>3</sub> )                  | Weak Acids<br>         | NO <sub>3</sub> <sup>-</sup>     |
| Hydrofluoric acid (HF)                           |                                                                                                         | F <sup>-</sup>                   |
| Nitrous acid (HNO <sub>2</sub> )                 |                                                                                                         | NO <sub>2</sub> <sup>-</sup>     |
| Formic acid (HCOOH)                              |                                                                                                         | HCOO <sup>-</sup>                |
| Acetic acid (CH <sub>3</sub> COOH)               | Negligible Acidity<br> | CH <sub>3</sub> COO <sup>-</sup> |
| Hydrocyanic acid (HCN)                           |                                                                                                         | CN <sup>-</sup>                  |
| Ammonia (NH <sub>3</sub> )                       |                                                                                                         | NH <sub>2</sub> <sup>-</sup>     |
| Methane (CH <sub>4</sub> )                       |                                                                                                         | CH <sub>3</sub> <sup>-</sup>     |

- Strong acid → weak conjugate base (stable, not eager to accept a proton back).
- Weak acid → strong conjugate base (unstable, eager to accept a proton).
- Strong base → weak conjugate acid.
- Weak base → strong conjugate acid.

◆ **Remember:** If an acid is strong, its conjugate base is weak, and vice versa.

e.g., HCl (a strong acid) has Cl<sup>-</sup> as the conjugate base (a very weak base that does not accept H<sup>+</sup> easily).

CH<sub>3</sub>COOH (weak acid) has CH<sub>3</sub>COO<sup>-</sup> as its conjugate base (a moderately strong base).

#### Advantages over Arrhenius

1. Works in any solvent (water, alcohol, liquid NH<sub>3</sub>) and even in the gas phase.
2. Explains NH<sub>3</sub> as a base (it accepts a proton from water: NH<sub>3</sub> + H<sub>2</sub>O ⇌ NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup>).
3. Explains H<sub>2</sub>O as amphiprotic (can act as an acid or base).
4. Explains metal oxides as bases (O<sup>2-</sup> + H<sub>2</sub>O → 2 OH<sup>-</sup>, then OH<sup>-</sup> accepts protons).

#### Limitation of Brønsted-Lowry

It still requires **protons**. It cannot explain acid-base reactions that do not involve proton transfer (e.g., BF<sub>3</sub> + NH<sub>3</sub> → F<sub>3</sub>B-NH<sub>3</sub>, or metal ions acting as acids).

### 3. Lewis Concept (Electronic Concept)

**Acid:** A species that accepts a pair of electrons from a base to form a coordinate covalent bond, i.e., an **electron pair acceptor**. An electrophile (electron-loving species) acts as a **Lewis acid**.

**Base:** A species (atoms, ions, molecules, etc.) that **donates a pair of electrons** to an acid to form a coordinate covalent bond. Nucleophiles (nucleus-loving species) act as Lewis bases.

#### Example 1: BF<sub>3</sub> + NH<sub>3</sub>

BF<sub>3</sub> — Boron has an incomplete octet → **Lewis Acid** (electron pair acceptor).

:NH<sub>3</sub> — Nitrogen has a lone pair → **Lewis Base** (electron pair donor).

Reaction: BF<sub>3</sub> + :NH<sub>3</sub> → F<sub>3</sub>B-NH<sub>3</sub> (a coordinate covalent bond forms from N to B)

#### Example 2: H<sup>+</sup> + :NH<sub>3</sub>

H<sup>+</sup> — Has an empty 1s orbital → **Lewis Acid**

:NH<sub>3</sub> — Lone pair on N → **Lewis Base**

Reaction: H<sup>+</sup> + :NH<sub>3</sub> → NH<sub>4</sub><sup>+</sup>

Merits of the Lewis concept:

1. **Includes non-proton reactions:** Covers coordination chemistry, metal complexes, and many



organic reactions (e.g., Friedel-Crafts alkylation using  $\text{AlCl}_3$  as a Lewis acid).

2. It also includes the basic properties of metallic oxides and the acidic properties of nonmetallic oxides.
3. It can also explain that  $\text{H}^+$  and  $\text{OH}^-$  are Lewis acids and Lewis bases, respectively.
4. **Explains acidity of salts like  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{FeCl}_3$ :** They are electron-deficient and accept electron pairs

Demerits of Lewis Concept:

1. Fails to arrange the acids and bases according to relative strength.
2. Says a coordinate covalent bond is formed between an acid and a base. However, **strong mineral acids** such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HNO}_3$  do not form any coordinate covalent bonds.
3. Most acid-base reactions (e.g.,  $\text{HCl} + \text{NaOH}$  in water) are very fast, but forming a coordinate covalent compound is slow. Such a rapid acid-base reaction is not accounted.

Comparison Table

| Feature                    | Arrhenius                         | Brønsted-Lowry                   | Lewis                    |
|----------------------------|-----------------------------------|----------------------------------|--------------------------|
| <b>Fundamental process</b> | Ion formation in water            | Proton ( $\text{H}^+$ ) transfer | Electron pair transfer   |
| <b>Acid</b>                | Gives $\text{H}^+$ in water       | Donates $\text{H}^+$             | Accepts an electron pair |
| <b>Base</b>                | Gives $\text{OH}^-$ in water      | Accepts $\text{H}^+$             | Donates an electron pair |
| <b>Main idea</b>           | $\text{H}^+/\text{OH}^-$ in water | Proton transfer                  | Electron-pair transfer   |
| <b>Solvent required?</b>   | Only water                        | Any (or none)                    | Any (or none)            |

### Summary of Progression

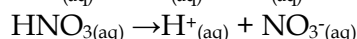
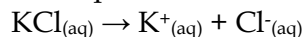
1. **Arrhenius** started the idea: acids give  $\text{H}^+$ , bases give  $\text{OH}^-$  in water.  
*Problem:* Too narrow.
2. **Brønsted-Lowry** expanded: acids donate  $\text{H}^+$ , bases accept  $\text{H}^+$  in any medium.  
*Problem:* Still requires protons.
3. **Lewis** gave the most general definition: acids accept electron pairs, bases donate electron pairs.  
*Problem:* Loses quantitative strength ordering.

