Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Technical chemistry laboratory

Laboratory exercise

pH of solutions

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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>
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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 measuring the 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 sulphuric acid is very small, and the effects are minor,
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 an individual student will be assessed on the basis of the solutions to tasks and problems presented in the report, given for independent solution/development: – mark 2,0 – the student has a general knowledge of pH and salt hydrolysis, but is not able to use it in practice to solve basic problems, – mark 3,0 – has basic chemical knowledge of pH and salt hydrolysis and is able to 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	**Literatura:** 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, Warsaw, 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:

- ionic product;
- the concept and scale of Ph;
- pH of the solution of acids, bases and salts and methods of its determination (indicators);
- strong and weak acids and bases.

2. THEORETICAL INTRODUCTION TO THE EXERCISE

2.1. Exponent of the concentration of hydrogen ions (pH)

2.1.1. Ionic product of water

Water is a very weak amphoteric electrolyte and it self-ionizes according to the scheme:

$$H_2O \quad + \quad H_2O \quad \rightleftarrows \quad H_3O^+ \quad + \quad OH^-$$

The equilibrium between H_3O^+ and OH^- ions and undissociated water can be expressed by the equilibrium constant of water auto-ionization

$$K_C = \frac{\left[H_3O^+\right] \cdot \left[OH^-\right]}{\left[H_2O\right]^2}$$

The concentration of pure water is a constant quantity, so the product $K_C[H_2O]^2 = K_W$ is also a constant quantity and is called the ionic product of water. The value of the ionic product of water at 298K is $1 \cdot 10^{-14}$

$$K_w = K_C\left[H_2O\right]^2 = \left[H_3O^+\right] \cdot \left[OH^-\right] = 1.00 \cdot 10^{-14}$$

Since in pure water the concentrations of hydronium and hydroxide ions are in equilibrium (they have the same values), the value of the ion product shows that their concentrations are

$$[H_3O^+] \quad = \quad [OH^-] \quad = \quad 1,00 \cdot 10^{-7}\ \text{mol/dm}^3$$

As with pure water, in all neutral solutions, $[H_3O^+] = 10^{-7}$ mol/dm^3. In acidic solutions $[H_3O^+] > 10^{-7}$ mol/dm^3, a in basic solutions $[H_3O^+] < 10^{-7}$ mol/dm^3.

Since the handling of such low concentrations is inconvenient, it is accepted in chemistry to operate with the negative decimal logarithm of the concentration of hydronium ions (according to Sörensen)

$$\mathrm{pH} = -\log\,[\mathrm{H}^+] \quad \text{or more correctly} \quad \mathrm{pH} = -\log\,[\mathrm{H_3O^+}]$$

and analogously

$$\mathrm{pOH} = -\log\,[\mathrm{OH}^-]$$

Taking the logarithm of the ionic product of water, we obtain a simple relationship

$$\mathrm{pH} + \mathrm{pOH} = 14$$

This relationship allows the conversion of pH to pOH and vice versa, e.g. pOH = 14 – pH.

As the temperature rises, the electrolytic dissociation of water increases. This is evidenced by the increase in the value of the ionic product of water (K_W) with increasing temperature.

Table 1

Ionic product of water at different temperatures

Temp. K	293	298	313	353	373
K_W	$8.6 \cdot 10^{-15}$	$1.0 \cdot 10^{-14}$	$1.3 \cdot 10^{-13}$	$3.4 \cdot 10^{-13}$	$7.4 \cdot 10^{-12}$

In the case of aqueous solutions of electrolytes with ionic strength J = 0 and factor F ≠ 1 the calculation of the pH value, using the simplified formulas for H_3O^+ and pH, may lead to significant deviations from the actual values. The above statement is true when high charge ions are present in the solution. In such circumstances, the expression for an activity constant taking into account the ionic strength which gives the specific values of the activity coefficients should be used. To calculate the activity of H_3O^+ hydronium ions then the relationship should be used

$$a_{\mathrm{H_3O^+}} = \left[\mathrm{H_3O^+}\right] \cdot f_{\mathrm{H_3O^+}}$$

where:

$f_{\mathrm{H_3O^+}}$ – hydronium ion activity coefficient,

$\left[\mathrm{H_3O^+}\right]$ – the concentration of hydronium ions at equilibrium.

