Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Technical chemistry laboratory

Laboratory exercise

Buffer mixtures

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EXERCISE SHEET

<table>
<tr><td rowspan="5">1</td><td colspan="3">Relation to subjects: ESO/25, 27 DiRMiUO/25, 27 EOUNiE/25, 27</td></tr>
<tr><td>Specialty/Subject</td><td>Learning outcomes for the subject</td><td>Detailed learning outcomes for the subject</td></tr>
<tr><td>ESO/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
SEKP6 – Performing determinations of selected indicators of technical water quality;</td></tr>
<tr><td>DiRMiUO/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
SEKP6 – Performing determinations of selected indicators of technical water quality;</td></tr>
<tr><td>EOUNiE/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
SEKP6 – Performing determinations of selected indicators of technical water quality;</td></tr>
<tr><td>2</td><td colspan="3">Purpose of the exercise:
mastering basic chemical concepts related to solutions of acids, bases and salts as well as acquiring practical skills in the field:
– determination of pH and pH of solutions,
– calculating the pH of solutions of strong and weak acids and bases,
– determining the reaction of individual types of salts after hydrolysis on the basis of the reaction,
– calculating the pH of specific salt solutions and buffer mixtures.</td></tr>
<tr><td>3</td><td colspan="3">Prerequisites:
general knowledge of pH, solution reaction, hydrolysis obtained from high school, knowledge of the key issues of ion dissociation acquired during the previous exercise, knowledge of the principles of work in a chemical laboratory</td></tr>
<tr><td>4</td><td colspan="3">Description of the laboratory workplace:
a set of laboratory glassware, a set of reagents and indicators for testing pH and hydrolysis,</td></tr>
<tr><td>5</td><td colspan="3">Risk assessment:
the likelihood of chemical burns from exposure to 0.2 M sulfuric acid is very small, and the effects are minimal,
Final assessment – VERY SMALL THREAT
Security measures required:
1. Lab coats, gloves and safety glasses.
2. Health and safety cleaning products, paper towels.</td></tr>
<tr><td>6</td><td colspan="3">The course of the exercise:
1. Getting to know the workplace manual (appendix 1).
2. Carrying out the experiments provided for in the manual.</td></tr>
<tr><td>7</td><td colspan="3">Exercise report:
1. Develop an exercise in accordance with the instructions contained in the workplace manual.
2. Solve the given task and/or answer the questions included in the set of tasks and questions to be completed by the student.</td></tr>
</table>

8	**Archiving of research results:** report on exercises – prepared in accordance with the rules applicable in the laboratory – should be submitted in writing to the academic teacher during the next classes.
9	**Assessment method and criteria:** a) EKP1, EKP2 – checking the knowledge of basic chemical concepts of pH and hydrolysis in class, b) SEKP4 – the detailed learning outcome for the student will be assessed on the basis of the observations, conclusions and solutions to tasks and problems given for independent solution/ development: – mark 2,0 – the student has a general knowledge of pH and salt hydrolysis, but is unable to use it in practice to solve basic problems, – mark 3,0 – has basic chemical knowledge of pH and salt hydrolysis and can use it to a small extent to solve potential problems in his specialty, – mark 3,5 – 4,0 – has extensive chemical knowledge in the field of pH, salt hydrolysis and is able to use it to a basic extent to determine the pH and calculate the pH of various electrolyte solutions and to solve problems on the ship, – mark 4,5 – 5,0 – has complete chemical knowledge in the field of pH and salt hydrolysis and is able to use in practice complex chemical knowledge to determine and calculate the pH of individual acid, alkali, salt and buffer solutions and to solve complex problems,
10	**Literature:** 1. Kozłowski A., Workplace instruction for laboratory exercises: *pH roztworów. Reakcje soli z wodą,* AM Szczecin, 2013. 2. Stundis H., Trześniowski W., Żmijewska S.: *Ćwiczenia laboratoryjne z chemii nieorganicznej*. WSM, Szczecin 1995. 3. Śliwa A., Chemical calculations. A collection of tasks. PWN Warsaw, 1994. 4. Jones L., Atkins P., *Chemia ogólna. Cząsteczki, materia reakcje*, WN PWN, Warszawa, 2004. 5. Bielański A., *Chemia ogólna i nieorganiczna*, PWN, Warsaw, 1996. 6. Kozłowski A., *Materiały dydaktyczne z chemii technicznej*, developed for the purposes of auditorium classes (not published).
11	Notes

APPENDIX 1 – MANUAL

1. SCOPE OF THE EXERCISE

Issues and keywords:

– buffer mixtures (buffer mechanism, types and examples of buffer mixtures, use of buffers).

