

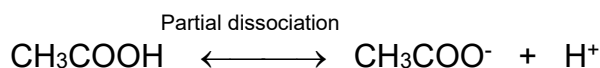
LABORATORY 2

ELECTROLYTE DISSOCIATION, pH

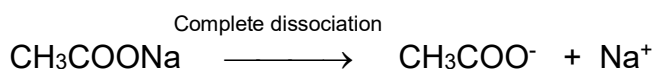
1. The influence of common ion on pH shift of a weak electrolyte

A. The influence of sodium acetate (CH_3COONa) addition on pH shift of CH_3COOH (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 $[\text{H}^+]$ 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:



Sodium acetate completely dissociates into acetate anions and sodium cations:

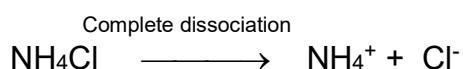
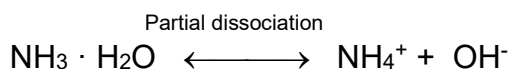


Adding acetate anions from completely dissociated sodium acetate to the solution of partially dissociated acetic acid shifts the equilibrium state (of acetic acid dissociation) to the left. There are less hydrogen ions, more undissociated molecules of acid, pH increases.

Procedure:

Add 0.1 M acetic acid (10 drops) and 1 drop of methyl orange indicator (at pH below 3.1 methyl orange is red; 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, mix and observe the change of the colour of the solution.

B. The influence of ammonium chloride (NH_4Cl) addition on pH shift of ammonia water ($\text{NH}_3 \cdot \text{H}_2\text{O}$) solution.



Procedure:

Add 0.1 M ammonia water solution (10 drops) and 1 drop of phenolphthalein indicator (at pH below 8.3 phenolphthalein is colourless and at pH above 8.3 it is pink) to two test tubes. Mix to obtain a pink-coloured solution. To one of the tubes add a few crystals of ammonium chloride. Mix and observe the decolourization of the solution.

Answer the question:

- Which ions from salts added to the solution of weak acid (point A) and weak base (point B) were responsible for the change of the colour of the solution and why?
- How pH and dissociation degree of weak electrolytes solutions were changed (increase, decrease or no change) after addition of the salts?

2. Calculation of dissociation degree and dissociation constant of acetic acid (CH₃COOH) 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:

$$(1) \quad \alpha \text{ (dissociation degree)} = \frac{[\text{H}^+]}{C \text{ (acid concentration)}} \times 100 \%$$

$$(2) \quad K \text{ (dissociation constant)} = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}] \text{ (undissociated residues of acid)}} = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{C_0 - [\text{H}^+]}$$

The equation is simplified when $[\text{H}^+] = [\text{CH}_3\text{COO}^-]$ and $\alpha \leq 2\%$ (undissociated acid = initial acid concentration C_0):

$$K = \frac{[\text{H}^+]^2}{C_0}$$

Procedure:

- Measure pH of acetic acid (0.1M and 1.0M) and formic acid (0.1M) (**demonstration**)
- Using the determined pH value, calculate hydrogen ions concentration and the dissociation degree of three acid solutions using equation (1)
- Calculate dissociation constant using equation (2)
- Fill the table below with the calculated data

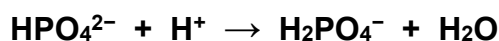
Solution	pH	[H ⁺]	α	K
CH ₃ COOH (1M)				
CH ₃ COOH (0.1M)				
HCOOH (0.1M)				

Answer the questions (using the data from the table):

- Which acid is stronger? Why?
- What is the relationship between dissociation degree, dissociation constant and concentration of acid (compare two acetic acids)?
- What is the relationship between dissociation constant and the strength of acid?