Each concept is still useful today – just in different contexts. For everyday aqueous chemistry, Arrhenius or Brønsted is fine. For coordination compounds and organic mechanisms, Lewis is essential.

## Ionisation of Electrolytes and Ostwald's Law

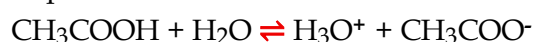
- **Electrolytes** are substances like acids, bases, and salts that can conduct electricity in their aqueous solution due to ionisation.
- Some electrolytes, like potassium chloride and sodium hydroxide, completely dissociate into their constituent ions in solution. These are known as **strong electrolytes**.

For example,



- **Weak electrolytes** ionise only partially in water.
- In the aqueous solution of weak electrolytes, the constituent ions are in equilibrium with undissociated molecules of the electrolyte.

Example:



- An equilibrium exists between ions and unionised molecules, called **ionic equilibrium**.
- **Weak acids** and **weak bases** are good examples of weak electrolytes.

**Degree of ionisation ( $\alpha$ ):** The fraction of the initial number of molecules (or formula units) that ionise into ions is called the degree of ionisation or dissociation. The degree of ionisation increases with dilution.

Ostwald's dilution law describes how the **degree of ionisation ( $\alpha$ )** of a weak electrolyte changes with **dilution** (i.e., when you add more solvent, usually water).

Consider a weak binary electrolyte **AB** with an initial concentration of the electrolyte,  $C$  (in mol/L), and degree of ionisation  $\alpha$  (fraction of AB that dissociates) that dissociates as:

|                                     | <b>AB</b>                     | $\rightleftharpoons$ | <b>A<sup>+</sup></b>        | <b>+</b> | <b>B<sup>-</sup></b>        |
|-------------------------------------|-------------------------------|----------------------|-----------------------------|----------|-----------------------------|
| Initial concentration               | $C$                           |                      | $0$                         |          | $0$                         |
| Change in concentration             | $-C\alpha$                    |                      | $+C\alpha$                  |          | $+C\alpha$                  |
| <b>Concentration at equilibrium</b> | <b><math>C-C\alpha</math></b> |                      | <b><math>C\alpha</math></b> |          | <b><math>C\alpha</math></b> |

The equilibrium constant or dissociation constant  $K$  is given by the law of mass action as:

$$K = \frac{[\text{A}^{+}][\text{B}^{-}]}{[\text{AB}]} = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

For a **weak electrolyte**,  $\alpha$  is very small ( $\alpha \ll 1$ ). Therefore,  $1-\alpha \approx 1$ .

The equation simplifies to:

$$K = C\alpha^2$$

Solving for  $\alpha$ :

$$\alpha = \sqrt{K/C}$$

**Therefore, when concentration  $C$  decreases,  $\alpha$  increases.**

If **one mole** of solute is dissolved in  **$V$  litres** of solution, the concentration is given as

$$\text{concentration } (C) = \frac{\text{number of moles (solute)}}{\text{volume in litres (solution)}} = \frac{n}{V}$$

$$\text{or, } C = \frac{1}{V}$$

Therefore,

$$\alpha = \sqrt{K \times V}$$

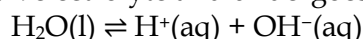
- For **weak electrolytes**, the ions in solution are far apart at equilibrium, so the approximation holds.
- For **strong electrolytes**, they are almost fully dissociated even at high concentration. Dilution does not increase  $\alpha$  (it's already  $\sim 1$ ), and the simple equilibrium constant expression does not correctly describe their behaviour due to interionic attractions.

✦ **Remember:** Ostwald's Dilution Law applies **ONLY** to weak electrolytes. For strong electrolytes, ionisation is already complete ( $\alpha \approx 1$ ) and does not depend on dilution.

## Autoionisation of Water and pH

### Ionisation of Water

Water is a weak electrolyte and undergoes very slight ionisation:



- This is a **reversible (equilibrium) reaction**.
- Only a **very small fraction** of water molecules ionise at any time.
- Most of the water remains as **unionised H<sub>2</sub>O molecules**.

☞ More accurately:

- H<sup>+</sup> exists as **H<sub>3</sub>O<sup>+</sup> (hydronium ion)**, but we write H<sup>+</sup> for simplicity.