Logarithm of the relationship (1), the actual $\mathrm{p_{aH}}$ value of the solution is obtained.

$$\mathrm{p_aH} = \mathrm{pH} - \log f_{\mathrm{H_3O^+}}$$

where:

pH – negative logarithm of the concentration of hydronium ions,

$f_{\mathrm{H_3O^+}}$ – hydronium ion activity coefficient.

In the presence of foreign ions, the $\mathrm{p_aH}$ of acid and hydroxide solutions differs significantly from the pH value due to the increased ionic strength of the solutions.

2.1.2. PH scale

The pH scale is a quantitative scale of acidity and alkalinity of aqueous solutions of chemical compounds, which is based on the activity of hydronium ions [H_3O^+] in aqueous solutions. Traditionally, pH is defined as:

$$pH = -\log[H_3O^+]$$

that is, the negative decimal logarithm of the concentration of hydronium ions, expressed in moles per cubic decimetre. Nowadays, however, it is not a strict definition of this size.

The pH scale covers strongly acidic solutions with pH = 0 ([H_3O^+] = 10^0 mol/dm^3) to strongly alkaline solutions with pH = 14 ([H_3O^+] = 10^{-14} mol/dm^3). For neutral solutions, pH = 7 ([H_3O^+] = 10^{-7} mol/dm^3).

In more concentrated solutions of strong acids and hydroxides, the pH scale may go beyond the given limits of 0 and 14.

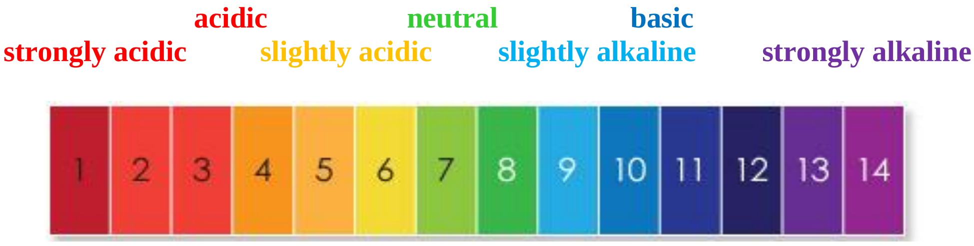

Fig. 1. The ranges of the pH of the solution and the corresponding colours of the universal indicator

To illustrate the typical reaction of solutions encountered in technology and in everyday life, a table is presented in Fig. 2, in which the solutions of these compounds were assigned the values of the pH scale and the corresponding colours of the universal indicator.

