# Institute of Mathematics, Physics and Chemistry

# Department of Chemistry


## Technical chemistry laboratory

## Laboratory exercise

# The rate of chemical reactions


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# EXERCISE SHEET

<table>
<tr><td rowspan="5">1</td><td colspan="3">Relation to subjects: ESO/26, DiRMiUO/26, EOUNIE/26</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/25 Technical chemistry</td><td>EKP1<br>K_W01,K_W02, K_U05<br>EKP2<br>K_U08, K_U09</td><td>SEKP7 – Mastering the experimental knowledge in studying the rate of chemical reactions and drawing conclusions from the conducted experiments.<br>Mastering the knowledge of the mechanism and type of catalysis as well as identifying catalysts and inhibitors.<br>Expanding knowledge on the use of catalysts in technology and environmental protection.</td></tr>
<tr><td>ESO/26 Chemistry of water, fuels and lubricants</td><td>EKP3<br>K_U014, K_U015, K_U016</td><td>SEKP6 – Determination of oxygen and ammoniacal nitrogen content in technical water.<br>SEKP6 – Determination of corrosion inhibitors in technical water.</td></tr>
<tr><td>DiRMiUO/26 Chemistry of water, fuels and lubricants</td><td>EKP3<br>K_U014, K_U015, K_U016</td><td>SEKP6 – Determination of oxygen and ammoniacal nitrogen content in technical water<br>SEKP6 – Determination of corrosion inhibitors in technical water.</td></tr>
<tr><td></td><td>EOUNIE/26 Chemistry of water, fuels and lubricants</td><td>EKP3<br>K_U014, K_U015, K_U016</td><td>SEKP6 – Determination of oxygen and ammoniacal nitrogen content in technical water<br>SEKP6 – Determination of corrosion inhibitors in technical water</td></tr>
<tr><td>2</td><td colspan="3">Purpose of the exercise:<br>1. Learning and consolidation of the basic concepts related to the rate of chemical reactions and catalysis.<br>2. Understanding the practical impact of selected factors on the rate of chemical reactions in laboratory conditions.<br>3. Analysing the theoretical way of influencing the acceleration or delay of chemical processes.</td></tr>
<tr><td>3</td><td colspan="3">Prerequisites:<br>general chemical knowledge of the rate of chemical reactions, catalysis and catalysts</td></tr>
<tr><td>4</td><td colspan="3">Description of the laboratory workplace:<br>Basic laboratory equipment – test tube rack, water baths, micro-spatula, stopwatch, chemical reagents – 0.1 M sulphuric acid(VI) $H_2SO_4$, 0.1 M potassium manganate(VII), $KMnO_4$; 0.1 M oxalic acid $H_2C_2O_4$, 0.1 M acetic acid; 3% hydrogen peroxide solution, $H_2O_2$, manganese(IV) oxide $MnO_2$, lead(IV) oxide $PbO_2$, manganese(II) sulphate(VI) $MnSO_4$, sodium sulphate(IV), $Na_2SO_3$;</td></tr>
</table>

| | |
|---|---|
| 5 | **Risk assessment:**<br>Chemical burns resulting from contact with 0.2 M sulphuric acid and caustic soda are very unlikely, the possible effects are minor,<br>Final assessment – **VERY SMALL THREAT**<br>**Security measures required:**<br>1. Lab coats, gloves and safety glasses.<br>2. Health and safety cleaning products, paper towels. |
| 6 | **The course of the exercise:**<br>1. Getting to know the workplace manual (appendix 1),<br>2. Performing individual exercises according to the instructions. |
| 7 | **Exercise report:**<br>1. Develop an exercise in accordance with the instructions contained in the workplace manual.<br>2. Solve the given task and/or answer the questions included in the set of tasks and questions to be completed by the student. |
| 8 | **Archiving of research results:** Submit the report on the exercise in the applicable form at the beginning of the next laboratory exercises. |
| 9 | **Assessment method and criteria:**<br>a. EKP1, EKP2 – control of the knowledge of basic chemical concepts regarding the rate of chemical reactions, catalysis, catalysts and inhibitors during the classes,<br>b. SEKP7 – 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:<br>– mark 2,0 – the student has too little knowledge of the rate of chemical reactions, factors influencing the rate of reaction, the catalysis process, catalysts and inhibitors, or is unable to solve simple tasks related to the above-mentioned concepts;<br>– mark 3,0 – has a basic chemical knowledge of the rate of chemical reactions, catalysis, catalysts and inhibitors and is able to solve simple problems in his profession related to the above-mentioned concepts;<br>– mark 3,5 – 4,0 – has extensive knowledge of chemistry and the rate of chemical reactions and the catalysis process, and has the ability to solve complex tasks in his specialty regarding the above-mentioned concepts;<br>– mark 4,5 – 5,0 – has the ability to apply complex knowledge regarding the rate of chemical reactions and the catalysis process, and is able to solve problem tasks in his specialty regarding the above-mentioned concepts. |
| 10 | **Literature:**<br>1. Stundis H., Trześniowski W., Żmijewska S.: *Ćwiczenia laboratoryjne z chemii nieorganicznej*. WSM, Szczecin 1995.<br>2. Kozłowski A., Gabriel-Półrolniczak U., Ćwirko K., *Instrukcja stanowiskowa do ćwiczeń laboratoryjnych: Szybkość reakcji chemicznych. Kataliza*, AM Szczecin, 2013.<br>3. Kozłowski A., *Materiały dydaktyczne z chemii technicznej*, developed for the purposes of auditorium classes (not published).<br>4. Cox. P.A. translation of Z. Zawadzki: *Chemia nieorganiczna*. PWN. Warsaw 2006.<br>5. Drapała T.: *Chemia ogólna i nieorganiczna*. SGGW, Warsaw 1994.<br>6. Bielański A.: *Chemia ogólna i nieorganiczna*. PWN, Warsaw 1994.<br>7. Jones L., Atkins P., *Chemia ogólna,. Cząsteczki, materia reakcje*, WN PWN, Warsaw 2004 |

