

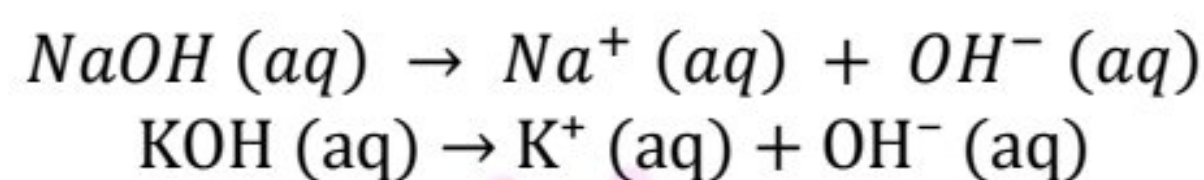
CHEMICAL EQUILIBRIA

Strong and Weak Bases

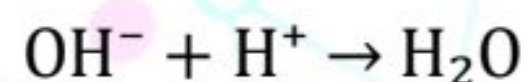
- **Strength of a base** refers to its ability to **accept a proton (H^+)** from a solvent (usually water).
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Strong Bases

- **Examples:** Hydroxides of alkali metals like **NaOH** (sodium hydroxide) and **KOH** (potassium hydroxide).
- These bases **ionize completely** in aqueous solution:

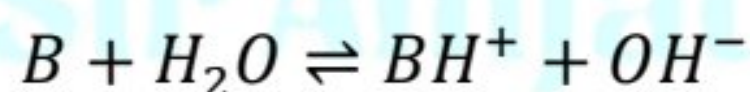


- The **OH^- ion** produced acts as a **Brønsted base** because it can accept a proton:



Weak Bases

- A **weak base** does **not ionize completely** in water.
- The reaction of a base (**B**) with water is shown as:



- Only a small fraction of **B** reacts to produce **OH^-** , so the solution contains fewer hydroxide ions.
-

Base Ionization Constant (K_b)

- The equilibrium constant for the above reaction is called the **base ionization constant (K_b)**:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- A **large K_b** $\rightarrow$ the base ionizes more $\rightarrow$ the base is **strong**.
 - A **small K_b** $\rightarrow$ the base ionizes less $\rightarrow$ the base is **weak**.
-

pK_b

- To make K_b values easier to work with, chemists use pK_b :

$$pK_b = -\log K_b$$

- Lower $pK_b \rightarrow$ stronger base (because K_b is large).
- Higher $pK_b \rightarrow$ weaker base.

Table 3.2 – K_b and pK_b Values of Some Common Bases

Name of Base	Formula	K_b (Base Ionization Constant)	pK_b
Diethylamine	$(C_2H_5)_2NH$	9.6×10^{-4}	3.02
Ethylamine	$C_2H_5NH_2$	5.6×10^{-4}	3.25
Methylamine	CH_3NH_2	4.5×10^{-4}	3.34
Ammonia	NH_3	1.7×10^{-5}	4.76
Pyridine	C_5H_5N	5.6×10^{-9}	8.25
Aniline	$C_6H_5NH_2$	4.3×10^{-10}	9.37

Key Observations

Relationship between K_b and pK_b :

- A high K_b means the base ionizes more $\rightarrow$ stronger base.
- A low pK_b means the base is stronger.

Order of Base Strength (Strongest $\rightarrow$ Weakest):



Important notes:

- Diethylamine** is the **strongest base** (highest K_b , lowest pK_b).
- Aniline** is the **weakest base** (lowest K_b , highest pK_b).
- Ammonia** (NH_3) is stronger than **Pyridine** and **Aniline**, but weaker than **alkylamines** (methyl-, ethyl-, diethylamine).

Buffer Solutions and Their Applications

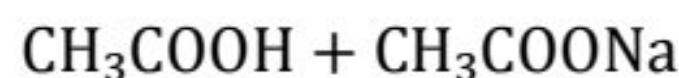
What is a Buffer Solution?

- A **buffer solution** is one whose **pH remains nearly constant** when a **small amount of acid or base** is added.
- Buffers **resist changes in pH**, keeping it stable for a long time.

Types of Buffer Solutions

Acidic Buffers

- Made by mixing a **weak acid** with its **salt formed from a strong base**.
- pH is **less than 7**.
- **Example:**



Basic Buffers

- Made by mixing a **weak base** with its **salt formed from a strong acid**.
- pH is **greater than 7**.
- **Example:**



Buffer Action (How Buffers Work)

Example: Buffer solution of CH_3COOH (weak acid) and CH_3COONa (its salt).