### Ionic Product of Water (K<sub>w</sub>)

The product of hydrogen ion and hydroxide ion concentrations is constant:

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

At 25°C (room temperature):

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

So,  $K_w = (10^{-7}) \times (10^{-7}) = 10^{-14}$

### Important Implications

- If  $[\text{H}^+]$  increases  $\rightarrow$   $[\text{OH}^-]$  must decrease
- If  $[\text{OH}^-]$  increases  $\rightarrow$   $[\text{H}^+]$  must decrease

☞ Because:  $[\text{H}^+] \times [\text{OH}^-] = 10^{-14}$

### Effect in Acidic Solutions

- Acids increase  $[\text{H}^+]$
- So  $[\text{OH}^-]$  decreases automatically

e.g., If  $[\text{H}^+] = 10^{-3}$ , then  $[\text{OH}^-] = 10^{-11}$  ✓ Solution is **acidic**

### Effect in Basic Solutions

- Bases increase  $[\text{OH}^-]$
- So  $[\text{H}^+]$  decreases

e.g., If  $[\text{OH}^-] = 10^{-2}$ , then  $[\text{H}^+] = 10^{-12}$  ✓ Solution is **basic**

### Neutral Solution Condition

- $[\text{H}^+] = [\text{OH}^-]$
- Both are  $10^{-7}$

✓ Solution is at 25 °C **neutral (pH = 7)**

- K<sub>w</sub> generally **increases with temperature**.

### What is pH?

pH is a measure of the **acidity or alkalinity** of a solution. It depends on the concentration of hydrogen ions (H<sup>+</sup>) present in the solution.

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

• Higher  $[H^+]$  → **lower pH** → more acidic

Lower  $[H^+]$  → **higher pH** → more basic

### pH Scale

The pH scale generally ranges from **0 to 14**:

- **pH < 7** → Acidic solution
- **pH > 7** → Basic (alkaline) solution

**pH = 7** → Neutral solution (pure water) at 25 °C

### Real-Life Importance of pH

- Biological systems: Blood pH  $\approx 7.4$  (slight change is dangerous)
- Agriculture: Soil pH affects crop yield
- Industry: Many reactions require controlled pH
- Daily life: Tooth decay occurs when the mouth pH < 5.5

### Worked Example

1. Potassium hydroxide, having a pH of 8, is diluted 1000 times. Calculate the pH of the diluted base. 4

Solution:

For the original KOH solution,

pH = 8

As we know,  $pH + pOH = 14$

$$\therefore pOH = 14 - pH = 14 - 8 = 6$$

Also, we know,  $pOH = -\log [OH^-]$

$$6 = -\log [OH^-]$$

$$[OH^-] = 10^{-6}$$

$$\text{or, } [KOH] = 10^{-6}$$

Now, when the solution is diluted 1000 times, the concentration of KOH decreases by a factor of 1000.

$$\text{i.e., new } [KOH] = 10^{-6}/1000 = 10^{-9}$$

This new concentration of KOH ions is too small. Even pure water has an  $OH^-$  ion concentration of  $10^{-7}$ .

In this case, the concentration of  $OH^-$  ions from water autoionization cannot be ignored.

KOH is a strong base, so:  $[K^+] = 1.0 \times 10^{-9} M$

Let,  $[H^+] = x$

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

we have

$$[OH^-] = 10^{-14}/x$$

Charge balance requires:  $[K^+] + [H^+] = [OH^-]$

$$\text{Therefore: } 10^{-9} + x = 10^{-14}/x$$

Multiplying by x:

$$x^2 + 10^{-9}x - 10^{-14} = 0$$

Solving gives approximately:

$$[H^+] = 9.995 \times 10^{-8} M$$

$$pH = -\log (9.995 \times 10^{-8}) \approx 7.0002$$

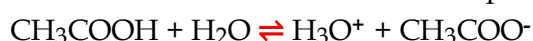
### Exam tips:

1. Make sure the concentration is expressed in Molarity or mol/L.

2. For very dilute solutions (of range  $10^{-7}$ ), also consider the autoionization of water.

## pKa and pKb

Weak acids like ethanoic acid dissociate partially as:





An equilibrium is established between the ions and undissociated molecules.  
The equilibrium constant characterises the equilibrium as

$$K_{eq} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

For dilute solutions, the concentration of water is relatively large and constant. Therefore,

$$K_{eq} \times H_2O = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

A higher value of  $K_a$  indicates that the acid is ionised to a larger extent; hence it's a strong acid, and vice versa.

Acid strength is often expressed as  $pK_a$ , where  $pK_a = -\log K_a$ .

The larger the  $K_a$ , the smaller the  $pK_a$ . Hence, a smaller  $pK_a$  value indicates a relatively stronger acid.

### Assignment

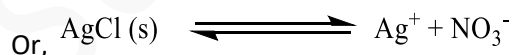
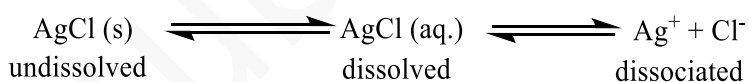
Accordingly, taking an example of a weak base like  $NH_4OH$ , write its dissociation, deduce the expression for  $K_b$  and  $pK_b$ , and deduce their meaning/ significance.

| Strong Acids                                                                   | Weak Acids                                                                                     | Strong Bases | Weak Bases                                | More soluble salts                                                                     | Sparingly soluble salts                                             |
|--------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|--------------|-------------------------------------------|----------------------------------------------------------------------------------------|---------------------------------------------------------------------|
| HCl<br>HNO <sub>3</sub><br>H <sub>2</sub> SO <sub>4</sub><br>HClO <sub>4</sub> | HCOOH<br>CH <sub>3</sub> COOH<br>C <sub>6</sub> H <sub>5</sub> COOH<br>HCN<br>H <sub>2</sub> S | NaOH<br>KOH  | NH <sub>4</sub> OH<br>Be(OH) <sub>2</sub> | NaCl<br>Na <sub>2</sub> SO <sub>4</sub><br>CH <sub>3</sub> COONa<br>NH <sub>4</sub> Cl | AgCl<br>Ag <sub>2</sub> CO <sub>3</sub><br>BaSO <sub>4</sub><br>CuS |

## Solubility Product and Solubility Product Principle

When a sparingly soluble salt like AgCl is dissolved in water, it dissolves only slightly and forms a saturated solution at a given temperature. At this stage, a **dynamic equilibrium** is established between the dissolved ions and the undissolved solid.

