LABORATORY 2

ELECTROLYTE DISSOCIATION, pH AND BUFFER SOLUTIONS

1. The influence of common ion on pH shift of a weak electrolyte

   A. The influence of sodium acetate (CH₃COONa) addition on pH shift of CH₃COOH (acetic acid) solution.

      Weak electrolytes at the same molar concentration as the strong ones, release to the solution considerably lower amount of ions. For example, the molar concentration of hydrogen ions [H⁺] in 0.1 M solution of strong hydrochloric acid is 10⁻¹ moles/L, but for the same 0.1 M concentration of acetic acid, hydrogen ions concentration reaches value 10⁻³ moles/L. Additionally, hydrogen ions concentration can be diminished after addition of sodium acetate:

      \[
      \text{Partial dissociation} \\
      \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \\
      \]

      Sodium acetate completely dissociates into acetate anions and sodium cations:

      \[
      \text{Complete dissociation} \\
      \text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+ \\
      \]

      Adding acetate anions from completely dissociated sodium acetate to the solution of partially dissociated acetic acid shifts the equilibrium state (of acetic acid dissociation) to the left. There are less hydrogen ions, more undissociated molecules of acid, pH increases.

   Procedure:
   Add 0.1 M acetic acid (10 drops) and 1 drop of methyl orange indicator (at pH below 3.1 methyl orange is pink; at pH above 4.4 it is yellow) to two test tubes. Mix until a pink solution is obtained. Add a few crystals of sodium acetate to one of the tubes and mix. The colour change of the solution is the result of a diminution of hydrogen ions concentration.

   B. The influence of ammonium chloride (NH₄Cl) addition on pH shift of ammonia water (NH₃•H₂O) solution.

   Procedure:
   Add 0.1 M ammonia water solution (10 drops) and 1 drop of phenolphthalein indicator (at pH below 8.3 phenolphthalein is colorless and at pH above 8.3 it is pink) to two test tubes. Mix to obtain a red-coloured solution. To one of the tubes add a few crystals of ammonium chloride. Mix and observe the decolourization of the solution. Write these chemical reactions down in your note book and explain the results of both tests.
2. Calculation of dissociation degree and dissociation constant of acetic acid (CH$_3$COOH) and formic acid (HCOOH)

Calculations will be performed for 0.1 M and 1.0 M solutions of acetic acid and 0.1 M solution of formic acid, after pH determination with pH-meter. The following equations should be used for calculations:

\[
\alpha (\text{dissociation degree}) = \frac{[H^+]}{c_{\text{acid concentration}}} \times 100 \%
\]

\[
K (\text{dissociation constant}) = \frac{[H^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\]

Procedure:

Fill the measuring vessel with the appropriate acetic acid solution (0.1 or 1.0 M) and measure the pH value. Measure also pH value of 0.1 M formic acid solution. Using the determined pH value, calculate hydrogen ions concentration and the dissociation degree using equation (1). Then calculate dissociation constant using equation (2): introduce your calculated hydrogen ions concentration raised to the power of 2 (hydrogen ions concentration is equal to concentration of acetate anions) to the numerator of the equation. Subtract the hydrogen ions concentration from molar concentration of acid and introduce the value to the denominator (concentration of un-dissociated acid molecules). Repeat the same calculations for 0.1 M formic acid solution. Fill the table below with the calculated data.

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>[H$^+$]</th>
<th>K</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$COOH (1 M)</td>
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<tr>
<td>CH$_3$COOH (0.1 M)</td>
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</tr>
<tr>
<td>HCOOH (0.1 M)</td>
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</tbody>
</table>

Buffer Solutions

Mixtures of a weak acid or a weak base, together with their hydrolysing salts, form a buffer solution. A buffer solution is resistant to pH change on addition of small amount of strong acid or strong base. In the presence of completely dissociated hydrolysing salt, the weak electrolyte (weak acid or weak base) does not dissociate. In the mixture of acetic acid and sodium acetate there are molecules and ions, that neutralize both H$^+$ and OH$^-$ ions added. So, acetate buffer consists of undissociated acetic acid and salt-origin acetate ions. After introduction of H$^+$ ions to the acetate buffer, the salt-derived acetate anions accept hydrogen ions, forming undissociated acetic acid. According to the Bronsted/Lowry theory of acids and bases, an anion of a weak acid is a strong base and accepts protons from the solution:
\[ \text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH} \]

\[ (\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}) \]

As the acetate anion concentration decreases, the acetic acid concentration increases.