- CH_3COOH is a **weak acid** $\rightarrow$ partially dissociates:



- CH_3COONa is a **strong electrolyte** $\rightarrow$ dissociates completely:

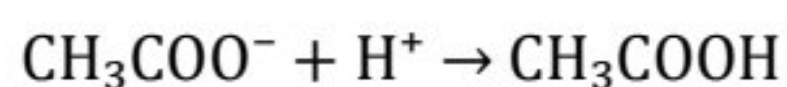


- The presence of CH_3COO^- ions (from the salt) suppresses further dissociation of CH_3COOH due to the **common ion effect**.

What happens if acid or base is added?

(i) When a strong acid (like HCl) is added:

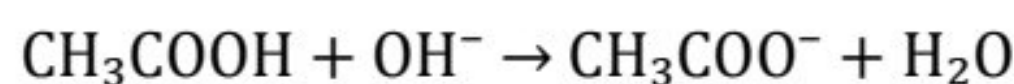
- H^+ ions from HCl react with CH_3COO^- ions to form more CH_3COOH :



This removes extra H^+ ions from the solution, so pH remains almost unchanged.

(ii) When a strong base (like NaOH) is added:

- OH^- ions from NaOH react with H^+ ions (from CH_3COOH) to form water:



This removes extra OH^- ions, keeping the pH stable.

Applications of Buffer Solutions

Buffers are very important in science and daily life.

Some key applications:

Biological systems – Blood is a natural buffer (maintains pH ~7.4).

Industrial processes – Used in fermentation, dyeing, and leather tanning.

Pharmaceuticals – Medicines (like eye drops) use buffers to match body pH.

Chemical analysis – Many chemical reactions require a constant pH.

Calculation of pH of Buffer Solution

Key Concept

- In a buffer solution, the **concentration of the conjugate base** (CH_3COO^-) mainly comes from the **salt** (CH_3COONa), which **ionizes completely**.
- The **acid** (CH_3COOH) only partially ionizes.
- pH is calculated using the **Henderson–Hasselbalch equation**:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Example 3.2

(a) Calculate the pH of an acetic acid–sodium acetate buffer solution containing 1.0 mole of each component.

- Given:
 - $[\text{CH}_3\text{COOH}] = 1.0 \text{ M}$
 - $[\text{CH}_3\text{COONa}] = 1.0 \text{ M}$
 - $K_a \text{ for acetic acid} = 1.8 \times 10^{-5}$

Step 1: Calculate pK_a

$$pK_a = -\log K_a$$
$$pK_a = -\log(1.8 \times 10^{-5}) = 4.745$$

Step 2: Use Henderson–Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$
$$pH = 4.745 + \log \frac{1.0}{1.0}$$
$$pH = 4.745 + 0 = \boxed{4.745}$$

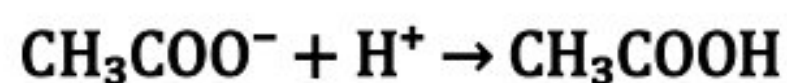
(b) What will be the pH after the addition of 0.01 mole of HCl to 1 dm³ of the solution?

Step 1: Understand reaction of added HCl

- HCl dissociates completely:



- H⁺ ions react with acetate ions (CH₃COO⁻):



- This reduces CH₃COO⁻ and increases CH₃COOH.
-

Step 2: Adjust concentrations

- Before addition:
 - CH₃COOH = 1.00 M
 - CH₃COO⁻ = 1.00 M
- After addition of 0.01 mole HCl:
 - CH₃COOH = 1.00 + 0.01 = 1.01 M
 - CH₃COO⁻ = 1.00 - 0.01 = 0.99 M

Step 3: Calculate new pH

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = 4.745 + \log \frac{0.99}{1.01}$$

Step 4: Simplify log term

$$\frac{0.99}{1.01} = 0.980$$

$$\log(0.980) = -0.009$$

Step 5: Final pH

$$\text{pH} = 4.745 - 0.009 = \boxed{4.736}$$

Conclusion

- pH changes only slightly:

$$4.745 \rightarrow 4.736 \text{ (a change of just 0.009!)}$$

Applications of Buffer Solutions

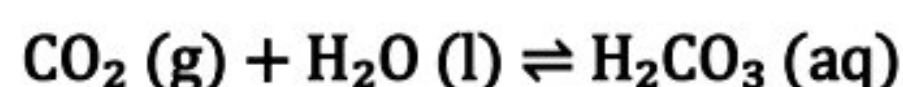
Buffers play a crucial role in everyday life, helping to maintain stability and prevent abrupt changes in pH in various systems.