This equilibrium can be represented as:



Applying the law of mass action to the above reversible equation at the equilibrium condition,

$$K_{eq} = \frac{[Ag^+][Cl^-]}{[AgCl(s)]}$$

The concentration of pure solid AgCl is treated as constant, so it is not included in the  $K_{sp}$  expression.

Hence, the above equation can be written as;

$$K_{eq} \times [AgCl(s)] = [Ag^+][Cl^-]$$

$$\text{Or, } K_{eq} \times \text{constant} = [Ag^+][Cl^-]$$

$$\text{Or, } K_{sp} = [Ag^+][Cl^-]$$

Where  $K_{sp}$  is known as the solubility product constant or solubility product; its value for a sparingly soluble salt is constant at a given temperature.

Thus, the **product of the concentrations of ions of a sparingly soluble salt in its saturated solution raised to the power equal to the stoichiometric coefficient** in a balanced equation **at a given temperature** is called the **solubility product** of a given salt.

Depending on the value of the ionic product in the given solution, the solution can be classified as saturated, unsaturated, or supersaturated. This is the **solubility product principle**.

1. If the ionic product (I.P.) < K<sub>sp</sub> (Solubility product), the solution will be unsaturated.
2. If I.P. = K<sub>sp</sub>, the solution will be saturated.
3. If I.P. > K<sub>sp</sub>, the solution will be supersaturated, favouring precipitation.

Application of Solubility product principle:

Precipitation of chlorides of Group I basic Radicals (Ag<sup>+</sup>, Pb<sup>2+</sup>, Hg<sub>2</sub><sup>2+</sup>)

When HCl is added to the solution containing various metal ions, the solubility product of only AgCl, PbCl<sub>2</sub> and Hg<sub>2</sub>Cl<sub>2</sub> is less than the Ionic product. On the other hand, the solubility product of the chlorides of other cations is higher than the ionic product. Hence, they remain in the solution without precipitation.

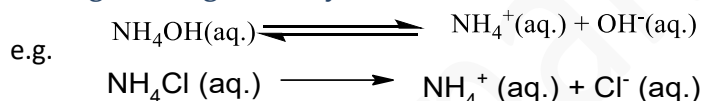
## Common Ion Effect

[www.youtube.com/watch?v=c9\\_Ab0BzIC4](http://www.youtube.com/watch?v=c9_Ab0BzIC4)

[The Common Ion Effect](http://www.youtube.com/watch?v=VVySeROOw7E)

[www.youtube.com/watch?v=VVySeROOw7E](http://www.youtube.com/watch?v=VVySeROOw7E)

The Common Ion Effect is the **suppression of the degree of ionisation of a weak electrolyte by adding a strong electrolyte with an ion common** to the weak electrolyte.



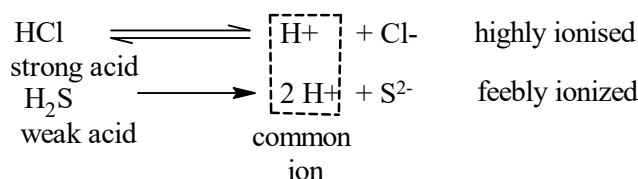
Due to the addition of NH<sub>4</sub>Cl, the concentration of NH<sub>4</sub><sup>+</sup> ions in solution increases. The increased concentration of NH<sub>4</sub><sup>+</sup> in the solution shifts the above equilibrium reaction towards the left. Thus, some NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> ions recombine to form unionised NH<sub>4</sub>OH. i.e., the degree of ionisation of the weak electrolyte is suppressed, thereby decreasing the concentration of OH<sup>-</sup> in the solution.

### Application of the Common Ion Effect:

A. In the selective precipitation of basic radicals in qualitative analysis:

1. Precipitation of sulphides of Group II basic radicals (Hg<sup>++</sup>, Pb<sup>++</sup>, Bi<sup>+++</sup>, Cu<sup>++</sup>)

The group reagent for the Group II basic radical is H<sub>2</sub>S in the presence of HCl. When H<sub>2</sub>S gas is passed through the solution containing HCl under hot conditions, the dissociation takes place as:

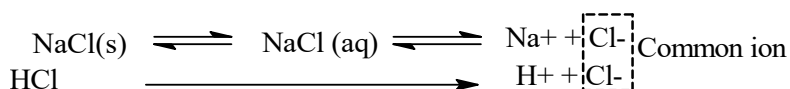


Addition of HCl increases [H<sup>+</sup>], which suppresses the ionisation of H<sub>2</sub>S and therefore decreases [S<sup>2-</sup>].

The concentration of metal ions is already present. For sufficiently insoluble Group II sulphides, the ionic product [M<sup>2+</sup>][S<sup>2-</sup>] can still exceed K<sub>sp</sub>, so they precipitate. Therefore, only the sulphides of the Group II metal ions get precipitated out.

### B. Purification of Common Salt:

The impure salt (Sea salt) can be made pure by passing HCl gas through the saturated sea salt solution.



Here, the increase in the concentration of  $\text{Cl}^-$  ions results in an increase in the ionic product of  $\text{Na}^+$  and  $\text{Cl}^-$  over the solubility product of  $\text{NaCl}$ . Hence, pure  $\text{NaCl}$  gets precipitated while all impurities remain in the solution.