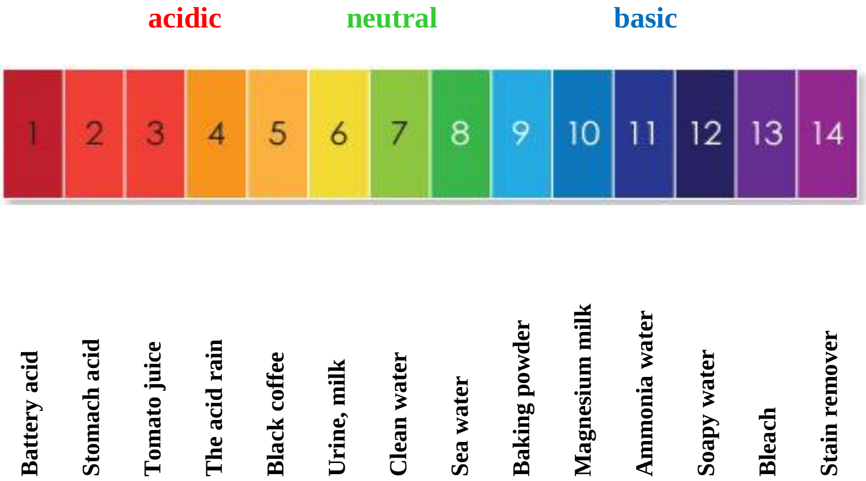

Fig. 2. Typical pH of solutions

2.1.3. Henderson–Hasselbalch equation

The Henderson-Hasselbalch equation is an equation that relates the pH value to the acid strength (pK_a). It is useful for estimating the pH of a buffer and finding the equilibrium pH of chemical reactions. This equation has the form:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

where:

pK_a – $-\log(K_a)$,

Ka – is the acid dissociation constant for the reaction.

$$HA + H_2O \rightleftarrows A^- + H_3O^+$$

is:

$$pK_a = -\log(K_a) = -\log\left(\frac{[H_3O^+][A^-]}{[HA]}\right)$$

where:

$[A^-]$ – is the concentration of anions formed from acid residues,

$[HA]$ – concentration of the undissociated form of the acid.

This equation cannot be used for strong bases and acids (pK values within a few units of 7), highly diluted or concentrated solutions (less than 1 mM or more than 1 M), and for large differences in the acid/base ratio (more than 1000 to one). Under such conditions, however, the pH scale itself loses its physical meaning.

3. PERFORMING THE EXERCISE

Experiment 1 – Testing the colour of the indicator in weak acid and weak hydroxide solutions

Materials and reagents:

Rack with test tubes, measuring cylinder, solutions: acetic acid (0.1M CH_3COOH), ammonium hydroxide (0.1M NH_4OH), indicators: methyl orange, methyl red, litmus, phenolphthalein, solution of the universal indicator.

Performance:

Pour 4 cm^3 of acetic acid (0.1M CH_3COOH), into five test tubes, and to the next five test tubes the same amount (4 cm^3) of ammonium hydroxide solution (0.1M NH_4OH). Place the test tubes in the rack so that the test tube containing the ammonium hydroxide solution is placed behind the test tube with acetic acid. Then, to each pair of test tubes (with acid and hydroxide), add successively three drops of the indicator given in the table.

Table 5

Summary of the results of the experiment 1

No	Indicator	Observed colours of indicators in test tubes		pH ranges of pH indicators
		CH_3COOH	NH_4OH ($NH_3 \cdot H_2O$)	
1.	Methyl orange			
2.	Methyl red			
3.	Litmus			
4.	Phenolphthalein			
5.	Universal			

Elaboration of the results:

1. Put the observed colours of the indicators in Table 5.
2. Enter the range of applicability (pH range) in which the characteristic colour of the indicator changes.
3. Calculate the pH of an aqueous acetic acid solution with a concentration of 0.01 mol/dm^3 if it is known that the dissociation constant of this acid is $K_a = 1.8 \cdot 10^{-5}$.
4. Calculate the pH of an aqueous solution of ammonium hydroxide with a concentration of 0,01 mol/dm^3 if it is known that the dissociation constant of this hydroxide is,
   $K_b = 1.8 \cdot 10^{-5}$.

Experiment 2 – Application of selected methods of pH determination to acidic and alkaline solutions

Materials and reagents:

50 cm^3 beakers, measuring cylinder, solutions: ammonium hydroxide (0.1M NH_4OH), acetic acid (0.1M CH_3COOH), indicators: neutral litmus paper, indicator papers with a selected range, solution of the universal indicator, pH-meter.

Performance:

Into the first 50 cm^3 beaker pour a solution of acetic acid (0.1M CH_3COOH), into the second 50 cm^3 beaker solution of ammonium hydroxide (0.1M NH_4OH). Then, in both beakers, determine the pH of solutions using neutral litmus paper, indicator papers with a selected range, solution of the universal indicator, pH-meter.