1. The Buffer System in Blood Plasma

- The **bicarbonate ion** (HCO_3^-) is the key component of the **bicarbonate buffer system**, which maintains the blood's pH.
- **Normal blood pH: 7.35 – 7.45**
 - **Below 6.8 or above 7.8** can be fatal.

How the Bicarbonate Buffer System Works

Formation of Carbonic Acid



Decomposition of Carbonic Acid

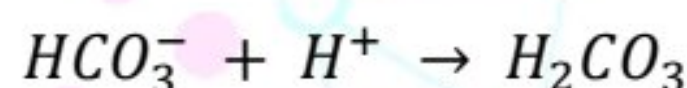


These reactions are **catalyzed by the enzyme carbonic anhydrase** (found in red blood cells).

Role in pH Regulation

Neutralization of Acids

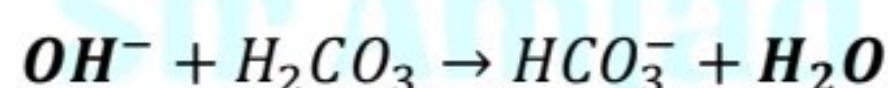
- When excess **H⁺ ions** are present, **bicarbonate (HCO₃⁻)** acts as a base:



- Carbonic acid then converts to **CO₂ and water**, and CO₂ is exhaled via the lungs.

Neutralization of Bases

- When excess **OH⁻ ions** are present, **carbonic acid (H₂CO₃)** donates **H⁺**:



- This prevents the blood from becoming too alkaline.
-

Why It's Important

- Maintains a **stable pH** for enzymes and metabolic processes.
- Works together with:
 - Respiratory system** (controls CO₂ levels through breathing)
 - Renal system** (regulates bicarbonate reabsorption and excretion).

Household Cleaning Products

- Detergents and cleaners** often contain buffers.
 - They maintain an **optimal pH** for cleaning **without damaging surfaces** or irritating skin.
-

Personal Care Products

- **Shampoos, soaps, and skincare products** use buffers.
 - Prevents **skin irritation** by keeping the product's pH **close to skin's natural pH (~5.5)**.
-

Swimming Pools

- Buffers are added to **pool water**.
 - Keeps pH stable to:
Prevent corrosion of pool equipment.
Provide a comfortable environment for swimmers.
-

Food and Beverage Industry

- **Food processing:** Buffers **control acidity**, preserve **flavour**, and keep foods stable.
 - **Beverages:** Buffers maintain **consistent taste** and **prevent spoilage**.
-

Photography

- **Photographic developer solutions** use buffers.
 - Maintains **stable pH** to ensure film and prints **develop consistently**.
-

The Partition Coefficient

When two **immiscible liquids** such as **ether** and **water** are placed in a separatory funnel and shaken, they form two distinct layers upon standing. **Ether**, being less dense, forms the **upper layer**, while water remains as the **lower layer**.

Distribution of Solute Between Layers

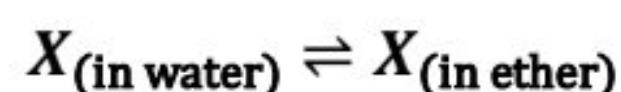
Suppose a solute **X** is initially dissolved in water. When ether is added and the mixture is shaken:

- Some solute remains in **water**.
- Some solute transfers into **ether**.

After standing, analysis shows that solute **X** is present in **both layers**. This indicates that the solute has **distributed** between the two solvents.

Dynamic Equilibrium

Eventually, a **dynamic equilibrium** is established between the solute molecules in both layers:



At this point, the **concentration of the solute** in each solvent becomes **constant**.

Partition Coefficient (K_{pc})

The **equilibrium constant** for this distribution is called the **Partition Coefficient** and is denoted as **K_{pc}**.

$$K_{pc} = \frac{[X]_{\text{in ether}}}{[X]_{\text{in water}}}$$

K_{pc} has:

- A **constant value** at a given temperature.
- **No units** (because it is a ratio of two concentrations).

Nernst Distribution Law

The **Nernst Distribution Law** states:

“A solute distributes itself between two immiscible solvents in a constant ratio of concentrations at a constant temperature, provided the solute exists in the same molecular form in both solvents.”

Key Points

- **High K_{pc}** → Solute prefers the **ether layer**.
- **Low K_{pc}** → Solute prefers the **water layer**.
- K_{pc} is only **constant** if the solute **does not react, dissociate, or change form** in either solvent.

Calculation of Partition Coefficient

The **partition coefficient (K)** can be calculated experimentally when a solute is distributed between **two immiscible solvents** (here: **water** and an organic solvent).