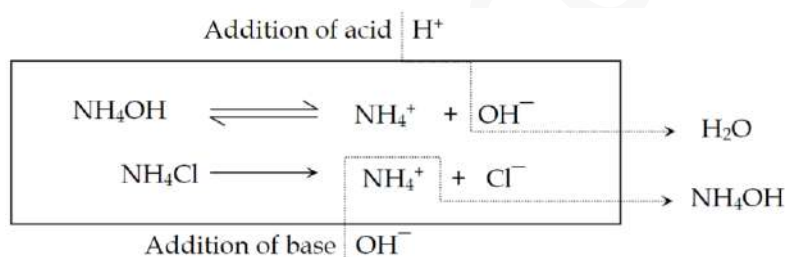
## Buffer solution and its application

A **buffer solution** is a solution that resists significant change in pH when small amounts of a strong acid or a strong base are added to it. Buffer solutions are vital in biological systems, industrial processes, and pharmaceutical preparations.

### B. Basic Buffer

Composed of a **weak base** and its **conjugate salt (formed with a strong acid)**.

**Example:**  $\text{NH}_4\text{OH}$  (ammonium hydroxide) +  $\text{NH}_4\text{Cl}$  (ammonium chloride)

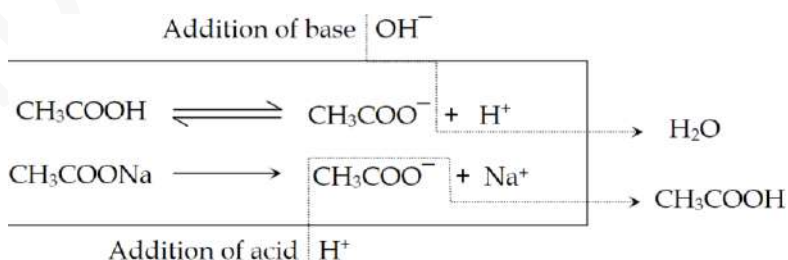


### B. Acidic Buffer

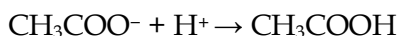
Composed of a **weak acid** and its **conjugate salt (formed with a strong base)**.

**Example:**  $\text{CH}_3\text{COOH}$  (acetic acid) +  $\text{CH}_3\text{COONa}$  (sodium acetate)

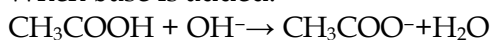
The weak acid provides an  $\text{H}^+$  reserve to neutralise added base; the conjugate base from the salt neutralises added acid.



When acid is added:



When base is added:



**Added acid is removed by the conjugate base.**

**Added base is removed by the weak acid.** Thus, keeping the pH constant.

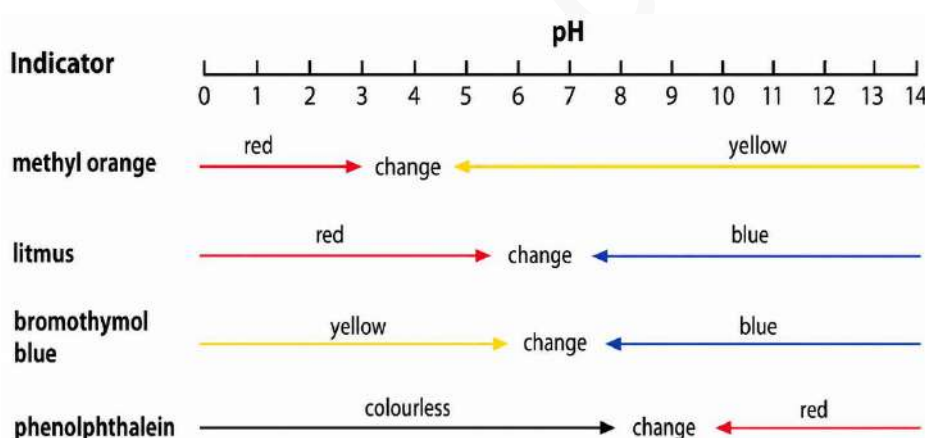
## Applications of Buffer Solutions

- **Blood buffer:** Blood is maintained at pH 7.35–7.45 by the  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  buffer system. Blood pH must remain within a narrow range for normal body function.
- **Industry:** Electroplating, fermentation, and dyeing industries require precise pH control using buffers.
- **Agriculture:** Soil buffers maintain optimal pH for plant growth.
- **Pharmaceuticals:** Medicines (especially injections) are buffered to prevent irritation or degradation.
- **Laboratory:** Buffer solutions are used to calibrate pH meters.

## Selection of Indicators in Acid-Base Titration and pH Curve

Indicators are generally weak organic acids or bases that indicate the endpoint of a reaction by changing their colours. The indicators have different colours in acidic and alkaline solutions. Some common indicators for acid-base titrations include methyl orange, phenolphthalein, and methyl red.

| Indicators      | Colour in acidic solution | Colour in alkaline solution | Colour in neutral solution | pH range |
|-----------------|---------------------------|-----------------------------|----------------------------|----------|
| Methyl orange   | Red                       | yellow                      | orange                     | 3.1-4.4  |
| Phenolphthalein | Colourless                | pink                        | colourless                 | 8.2-10   |
| Methyl red      | Red                       | yellow                      | Light orange               | 4.4-6.2  |



The choice of a suitable indicator for a particular acid-base titration depends upon the nature of the acid and base used.

