CHEMICAL EQUILIBRIA

Strong and Weak Bases

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

Strong Bases

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

$$NaOH\ (aq) \rightarrow Na^+\ (aq) + OH^-\ (aq)$$
$$\mathrm{KOH\ (aq) \rightarrow K^+\ (aq) + OH^-\ (aq)}$$

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

$$\mathrm{OH^- + H^+ \rightarrow H_2O}$$

Weak Bases

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

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

- 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** → the base ionizes more → the base is **strong**.
- A **small K_b** → the base ionizes less → the base is **weak**.

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pK_b

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

$$pK_b = -\log K_b$$

- **Lower pK_b → stronger base** (because K_b is large).
- **Higher pK_b→ weaker base**.

Table 3.2 – K_β and pK_β Values of Some Common Bases

Name of Base	Formula	K_β (Base Ionization Constant)	pK_β
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_β and pK_β:

- A **high K_β** means the base ionizes **more → stronger base**.
- A **low pK_β** means the base is **stronger**.

Order of Base Strength (Strongest → Weakest):

$$Diethylamine > Ethylamine > Methylamine > Ammonia > Pyridine > Aniline$$

Important notes:

- **Diethylamine** is the **strongest base** (highest K_β, lowest pK_β).
- **Aniline** is the **weakest base** (lowest K_β, highest pK_β).
- **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:**

$$CH_3COOH + CH_3COONa$$

Basic Buffers

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

$$NH_4OH + NH_4Cl$$

Buffer Action (How Buffers Work)

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

- **CH_3COOH** is a **weak acid** → partially dissociates:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

- **CH_3COONa** is a **strong electrolyte** → dissociates completely:

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

- 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:

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

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:

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

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**:

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

Example 3.2

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

- Given:
  - $[CH3COOH] = 1.0\ M$
  - $[CH3COONa] = 1.0\ M$
  - $K_a\ for\ acetic\ acid = 1.8 \times 10^{-5}$

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

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

$$\text{pH} = 4.745 + \log \frac{1.0}{1.0}$$

$$\text{pH} = 4.745 + 0 = \boxed{4.745}$$

(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:

$$HCl \rightarrow H^+ + Cl^-$$

- H^+ ions react with acetate ions (CH_3COO^-):

$$\mathbf{CH_3COO^- + H^+ \rightarrow CH_3COOH}$$

- This **reduces CH_3COO^-** and **increases CH_3COOH**.

Step 2: Adjust concentrations

- Before addition:
  - CH_3COOH = 1.00 M
  - CH_3COO^- = 1.00 M
- After addition of 0.01 mole HCl:
  - $CH_3COOH = 1.00 + 0.01 = 1.01$ M
  - $CH_3COO^- = 1.00 - 0.01 = 0.99$ M

Step 3: Calculate new pH

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

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

Step 4: Simplify log term

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

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

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

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

Decomposition of Carbonic Acid

$$H_2CO_3\,(aq) \rightleftharpoons HCO_3^-\,(aq) + H^+\,(aq)$$

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 (HCO_3^-)** acts as a base:

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

- Carbonic acid then converts to **CO_2 and water**, and CO_2 is exhaled via the lungs.

Neutralization of Bases

- When excess **OH^- ions** are present, **carbonic acid (H_2CO_3)** donates **H^+**:

$$\boldsymbol{OH^-} + H_2CO_3 \rightarrow HCO_3^- + \boldsymbol{H_2O}$$

- 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 CO_2 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:

$$X_{\text{(in water)}} \rightleftharpoons X_{\text{(in ether)}}$$

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

Partition Coefficient (Kpc)

The **equilibrium constant** for this distribution is called the **Partition Coefficient** and is denoted as **Kpc**.

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

Kpc 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 Kpc** → Solute prefers the **ether layer**.
- **Low Kpc** → Solute prefers the **water layer**.
- Kpc 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 (CH_3NH_2)** 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

$$CH_3NH_2\ (aq) \rightleftharpoons CH_3NH_2\ (organic)$$

Step 2: Write the expression for partition coefficient

$$K = \frac{[CH_3NH_2]_{organic}}{[CH_3NH_2]_{aqueous}}$$

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 CH_3NH_2 in aqueous layer

- From titration:

$$\text{moles HCl} = C \times V$$

$$= 0.225 \times \frac{7.05}{1000} = 0.001586 \text{ mol}$$

- 1 mole of HCl reacts with 1 mole of CH_3NH_2:

$$\text{moles } CH_3NH_2 \text{ in } 25 \text{ cm}^3 = 0.001586 \text{ mol}$$

Scale up to **100 cm³**:

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

Step 5: Moles of CH_3NH_2 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**:

$$[CH_3NH_2]_{\text{aqueous}} = \frac{0.00634}{0.100} = 0.0634 \text{ mol dm}^{-3}$$

- **In organic layer**:

$$[CH_3NH_2]_{\text{organic}} = \frac{0.00866}{0.075} = 0.115 \text{ mol dm}^{-3}$$

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:

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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 → K favours the polar phase.

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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 → higher K in favour of the non-polar phase.

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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 → 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., –OH, –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:**

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

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

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

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

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

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

- Example: NH_3, CH_3NH_2.

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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:** $CH_3COOH + CH_3COONa$
  - **Basic buffer:** $NH_4OH + NH_4Cl$.

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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:

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

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

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

The pH remains **nearly constant**.

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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.

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

- **Bicarbonate buffer system** in blood:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

If blood becomes **too acidic** (↑ H^+):

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

If blood becomes **too basic** (↑ OH^-):

$$OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O$$

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

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8. Calculate the concentration of a slightly soluble salt given its solubility product constant (Ksp).

Formula:
For a salt **AB ⇌ A^+ + B^-**:

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

If the solubility is **s** mol/dm³:

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

For salts like **A_2B** or **AB_2**, adjust the expression accordingly (e.g., Ksp = $4s^3$ for AB_2)

For More Information:

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