Introduction of OH\(^-\) ions to the buffer solution, causes the following reaction (acetic acid acts as the Bronsted/Lowry acid because it donates H\(^+\)):

\[ \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]

As the concentration of acetic acid decreases, the acetate ion concentration increases. A buffer's capacity (\(\beta\)) to hold a constant pH depends on the molar concentration of its components. To calculate the buffer's capacity we can use equation:

\[ \beta = \frac{\text{amount of acid or base added to buffer (mole/L)}}{\Delta \text{pH}} \]

A buffer's initial pH value depends on both the weak electrolyte dissociation constant \(K\) and the ratio of buffer components:

\[
[H^+] = K \frac{\text{acid concentration}}{\text{salt concentration}} \quad \text{(for weak acids)}
\]

\[
[OH^-] = K \frac{\text{base concentration}}{\text{salt concentration}} \quad \text{(for weak bases)}
\]

\[
\text{pH} = -\log [H^+]; \quad \text{pOH} = -\log [OH^-] \]

\[ [H^+] \times [OH^-] = 10^{-14} \]

\[ \text{pH} + \text{pOH} = 14 \]

3. The influence of buffer concentration on pH value and buffer capacity

**Procedure:**

Add the following solutions to three beakers:

A) 40 mL of 0.1 M acetic buffer (concentration ratio of acid to salt is 1:1),
B) 40 mL of 0.01 M acetic buffer (concentration ratio of acid to salt is 1:1),
C) 40 mL of water.

Accurately mix each solution and measure the pH value via a pH-meter and note. Next add 2 ml of 0.01M HCl to each beaker and determine the pH value again. Calculate buffers capacities. Draw the conclusions from this experiment.
4. The influence of acid to salt molar ratio on pH of buffer

**Procedure:**

Add the following solutions to two beakers:
A) 20 mL of 0.1 M CH₃COOH, 10 mL of 0.1 M CH₃COONa, and 10 mL of water,
B) 10 mL of 0.1 M CH₃COOH and 20 mL of 0.1 M CH₃COONa, and 10 mL of water
Mix the solutions and determine the pH value via a pH meter. Calculate the acid-to-salt molar ratio and draw a conclusion.

**Problems:**

1. Dissociation degree of 0.1 M hydrogen cyanide (HCN) is 0.007%. Count dissociation constant of HCN. (Answer: \( K = 4.9 \times 10^{-10} \))
2. Calculate molar concentration of water solution of ammonia (\( \text{NH}_3 \cdot \text{H}_2\text{O} \)) pH = 8 and \( \alpha = 0.01 \% \). (Answer: \( C_m = 0.01 \text{ moles/L} \))
3. What will be pH change after addition of 1 drop of 2 mol/L HCl solution to 1 L of water (the volume of 1 drop = 0.05 mL). (Answer: pH changes from 7 to 4)
4. 0.11 moles of HCl and 0.01 moles of NaOH were mixed in a final volume of 1 liter of water. Count pH of the solution. (Answer: pH = 1)
5. 1.2 mL of 0.1 M HCl was added to 10 mL of acetate buffer pH 5.4. pH decreased to 4.2. Calculate the buffer’s capacity. (Answer: \( \beta = 8.9 \times 10^{-3} \))
6. In 1 mL of gastric juice there are 3 mg of HCl (HCl = 36.5 g/mole). What is pH of gastric juice? (Answer: pH = 1.09)
7. Enzymatic reaction was performed in 0.25 M phosphate buffer (0.125 mol/L \( \text{H}_2\text{PO}_4^- \) and 0.125 mol/L \( \text{HPO}_4^{2-} \)), pH 6.8. As the result of the reaction 0.05 moles of H⁺ were produced. What was the final pH of the solution? What would be pH in case of a lack of a buffer? \( K_{\text{H}_2\text{PO}_4^-} = 1.58 \times 10^{-7} \). (Answer: pH₁ = 6.43, pH₂ = 1.3)
8. The concentration of \( \text{H}_2\text{CO}_3 \) in the human plasma is \( 1.25 \times 10^{-3} \text{ mol/L} \). What is concentration of \( \text{HCO}_3^- \) if pH of the blood is 7.4? \( K_{\text{H}_2\text{CO}_3} = 8 \times 10^{-7} \). (Answer: 25 mmol/L).
9. Bicarbonate buffer is the main buffer of human plasma responsible for regulation of blood pH. At pH 7.4, \( \text{HCO}_3^- \) ions concentration is 25 mM, \( \text{CO}_2^- \) – 1.2 mM. What will be pH change after addition 0.005 moles of H⁺ to 1 L of the blood? pK = 6.1. In the human body the excess of \( \text{CO}_2 \) is removed together with exhaled air and \( \text{CO}_2 \) concentration is not changed. (Answer: pH = 7.3 is the final pH)
10. What is \( p_{\text{CO}_2} \) in the patient blood if pH = 7.25, \( \text{HCO}_3^- = 25 \text{ mmol/L} \), \( K_a = 8 \times 10^{-7} \), \( \alpha = 0.03 \text{ mmol/L} \cdot \text{mmHg} \) (\( \text{[CO}_2] = \alpha \times p_{\text{CO}_2} \))? What type of abnormality does the patient have? (Answer: 59 mmHg, respiratory acidosis)