During acid-base titration, neutralisation of an acid by a base and vice versa. During neutralisation,  $\text{H}^+$  ions and  $\text{OH}^-$  ions combine, forming water molecules. Hence, the pH of the resulting solution changes.

A plot of the pH of the solution against the volume of acid or base added from the burette is called a titration curve or pH curve. Such a titration curve graphically shows the equivalence point and helps select the proper indicators.

Acid-base titrations are of the following types;

### 1. Strong acid-strong base (HCl vs NaOH) titration:

When a strong acid is titrated against a strong base, a pH curve with a sharp pH change from approx. 3-11 is obtained. Therefore, the indicators methyl orange, with a pH range of 3.1-4.4, and phenolphthalein, with a pH range of 8.2-10, can be used as suitable indicators.

### 2. Strong acid-weak base (HCl vs $\text{NH}_4\text{OH}$ ) titration:

When a strong acid is titrated against a weak base, a pH curve with a sharp change in pH from approx. 3-8 is obtained. Therefore, the indicator methyl orange, having a pH range of 3.1-4.4, can

be used as a suitable indicator.

### 3. Weak acid-strong base ( $\text{CH}_3\text{COOH}$ vs $\text{NaOH}$ ) titration:

When a weak acid is titrated against a strong base, a pH curve with a sharp pH change from 6-11 (approx.) is obtained. Therefore, the indicator phenolphthalein, having a pH range of 8.2-10, can be used as a suitable indicator.

### 4. Weak acid-weak base ( $\text{CH}_3\text{COOH}$ vs $\text{NH}_4\text{OH}$ ) titration:

When a weak acid is titrated against a weak base a pH curve with no sharp (narrow) change in pH (6-7.5) is obtained. Therefore, there is no suitable indicator available for this type of titration.

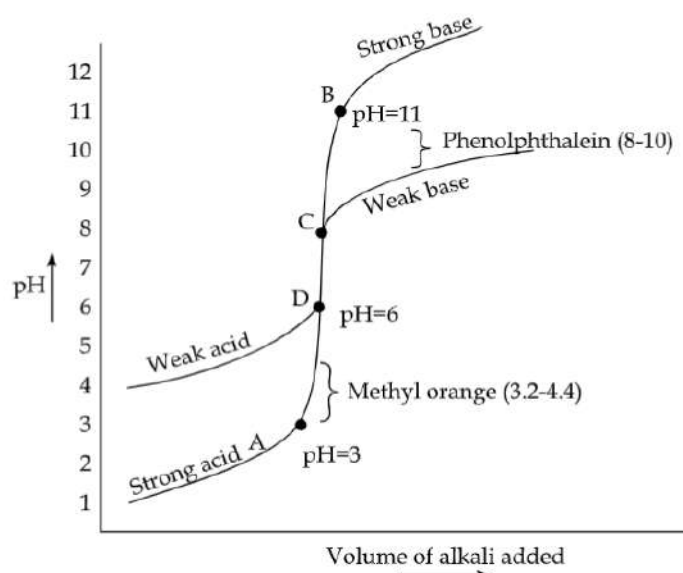


Fig: pH curves for acid-base titration

## Types of salts

When you hear the word **salt**, the first thing that probably comes to mind is the white crystals you sprinkle on food. But chemistry reveals a far richer story. Baking soda that makes your cake rise, washing soda that cleans your clothes, alum that purifies drinking water, blue vitriol used in laboratories — all of these are salts!

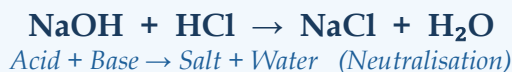


Salts are **everywhere** — in industry, agriculture, medicine, water treatment, and in every biological cell of your body.

A **salt** is an **ionic compound** formed when the hydrogen ion ( $\text{H}^+$ ) of an acid is wholly or partially replaced by a metal ion or an ammonium ion ( $\text{NH}_4^+$ ).



In practical terms, salts are most commonly produced during a **neutralisation reaction** between an acid and a base:



Every salt is made up of two essential components:

| Component              | Type                   | Examples                                                                         |
|------------------------|------------------------|----------------------------------------------------------------------------------|
| Cation (Basic Radical) | Positively charged ion | $\text{Na}^+$ , $\text{K}^+$ , $\text{Cu}^{2+}$ , $\text{NH}_4^+$                |
| Anion (Acid Radical)   | Negatively charged ion | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , $\text{CH}_3\text{COO}^-$ |

Salts can be classified as:

#### A. Based on composition

- Simple salts      Double salts      Complex salts      Acid salts

#### B. Based on behaviour in water

- Neutral salts      Acidic salts      Basic salts

### Simple Salts

Simple salts contain only **one type of cation** and **one type of anion**. When soluble simple salts dissolve in water, they generally dissociate into their constituent ions. For example:



Common examples include:

| Salt Name        | Chemical Formula            |
|------------------|-----------------------------|
| Sodium chloride  | $\text{NaCl}$               |
| Copper sulphate  | $\text{CuSO}_4$             |
| Sodium acetate   | $\text{CH}_3\text{COONa}$   |
| Ammonium acetate | $\text{CH}_3\text{COONH}_4$ |

Simple salts are further classified based on the nature of the solution they produce when dissolved in water:

#### Acidic Salts ( $\text{pH} < 7$ )

These salts produce an **acidic solution** when dissolved in water. They are typically formed from a **strong acid + weak base** combination.