Activity 3.1: Calculating the Partition Coefficient**Procedure:**

1. Measure **100 cm³** of a **0.150 M** aqueous methylamine (**CH₃NH₂**) solution into a separatory funnel.
2. Add **75 cm³** of an organic solvent.
3. Shake well and allow the system to reach equilibrium (5–10 min).
4. Let the two layers separate and collect them.
5. Take **25 cm³** of the aqueous layer and titrate against **0.225 M HCl**.
6. Note the volume of HCl used (**7.05 cm³**).

Data Given

- Volume of aqueous methylamine solution: **100 cm³**
- Initial concentration of methylamine: **0.150 mol dm⁻³**
- Volume of organic solvent: **75.0 cm³**
- Volume of aqueous layer titrated: **25.0 cm³**
- Volume of HCl used: **7.05 cm³**
- Concentration of HCl: **0.225 mol dm⁻³**

Step-by-Step Solution

Step 1: Write the equilibrium equation



Step 2: Write the expression for partition coefficient

$$K = \frac{[\text{CH}_3\text{NH}_2]_{\text{organic}}}{[\text{CH}_3\text{NH}_2]_{\text{aqueous}}}$$

Step 3: Calculate total moles of methylamine initially present

$$n = C \times V = 0.150 \times \frac{100}{1000} = 0.015 \text{ mol}$$

Step 4: Calculate moles of CH₃NH₂ in aqueous layer

- From titration:

$$\begin{aligned}\text{moles HCl} &= C \times V \\ &= 0.225 \times \frac{7.05}{1000} = 0.001586 \text{ mol}\end{aligned}$$

- 1 mole of HCl reacts with 1 mole of CH₃NH₂:

$$\text{moles CH}_3\text{NH}_2 \text{ in } 25 \text{ cm}^3 = 0.001586 \text{ mol}$$

Scale up to 100 cm³:

$$0.001586 \times \frac{100}{25} = 0.00634 \text{ mol in aqueous layer}$$

Step 5: Moles of CH₃NH₂ in organic layer

$$\text{Moles in organic layer} = \text{Total moles} - \text{Moles in aqueous layer}$$

$$0.015 - 0.00634 = 0.00866 \text{ mol}$$

Step 6: Calculate concentrations

- In aqueous layer:

$$[\text{CH}_3\text{NH}_2]_{\text{aqueous}} = \frac{0.00634}{0.100} = 0.0634 \text{ mol dm}^{-3}$$

- In organic layer:

$$[\text{CH}_3\text{NH}_2]_{\text{organic}} = \frac{0.00866}{0.075} = 0.115 \text{ mol dm}^{-3}$$

Step 7: Calculate the partition coefficient

$$K = \frac{0.115}{0.0634} \approx \boxed{1.8}$$

Conclusion

- Since $K > 1$, methylamine is **more soluble in the organic solvent** than in water.

Factors Affecting the Numerical Value of the Partition Coefficient

The partition coefficient (K) indicates how a solute distributes itself between two immiscible phases—commonly a polar solvent (like water) and a non-polar solvent (like octanol or ether).

Several factors influence its numerical value:

1. Polarity of the Solute

- Polar solutes have a greater affinity for polar solvents because of:
 - Dipole–dipole interactions
 - Hydrogen bonding
 - Example:
 - *Ethanol* (polar due to --OH group) partitions between octanol and water.
 - Ethanol is more soluble in water $\rightarrow K$ favours the polar phase.
-

2. Solvent Polarity

- The nature of the solvents strongly affects partitioning:
 - Non-polar solvents dissolve non-polar solutes better.
 - Polar solvents dissolve polar solutes better.
 - Example:
 - *Benzene* (non-polar) partitions between octanol and water.
 - Benzene dissolves more in octanol $\rightarrow$ higher K in favour of the non-polar phase.
-

3. Temperature

- Temperature changes affect:
 - Solubility of the solute in each solvent.
 - Kinetic energy of solute molecules.
- Generally, higher temperature:
 - Increases solubility of many solutes in polar solvents.
- Example:
 - The partitioning of *aspirin* between octanol and water shows different K values at different temperatures.
 - At higher temperatures $\rightarrow$ aspirin becomes more soluble in water.

4. Molecular Structure & Size

- Larger molecules or those with bulky groups experience:
 - Steric hindrance, reducing solubility in certain solvents.
- Functional groups (e.g., $-\text{OH}$, $-\text{COOH}$) also influence solubility by forming hydrogen bonds.
- Example:
 - *Ethyl acetate* vs. *Butyl acetate* between octanol and water:
 - Butyl acetate (larger) shows a lower K in favour of the non-polar phase due to size and steric effects.