Elaboration of the results:

Summarize the obtained results in the table:

No	Measurement methods	Acidic solution CH_3COOH	Basic (alkaline) solution NH_4OH
1	Neutral litmus paper *		
2	Indicator papers with a selected range		
3	Solution of the universal indicator		
4	pH-meter		

* Neutral litmus paper stains pink in an acidic environment, blue in an alkaline environment.

Experiment 3 – (theoretical) – Calculation of the pH value of strong acids and strong hydroxides as well as the pH and pOH values of solutions in which the concentrations of H_3O^+ and OH^- ions are given, respectively

Development of the experiment 3:

1. Calculate the pH of the $HClO_4$ solution with concentration 0.1 mol/dm^3.
2. Calculate the pH of the KOH solution with concentration 0.01 mol/dm^3.
3. Calculate the pH of the $Sr(OH)_2$ solution with concentration 0.01 mol/dm^3.
4. Calculate the pH and pOH of the solution in which the ion concentration OH^- is 4.5 10^{-2} mol/dm^3.
5. Calculate the pH and pOH of the solution in which the ion concentration H_3O^+ is 2.0 10^{-2} mol/dm^3.

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

Calculation of the pH of solutions of strong acids and strong hydroxides

It follows from the definition that strong electrolytes are completely dissociated into ions, so for H – R monoprotic acid the concentration of hydrogen ions [H^+] is equal to the initial concentration of the acid. Similarly, for hydroxides, the concentration of hydroxide ions is equal to the initial concentration of hydroxide.

Example 1

Calculate the pH of 0.01 M hydrochloric acid.

Solution:

$$\begin{array}{ccc} \mathrm{HCl} & \longrightarrow & \mathrm{H^+ \; + \; Cl^-} \\ & & \\ 1\ \mathrm{mol} & & 1\ \mathrm{mol} \\ 0.1\ \mathrm{mol/dm^3} & & 0.1\ \mathrm{mol/dm^3} \end{array}$$

If $[H^+] = 0.01\ mol/dm^3 = 10^{-2}$ then $pH = -\log[H+] = -\log 10^{-2} = -(-2) = 2$

Answer: Exponent pH = 2.

Example 2

Calculate the exponent of the hydrogen ion concentration of the barium hydroxide solution at 0.005 mol/dm^3.

Solution:

$$\begin{array}{ccccc} \mathrm{Ba(OH)_2} & \longrightarrow & \mathrm{Ba^{2+}} & + & \mathrm{2OH^-} \\ 1\ \mathrm{mol} & & & & 2\ \mathrm{mole} \\ 0.005\ \mathrm{mol/dm^3} & & & & 0.01\ \mathrm{mol/dm^3} \end{array}$$

If $[OH^-] = 0.01\ mol/dm^3 = 10^{-2}$ then pOH = 2, hence pH = 14 – 2 = 12

Answer: Exponent pH = 12.

Calculation of the pH of solutions of weak acids and weak hydroxides

In the case of weak acids and weak hydroxides, the concentration of hydrogen ions is limited by the acid dissociation constant:

$$\mathrm{H-R} \rightleftharpoons \mathrm{H}^{\oplus} + \mathrm{R}^{\ominus}$$

$$K_a = \frac{[\mathrm{H}^+] \cdot [\mathrm{R}^-]}{[\mathrm{H-R}]}$$

However, the equilibrium concentration of the hydrogen ion [H^+], the acid residue [R^-] and the acid [H   R] is unknown. We only know from the dissociation equation that;

$[H^+] = [R^-]$, and $[H-R] = C_0 - [H^+]$ (provided that the H^+ ions come only from an acid).