When dissolved in water, they undergo hydrolysis and increase the concentration of  $\text{H}^+$  ions:



*$\text{NH}_4^+$  hydrolyses to release  $\text{H}^+$ , making the solution acidic*

Examples of acidic salts:

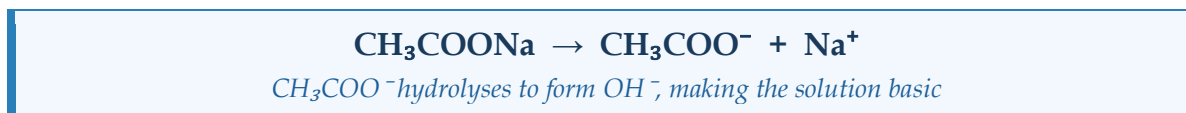
| Salt Name       | Formula                    | Formed from                                                                  |
|-----------------|----------------------------|------------------------------------------------------------------------------|
| Copper sulphate | $\text{CuSO}_4$            | $\text{H}_2\text{SO}_4$ (strong acid) + $\text{Cu}(\text{OH})_2$ (weak base) |
| Zinc nitrate    | $\text{Zn}(\text{NO}_3)_2$ | $\text{HNO}_3$ (strong acid) + $\text{Zn}(\text{OH})_2$ (weak base)          |

| Salt Name         | Formula            | Formed from                                        |
|-------------------|--------------------|----------------------------------------------------|
| Ammonium chloride | NH <sub>4</sub> Cl | HCl (strong acid) + NH <sub>4</sub> OH (weak base) |

### Basic Salts (pH > 7)

These salts produce a **basic solution** when dissolved in water. They are formed from a **weak acid + strong base** combination.

Upon hydrolysis, they increase the concentration of OH<sup>-</sup> ions:



Examples of basic salts:

| Salt Name         | Formula               | Formed from                                           |
|-------------------|-----------------------|-------------------------------------------------------|
| Sodium acetate    | CH <sub>3</sub> COONa | CH <sub>3</sub> COOH (weak acid) + NaOH (strong base) |
| Potassium formate | HCOOK                 | HCOOH (weak acid) + KOH (strong base)                 |

### Neutral Salts (pH ≈ 7)

These salts produce a **neutral solution** in water with a pH close to 7. They are formed from a **strong acid + strong base** combination.

**Why neutral?** Neither the cation nor the anion undergoes significant hydrolysis, so there is no net change in H<sup>+</sup> or OH<sup>-</sup> concentration.

Examples of neutral salts:

| Salt Name         | Formula          | Formed from                                        |
|-------------------|------------------|----------------------------------------------------|
| Sodium chloride   | NaCl             | HCl (strong acid) + NaOH (strong base)             |
| Potassium nitrate | KNO <sub>3</sub> | HNO <sub>3</sub> (strong acid) + KOH (strong base) |

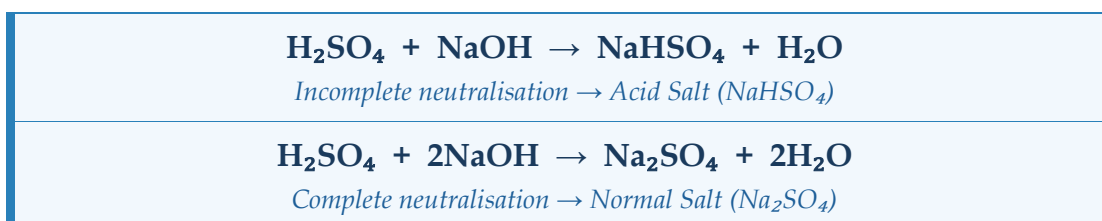
### Double salts:

Compounds formed by the combination of two simple salts in a definite ratio and which dissociate completely into their constituent ions in solution. Example: Mohr's salt, FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O.

### Acid Salts

Acid salts are formed by the **partial neutralisation of a polybasic acid**. They still retain one or more **replaceable hydrogen atoms** in their formula.

Compare what happens when sulphuric acid (a dibasic acid) reacts with NaOH:



Common acid salts include:

| Acid Salt Name | Formula | Replaceable H <sup>+</sup> |
|----------------|---------|----------------------------|
|----------------|---------|----------------------------|

| Acid Salt Name              | Formula            | Replaceable H <sup>+</sup> |
|-----------------------------|--------------------|----------------------------|
| Sodium hydrogen sulphate    | NaHSO <sub>4</sub> | 1                          |
| Sodium hydrogen carbonate   | NaHCO <sub>3</sub> | 1                          |
| Potassium hydrogen sulphate | KHSO <sub>4</sub>  | 1                          |

### ⚠ Critical NEB Distinction: Acidic Salt vs Acid Salt

This is one of the **most frequently tested distinctions** in NEB examinations. Students often confuse these two terms — make sure you don't!

| Feature            | Acidic Salt                                                  | Acid Salt                                                    |
|--------------------|--------------------------------------------------------------|--------------------------------------------------------------|
| Definition         | Gives an acidic solution in water                            | Contains replaceable H <sup>+</sup> in the formula           |
| Based on           | Behaviour in water (hydrolysis)                              | Composition of the salt                                      |
| Example            | NH <sub>4</sub> Cl                                           | NaHSO <sub>4</sub>                                           |
| Key test           | Check pH < 7 in aqueous solution                             | Check for H in the formula                                   |
| Are they the same? | No — an acid salt can give a neutral or even basic solution! | No — an acidic salt need not have replaceable H <sup>+</sup> |

#### Important Point

An acid salt is defined by its composition, not by the pH of its aqueous solution.

Example: NaHCO<sub>3</sub> is an acid salt but gives a slightly basic solution!