Review Exercise

1. Explain the common ion effect with a suitable example.

- **Definition:** The **common ion effect** is the suppression of the ionization of a weak acid or weak base by the addition of a strong electrolyte containing a common ion.
- **Example:**



Adding CH_3COONa (which provides CH_3COO^- ions) **suppresses** the ionization of acetic acid due to the presence of the **common ion** (CH_3COO^-).

2. Differentiate between strong and weak acids using the extent of ionization and K_a .

- **Strong acids:**
 - **Completely ionize** in water.
 - Have **very large K_a** values ($K_a \rightarrow \infty$).
 - Example: HCl , HNO_3 .
- **Weak acids:**
 - **Partially ionize** in water.
 - Have **small K_a** values.
 - Example: CH_3COOH .

3. Differentiate between strong and weak bases using the extent of ionization and K_b .

- **Strong bases:**
 - **Completely ionize** in water.
 - Have **large K_b** values.
 - Example: NaOH , KOH .
- **Weak bases:**
 - **Partially ionize** in water.
 - Have **small K_b** values.

- Example: NH_3 , CH_3NH_2 .

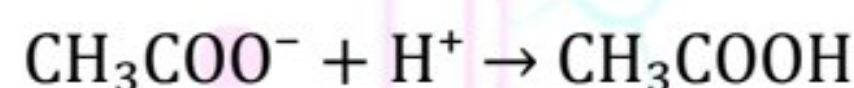
4. Define a buffer solution and provide an example of how it can be made.

- **Definition:** A buffer solution is one that **resists changes in pH** when small amounts of acid or base are added.
- **Examples:**
 - **Acidic buffer:** $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
 - **Basic buffer:** $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.

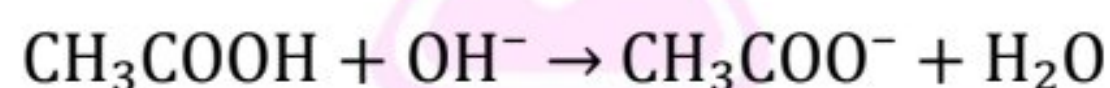
5. How does a buffer solution control pH? Include chemical equations in your explanation.

- **Mechanism:** Buffers **neutralize** added acids or bases using weak acid/base equilibrium.
- **Example (Acetic acid–Sodium acetate buffer):**

When **acid (H^+)** is added:



When **base (OH^-)** is added:



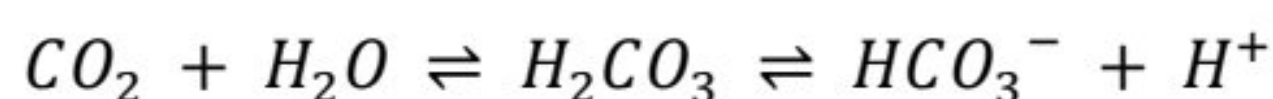
The pH remains **nearly constant**.

6. Describe the uses of buffer solutions in various applications.

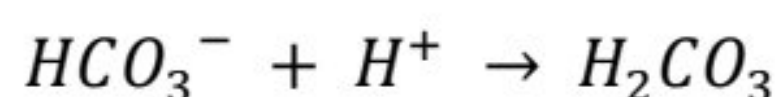
- **Blood plasma:** Maintains pH (7.35–7.45).
- **Shampoos & soaps:** Prevents skin irritation.
- **Swimming pools:** Keeps pH stable.
- **Food industry:** Controls acidity & flavour.
- **Photography:** Keeps developer solutions at the right pH.

7. Explain how HCO_3^- plays a role in controlling pH in the blood.

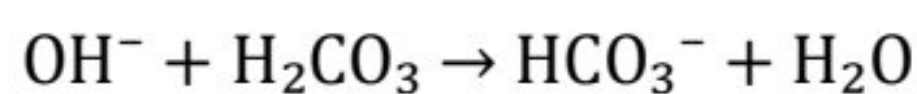
- **Bicarbonate buffer system** in blood:



If blood becomes **too acidic** ($\uparrow H^+$):



If blood becomes **too basic** ($\uparrow OH^-$):



This maintains blood pH in the **normal range**.

8. Calculate the concentration of a slightly soluble salt given its solubility product constant (K_{sp}).

Formula:

For a salt $AB \rightleftharpoons A^+ + B^-$:

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

If the solubility is s mol/dm³:

$$K_{sp} = s^2 \Rightarrow s = \sqrt{K_{sp}}$$

For salts like A_2B or AB_2 , adjust the expression accordingly (e.g., $K_{sp} = 4s^3$ for AB_2)

For More Information:

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