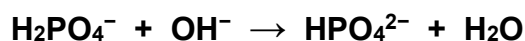
BUFFER SOLUTIONS

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. **Phosphate buffer** consists of two phosphate salts which introduce two phosphate ions to the solution: **H₂PO₄⁻** and **HPO₄²⁻**. **These ions neutralize** both H⁺ and OH⁻ ions added. After introduction of H⁺ ions to the phosphate buffer, **HPO₄²⁻** anions accept hydrogen ions (act as a Bronsted/Lowry base), forming **H₂PO₄⁻** ions:



As the hydrogen phosphate anion (**HPO₄²⁻**) concentration decreases, the dihydrogen phosphate anion (**H₂PO₄⁻**) concentration increases.

Introduction of **OH⁻** ions to the buffer solution, causes the following reaction (**H₂PO₄⁻** ions act as a Bronsted/Lowry acid because they donate H⁺):



As the concentration of dihydrogen phosphate anion (**H₂PO₄⁻**) decreases, the concentration of hydrogen phosphate anion (**HPO₄²⁻**) increases.

A **buffer's capacity** (β) to hold a constant pH depends on the molar concentration of buffer components. To calculate the buffer's capacity we can use equation:

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

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

- Prepare three beakers with two buffer solutions and water according to the table presented below:

Beaker number	V (cm ³) phosphate buffer		V (cm ³) H ₂ O	pH ₁	V (cm ³) 0,05M HCl	pH ₂	ΔpH	n _{HCl}	β
	0,1M	0,01M							
1	40	—	—		2				
2	—	40	—		2				
3	—	—	40		2				

- Measure initial pH (pH₁) of the solutions and water
- Add 2 ml of 0,05 M HCl to each beaker, mix and again measure pH (pH₂)
- Calculate pH difference (ΔpH) and moles of acid (n) added to 1 liter of buffers or water
- Calculate buffer capacity for buffers (not for water)

Answer the question (using the data from the table):

- What is a relationship between the buffer's concentration and capacity?

Problems:

- Dissociation degree of 0.1 M hydrogen cyanide (HCN) is 0.007%. Count dissociation constant of HCN. (Answer: $K = 4.9 \times 10^{-10}$)
- Calculate molar concentration of water solution of ammonia (NH₃ · H₂O) pH = 8 and $\alpha = 0.01$ %. (Answer: $C_m = 0.01$ moles/L)
- 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)
- 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)
- 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: $\beta = 0.01$)
- 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)
- Enzymatic reaction was performed in 0.25 M phosphate buffer (0.125 mol/L H₂PO₄⁻ and 0.125 mol/L HPO₄²⁻), pH 6.8. As the result of the reaction 0.05 moles of H⁺ were produced (per 1 L of the buffer). What was the final pH of the solution? What would be pH in case of a lack of a buffer ? $K_{H_2PO_4^-} = 1.58 \times 10^{-7}$. (Answer: pH₁ = 6.43, pH₂ = 1.3)
- The concentration of H₂CO₃ in the human plasma is 1.25×10^{-3} mol/L. What is concentration of HCO₃⁻ if pH of the blood is 7.4? $K_{H_2CO_3} = 8 \times 10^{-7}$. (Answer: 25 mmol/L)

9. Bicarbonate buffer is the main buffer of human plasma responsible for regulation of blood pH. At pH 7.4, HCO_3^- ions concentration is 25 mM, CO_2 – 1.2 mM. What will be pH change after addition 0.005 moles of H^+ to 1 L of the blood? $\text{pK} = 6.1$. In the human body the excess of CO_2 is removed together with exhaled air and CO_2 concentration is not changed. (Answer: 7.3 is the final pH)
10. What is pCO_2 in the patient blood if $\text{pH} = 7.25$, $\text{HCO}_3^- = 25 \text{ mmol/L}$, $K_a = 8 \times 10^{-7}$, $\alpha = 0.03 \text{ mmol/L} \cdot \text{mmHg}$ ($[\text{CO}_2] = \alpha \times \text{pCO}_2$)? What type of abnormality does the patient have? (Answer: 59 mmHg, acidosis)