2. THEORETICAL INTRODUCTION TO THE EXERCISE

2.1. Buffer mixtures

Buffer mixtures are mixtures of weak bases or acids with their salts, e.g. $CH_3COOH + CH_3COONa$ or $NH_4OH + NH_4Cl$ and mixtures of salts of weak polyprotonic acids with different degrees of neutralization, e.g. $NaH_2PO_4 + Na_2HPO_4$ or $Na_2HPO_4 + Na_3PO_4$.

Buffer mixtures have a certain pH, the value of which changes slightly when some excess ions H_3O^+ or $OH^–$ are introduced into the solution. In other words, these mixtures have a „buffering effect”, that is, they prevent a sudden change in the pH of the solution. Similarly, diluting or increasing the concentration of buffer solutions has no effect on their pH value.

For an acidic buffer, e.g. CH_3COONa + CH_3COOH, the concentration of hydronium ions $[H_3O^+]$ is calculated from the formula

$$[\mathrm{H_3O^+}] = \mathrm{K_a}\frac{C_a}{C_s}$$

where:

K_a – weak acid dissociation constant,
C_a – acid concentration,
C_s – salt concentration.

The mechanism of action of the buffering solution is as follows: after adding an acid to the buffer mixture – the anion of the salt contained in the buffer with the H_3O^+ ion creates a weakly dissociated acid, while after adding a base – the hydronium ion of the acid contained in the mixture forms with the $OH^–$ ion poorly dissociated water molecules. Due to the formation of poorly dissociated acid and water particles, the pH of the solution changes slightly.

After adding CH_3COOH and CH_3COONa of hydrochloric acid to the acetate buffer, the $CH_3COO^–$ anion from sodium acetate forms with H_3O^+ acetic acid

$$CH_3COO^- + H_3O^+ \rightleftarrows CH_3COOH + H_2O$$

After the addition of e.g. sodium hydroxide, NaOH, a neutralization reaction takes place between the hydronium ions from acetic acid and the hydroxyl ions from the base.

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$
$$H_3O^+ + OH^- \rightleftarrows 2H_2O$$

The introduction of acid to the buffer mixture causes an increase in the concentration of weak acid, while the introduction of a base – an increase in the concentration of the appropriate salt. Changes in the concentration of the components of the buffer mixture have a slight effect on the pH of the solution.

In the case of an alkaline buffer, e.g. NH_4OH + NH_4Cl, the equation is used to calculate the concentration of hydronium $[H_3O^+]$

$$[H_3O^+] = \frac{10^{-14} \cdot C_s}{K_b \cdot C_b}$$

where:

- C_s – salt concentration,
- C_b – base concentration,
- K_b – the weak base dissociation constant of a given buffer.

The basic buffer (NH_4OH, NH_4Cl) mechanism of action is as follows:

Dissociation has occurred in the solution and ions NH_4^+, Cl^- are present and the molecule NH_3. By introducing a small amount of hydronium ions from the acid, the reaction will take place

$$NH_3 + H_3O^+ \rightleftarrows NH_4^+ + H_2O$$

which confirms that the pH does not change.

If a strong base is introduced into the buffer mixture, the ammonium ion will react according to the equation

$$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$$

and in this case the pH of the solution did not change.

Table 1

Exemplary buffer mixtures

Buffer name	The composition of the buffer with a concentration of 1 : 1	pH
ammonium	ammonium hydroxide NH_4OH, ammonium chloride NH_4Cl	9.3
benzoate	benzoic acid C_6H_5COOH, sodium benzoate C_6H_5COONa	4.2
phosphate	sodium hydrogenorthophosphate Na_2HPO_4, sodium dihydrogenorthophosphate NaH_2PO_4	6.8
formate	formic acid HCOOH, sodium formate HCOONa	3.7
acetate	acetic acid CH_3COOH, sodium acetate CH_3COONa	4.7

3. PERFORMING THE EXERCISE

Experiment 1 – Preparation of ammonium chloride and ammonium hydroxide buffer mixtures

Materials and reagents:

50 cm^3 beakers, measuring cylinder, solutions: ammonium chloride (0.1 M NH_4Cl), ammonium hydroxide (0.1 M NH_4OH), ammonium chloride (0.2 M NH_4Cl), ammonium hydroxide (0.2 M NH_4OH), solution of the universal indicator.