Therefore, acid salt ≠ acidic salt.

### Complex Salts

Complex salts contain a **complex ion** along with a counter ion. A complex ion consists of a **central metal ion** surrounded by **ligands** — atoms, molecules, or ions that donate a lone pair of electrons to the metal. Common ligands include:

| Ligand       | Formula          | Type             |
|--------------|------------------|------------------|
| Ammonia      | NH <sub>3</sub>  | Neutral molecule |
| Water        | H <sub>2</sub> O | Neutral molecule |
| Chloride ion | Cl <sup>-</sup>  | Anionic ligand   |
| Cyanide ion  | CN <sup>-</sup>  | Anionic ligand   |

Formation of a Complex Salt — A Striking Example:

Consider what happens when ammonium hydroxide (NH<sub>4</sub>OH) is added to a copper sulphate (CuSO<sub>4</sub>) solution step by step:

#### Step 1: Small amount of NH<sub>4</sub>OH added

A pale blue precipitate of copper hydroxide forms:



## Step 2: Excess $\text{NH}_4\text{OH}$ added

The pale blue precipitate dissolves, and a stunning deep blue complex ion forms!



In a solution containing sulfate ions, this corresponds to the complex salt  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  (Tetraamminecopper(II) sulphate)

Understanding the structure of this complex salt:

| Component                         | Identity          | Role                                    |
|-----------------------------------|-------------------|-----------------------------------------|
| $\text{Cu}^{2+}$                  | Central metal ion | Accepts electron pairs from ligands     |
| $\text{NH}_3$ ( $\times 4$ )      | Ligand            | Donates a lone pair to $\text{Cu}^{2+}$ |
| $[\text{Cu}(\text{NH}_3)_4]^{2+}$ | Complex ion       | Core of the complex salt                |
| $\text{SO}_4^{2-}$                | Counter ion       | Balances the positive charge            |

Complex salts:

- Contain one or more complex ions enclosed in square brackets [ ].
- Usually exhibit characteristic, vivid colours (e.g., deep blue, red, yellow).
- Show special chemical properties not seen in simple salts.
- Are widely used in analytical chemistry, medicine, and industrial processes.

## Hydrolysis of Salts

The reaction of the cation or anion (or both) of a salt with water to produce an acidic or basic solution is called **hydrolysis of salts**.

Based on the relative strength of the acid and base produced (parent acid and base), the solution may be acidic, basic, or neutral, and the salts are divided into 4 classes.

### A. Salt of a strong acid and a strong base:

Halides, nitrates, and sulphates of Na and K, like  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{K}_2\text{SO}_4$ , are strong electrolytes which give cations and anions when dissolved in water. These ions do not interact with water (these ions do not get hydrolysed). Therefore, the concentration of  $\text{H}^+$  and  $\text{OH}^-$  ions will not change.

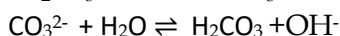
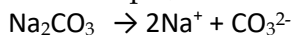


Hence, in general, **the salt of a strong acid and a strong base does not undergo hydrolysis**. Hence, the resulting solution is neutral.

### B. Salt of a weak acid and a strong base:

Salts like  $\text{Na}_2\text{CO}_3$ ,  $\text{CH}_3\text{COONa}$ , and  $\text{K}_2\text{CO}_3$  are examples of this type. When these salts are dissolved in water, it produces strong base and a weak acid.

For example, when  $\text{Na}_2\text{CO}_3$  is dissolved in water, it dissociates into sodium and carbonate ions.

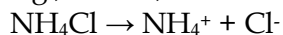


Thus,  $\text{OH}^-$  is produced  $\rightarrow$  the solution is basic.

### C. Salt of strong acid and weak base:

Salts like  $\text{CaCl}_2$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{FeCl}_3$  are examples of this category. When such salts are dissolved in water, they produce a strong acid and a weak base.

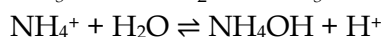
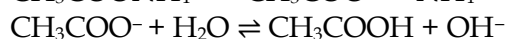
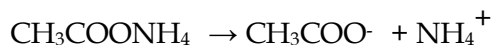
e.g.,  $\text{NH}_4\text{Cl}$ , when dissolved in water, dissociates as:



Thus,  $\text{H}^+$  is produced  $\rightarrow$  the solution is acidic.

#### D. Salt of a weak acid and a weak base:

Salts like  $\text{CH}_3\text{COONH}_4$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $(\text{CH}_3\text{COO})_2\text{Ca}$ , and  $\text{HCOONH}_4$  are examples of this category. When such salts are dissolved in water, they produce weak acids and weak bases.



Therefore, the resulting solution may be neutral, acidic, or alkaline depending on the relative strength of weak acids and bases produced.

#### Summary: Hydrolysis of Salts

| Salt Type                 | Hydrolysis          | pH                         | Example                                  |
|---------------------------|---------------------|----------------------------|------------------------------------------|
| Strong acid + Strong base | Negligible          | = 7                        | $\text{NaCl}$ , $\text{KNO}_3$           |
| Weak acid + Strong base   | Anion hydrolysis    | > 7                        | $\text{CH}_3\text{COONa}$                |
| Strong acid + Weak base   | Cation hydrolysis   | < 7                        | $\text{NH}_4\text{Cl}$ , $\text{FeCl}_3$ |
| Weak acid + Weak base     | Both ions hydrolyse | Depends on $K_a$ and $K_b$ | $\text{CH}_3\text{COONH}_4$              |

\*\*\* ... \*\*\*

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