Let's substitute these relationships into the equation for the dissociation constant:

$$K_a = \frac{\left[\mathrm{H}^+\right]^2}{c_0 - \left[\mathrm{H}^+\right]}$$

In this way, we obtained a quadratic equation (after transformation) with one unknown ($[\mathrm{H}^+]$). Depending on the acid strength, this equation can be simplified (but only when the calculation error from the simplified formula is less than 5%).

The following cases should be considered:

a) weak acids of moderate concentration:
If the acid is weak then a small fraction of it dissociates. We can assume that $c_0 - [\mathrm{H}^+] = c_0$. The formula for K_a will simplify to form:

$$K_a = \frac{\left[\mathrm{H}^+\right]^2}{c_0} \qquad \text{so} \qquad \left[\mathrm{H}^+\right] = \sqrt{K_a c_0}$$

b) medium-strength acids:
For medium-strength acids, the concentration of hydrogen ions should be calculated from the converted formula for K_a:

$$K_a C_0 - K_a \left[\mathrm{H}\right]^+ = \left[\mathrm{H}^+\right]^2 \qquad \text{so} \qquad \left[\mathrm{H}^+\right]^2 + K_a\left[\mathrm{H}^+\right] - K_a C_0 = 0$$

After solving the quadratic equation, the value $[\mathrm{H}^+]$ is calculated from the formula:

$$\left[\mathrm{H}^+\right] = \frac{-K_a + \sqrt{K_a^2 + 4K_a c_0}}{2}$$

Example 3

Calculate the exponent of the pH of the single-proton weak acid HR (K_c = 10^{-5} mol/dm^3) knowing that its initial concentration is 0.4 mol/dm^3.

Solution:

Using the formula: $\left[\mathrm{H}^+\right] = \left(K_c C_0\right)^{\frac{1}{2}}$ we calculate that $\left[\mathrm{H}^+\right] = 2 \cdot 10^{-3} = 0{,}002 \ \mathrm{mol/dm}^3$.

Hence: pH = $-\log[\mathrm{H}^+] = -\log 2 \cdot 10^{-3} = -0.3 + 3 = 2.7$

Answer: Exponent pH = 2.7

Example 4

Calculate the pH of the NH_4NO_3 solution with a concentration of 0.001 mol/dm^3, knowing that $K_z = 1.7 \cdot 10^{-5}$

Solution:

You can use the formula for calculating the pH of a strong acid salt and a weak base, derived earlier and given in Table 3.:

$$\mathrm{pH} = 7 + \frac{1}{2}\log K_z - \frac{1}{2}\log \mathrm{C_s} = 7 + \frac{1}{2}\left(0{,}2 - 5\right) - \frac{1}{2}\left(-3\right) = 6{,}1$$

Answer: Exponent pH = 6.1

II. Tasks and questions to be completed by the student

1. What is the pH of the solution, if:
   a) a) $[H_3O^+] = 5.50\ \ 10^{-6}$ mol/ dm^3,
   b) b) $[OH^-] = 1.82 \cdot 10^{-9}$ mol/ dm^3?

2. What is the concentration of H_3O^+ and OH^- at t = 25 °C in solutions:
   c) 0.005 M solution of $Ba(OH)_2$,
   d) 0.055 M solution of KOH?

3. What is the pH of:
   a) human blood, in which the concentration of oxonium ions is $4 \cdot 10^{-8}$ mol/dm^3
   b) 0.03 M solution of HC1,
   c) 0.05 M solution of KOH.

4. Calculate the molar concentration of the potassium hydroxide solution with pH = 12.

5. Calculate the pH of the solution obtained after dissolving 0.05 g NaOH in 0.5 dm^3 of water.

6. Calculate the pH and the degree of dissociation of acetic acid, CH_3COOH in its solution concentration 0.2 mol/ dm^3; dissociation constant $Kc = 1.8 \cdot 10^{-5}$.

7. Calculate the pH value of a monoprotic acid solution with a concentration of 0.01 mol/dm^3, knowing that the dissociation constant of this acid is $K_a = 5.0 \cdot 10^{-3}$.