Performance:

Using 0.1 M and 0.2 M solutions, prepare buffer mixtures by mixing them at the following volumetric ratios:

ammonium chloride	1	1	10
ammonium hydroxide	10	1	1

Then add 5 drops of the universal indicator solution to every single buffer mixture and determine the pH using Yamada Table:

Colour change of the universal indicator solution according to Yamada depending on the exponent of the concentration of the hydronium ion (depending on the pH)

pH	Colour of the indicator
4.0	red
5.0	orange
6.0	yellow
7.0	green
8.0	blue
9.0	dark blue
10.0	purple

Elaboration of the results:

Provide the obtained results in the table

Compound	The volume ratio of the solutions		
0.1 M ammonium chloride	1	1	10
0.1 M ammonium hydroxide	10	1	1
pH value			
0.2 M ammonium chloride	1	1	10
0.2 M ammonium hydroxide	10	1	1
pH value			

Experiment 2 – Preparation of acetic acid and sodium acetate buffer mixtures. Effect of the addition of acid solution and hydroxide solution on the prepared buffer mixture: acetic acid: sodium acetate (1:1)

Materials and reagents:

50 cm^3 beakers, rack with test tubes, measuring cylinder, solutions: acetic acid (0.1 M CH_3COOH), sodium acetate (0.1 M CH_3COONa), hydrochloric acid (0.1M HCl), sodium hydroxide (0.1M NaOH), the universal indicator solution.

Performance:

Using 0.1 M solutions, prepare buffer mixtures by mixing them in the following volumetric ratios:

acetic acid	1	1	10
sodium acetate	10	1	1
PH value			

Then add 5 drops of the universal indicator solution to every single buffer mixture and determine the pH using Yamada Table:

Colour change of the universal indicator solution according to Yamada depending on the exponent of the concentration of the hydronium ion (depending on the pH)

pH	Colour of the indicator
4.0	red
5.0	orange
6.0	yellow
7.0	green
8.0	blue
9.0	dark blue
10.0	purple

Then take the prepared buffer mixture (1:1) and pour it into 4 test tubes. Into the first two test tubes add 2 drops (the first test tube) and 4 drops (the second test tube) of the 0.1M hydrochloric acid (HCl) solution and into the next two test tubes 2 drops (the third test tube) and 4 drops (the fourth test tube) of the 0.1M sodium hydroxide solution (NaOH). Determine the pH.

Elaboration of the results:

Fill in the table below and write definition of buffer capacity.

Test tube	1	2	3	4
pH value				

Experiment 3 – Testing the pH of buffer solutions

Materials and reagents:

Beakers, measuring cylinder, solutions: ammonium chloride (0.1M NH_4Cl), ammonium hydroxide (0.1M NH_4OH), sodium acetate (0.1M CH_3COONa), acetic acid (0.1M CH_3COOH), indicators: litmus paper, indicator papers, universal indicator.

Performance:

Pour 4 cm^3 of ammonium chloride solution (0.1M NH_4Cl) and 8 cm^3 of ammonium hydroxide solution (0.1M NH_4OH) into the first beaker with a capacity of 50 cm^3. Pour 4 cm^3 of sodium acetate (0.1M CH_3COONa) and 8 cm^3 of acetic acid (0.1M CH_3COOH) into the second beaker. Then, in both beakers, determine the color and pH of the prepared solutions using the indicators given in Table 5, and finally measure the pH with a pH-meter.

Summary of results for experiment 3

No.	Method	Beaker 1		Beaker 2	
		Buffer solution		Buffer solution	
		Colour	pH/reaction	Colour	pH/reaction
1.	Litmus paper				
2.	Indicator papers with a selected range, 1 – 7 and 7 – 14				
3.	Universal indicator (alcoholic solution)				
4.	Measurement – with a pH meter				
5.	Calculation of the pH value				

Elaboration of the results

1. Determine the type of buffer solution in beakers 1 and 2.
2. Enter the colours and pH values obtained into Table 8.
3. Calculate the pH of the tested buffer solutions using the following formulas for calculating the concentration of hydronium ions: acidic buffer (acetate buffer) $[H_3O^+] = K_a \frac{C_a}{C_s}$, alkaline buffer (ammonium buffer) $[H_3O^+] = \frac{10^{-14} \cdot C_s}{K_b \cdot C_b}$; pH = –log$[H_3O^+]$.
4. Compare the methods used to determine the pH of buffer solutions.

4. DEVELOPMENT OF THE EXERCISES

1. Prepare a report according to the guidelines in the experimental section.
2. Place the cover sheet as the first page of the report.
3. After the theoretical part has been concisely developed, include in the report the study of individual experiments and the solved task/additional tasks given by the academic teacher.

5. THE FORM AND CONDITIONS FOR PASSING THE LABORATORY EXERCISE

1. Passing the so-called „entry test" before starting the exercise.
2. Submission of a correct written laboratory report on the performed exercise in accordance with the guidelines for the preparation of the laboratory report, please see the link below: https://www.am.szczecin.pl/en/facilities/institute-of-mathematics-physics-and-chemistry/department-of-chemistry/technical-chemistry/tech-chemistry-lab-manuals/

I. Examples of a tasks with a solution

Example 1

What is the pH of the solution obtained by mixing 100 cm^3 of 0.1 mol/dm^3 acetic acid solution with 100 cm^3 of 0.05 mol/dm^3 sodium acetate solution; pKa = 4.75.

In the first step, the „new" molar concentration of the acid (CH_3COOH) and salt (CH_3COONa) in the resulting solution:

$$C_{CH3COOH} = 0.1\ mol/dm^3 \cdot 0.1\ dm^3 / 0.2\ dm^3 = 0.05\ mol/dm^3$$
$$C_{CH3COONa} = 0.05\ mol/dm^3 \cdot 0.1\ dm^3 / 0.2\ dm^3 = 0.025\ mol/dm^3$$

After substituting into the formula on $[H_3O^+]$ for an acidic buffer, we get:

$$[H_3O^+] = K_a \cdot C_a / C_s = 1{,}8 \cdot 10^{-5} \cdot 0.05\ mol/dm^3 / 0.025\ mol/dm^3 = 0.000036\ mol/dm^3$$
hence pH= –log $[H_3O+]$ = **4.44**.

Example 2

1 cm^3 of ammonium chloride (NH_4Cl) solution and 9 cm^3 of NH_3 solution with concentrations equal to 0.2 mol/dm^3 each were mixed. Calculate the pH of the buffer obtained.

In the first step, you need to calculate the molar concentrations of salt and base in the resulting solution:

$$C_s = 0.2\ mol/dm^3 \cdot 0.001\ dm^3 / 0.01\ dm^3 = 0.02\ mol/dm^3$$
$$C_b = 0.2\ mol/dm^3 \cdot 0.009\ dm^3 / 0.01\ dm^3 = 0.18\ mol/dm^3$$

After substituting into the formula for a buffer of a basic nature, we get:

$$[H_3O^+] = 10^{-14} \cdot C_s / K_b \cdot C_b = 6.17 \cdot 10^{-11}\ mol/dm^3$$
hence pH= **10.21**.

II. Tasks and questions to be completed by the student

1. Calculate the pH of the buffer solution containing 0.04 mol/dm^3 sodium acetate and 0.08 mol/dm^3 acetic acid at 25ºC. Answer: 4.44.
2. Calculate the pH of the buffer solution containing 0.04 mol/ dm^3 ammonium chloride and 0.03 mol/ dm^3 NH_3. Answer: 9.13.
3. Calculate the pH of the buffer solution obtained by mixing 80 cm^3 of acetic acid with 20 cm^3 of sodium acetate at concentrations 0.2 mol/dm^3; K (acetic acid) = $1.8 \cdot 10^{-5}$. Answer: 4.16.
4. How many cm^3 of sodium acetate solution with a concentration of 0.2 mol/dm^3 should be added to 10 cm^3 of acetic acid solution with a concentration of 0.1 mol/dm^3, so that the pH is 5. Answer: 8.95 cm^3.
5. Provide a definition of buffer.
6. Where are the buffer solutions used?