| | |
|---|---|
| | 8. Mastalerz P.: *Elementarna chemia nieorganiczna*. Wydawnictwo Chemiczne. Warsaw 2000.<br>9. Śliwa A.: *Obliczenia chemiczne. Zbiór zadań.* PWN. Warsaw 1994<br>10. Pazdro M. *Zbiór zadań z chemii dla szkół średnich*.<br>11. Resources Open AGH. http://open.agh.edu.pl/open2/<br>12. http://autokult.pl/2011/06/30/reaktor-katalityczny-czyli-nasz-stary-dobry-katalizator |
| 11 | Notes |

# APPENDIX 1 – MANUAL

## 1. SCOPE OF THE EXERCISE

**Issues and keywords:**

- basic concepts and formulas of chemical reaction kinetics (reaction rate, chemical equilibrium, equilibrium constant ($K_c$), half-life, activation energy);
- kinetic equations of reactions, order of reaction;
- law of mass action (Guldberg-Waage);
- Le Chatelier-Braun principle (the equilibrium law);
- factors affecting the rate of a chemical reaction (van't Hoff's rule, Arrhenius equation).

## 2. THEORETICAL INTRODUCTION TO THE EXERCISE

### 2.1. The rate of chemical reactions

Quantitatively average reaction rate is defined as the change in molar concentration of a substrate or product per unit time. The reaction rate is described by the equation:

$$v = \pm \frac{\Delta c}{\Delta t} \left[ \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \right]$$

where:

$v$ – chemical reaction rate [mol/(dm$^3$ · s)],
$\Delta c$ – change in concentration of products / substrates [mol/dm$^3$],
$\Delta t$ – the period of time considered [s].

So that the value of $\Delta c = c_2 - c_1$ (and thus the reaction rate – $v$) is not negative, when calculating $\Delta c$ we consider the concentration of substrates, which decreases during the course of the reaction and $c_1 > c_2$ we use the „–” sign, and when we consider the concentration products that grow during the reaction and $c_2 > c_1$, we use the „+” sign.

The instantaneous reaction rate ($v_{ch}$) varies during the reaction as it determines the ratio of the infinitely small changes in the concentration of reactants or products to the infinitely small time interval over which these changes in concentration take place. For the first order reaction:

$$A \rightarrow B$$

shows the kinetic equation

$$v = \frac{dc_B}{dt} = \frac{-dc_A}{dt} = k \cdot c_A$$

where:

$v$ – reaction rate [mol/dm$^3$ · s];
$c_A$ – concentration of substrate A [mol/dm$^3$];
$c_B$ – concentration of product B [mol/dm$^3$];
$t$ – time [s];
$k$ – reaction rate constant – value characteristic for a given reaction, independent of the concentration of reacting substrates, but dependent on the temperature and the presence of the catalyst.

Practical measurements have shown that the rate of the reaction changes during its course.

Often the reaction rate is characterized by the so-called half-life. The half-life $t_{1/2}$ is the time during which the substrate concentration is reduced to half

$$t_{1/2} = \frac{2,303}{k} \log \frac{C_A^o}{\frac{C_A}{2}} = \frac{2,303}{k} \log 2 = \frac{0,693}{k}$$

For first order reactions, the half-life is therefore independent of the initial concentration and is inversely proportional to the reaction rate constant (k).

## 2.2. The order of the chemical reaction

The course of the chemical reactions is more complex than the stoichiometric equation might suggest. Most reactions are multi-stage reactions. Sometimes several reactants occur, and the rate of reaction depends only on the concentration of one or two of them.

Only on the basis of experience it is possible to establish the relationship between the reaction rate and the concentration of the substrates. They give the kinetic equation of a given reaction. The sum of the exponents in this equation for the concentrations of the reactants that affect the rate of the reaction determines the **order of the reaction**. One can talk about:

- zero-order reactions $v = k$ (the rate of this reaction does not depend on the concentration of the reactants),
- first order reactions $v = k \cdot c_A$,
- second order reactions $v = k \cdot c_A \cdot c_B$ or $v = k \cdot c_A^2$,
- third order reactions $v = k \cdot c_A \cdot c_B \cdot c_C$ or $v = k \cdot c_A^3$.

Higher order reactions are unknown. This is because one, two, or at most three molecules are involved in each reaction step.

## 2.3. Mechanism of the course of the reaction

The variety of kinetic phenomena and the influence of a number of factors on the reaction rate are best explained by two kinetic theories:

1. Collision theory (only applies to gas phase reactions).
2. Active complex theory (concerns gas and liquid phase reactions).

Ad 1

1. The condition for the reaction to take place is the collision of the relevant particles. Not every collision is chemically effective. The number of effective events is usually a small fraction of all collisions. The greater the number of collisions, the more effective collisions among them, and therefore the greater the reaction rate.

2. The chemical reaction is a series of elementary acts. An elementary act is a single event. Many of the same collisions constitute a reaction step. The sequence of elementary acts is called the reaction mechanism. We call one-stage reactions simple, and multi-stage reactions – complex.

The slowest stage, the so-called limiting stage, decides the rate of multistage reaction.

Ad 2.

1. The collision of particles can lead to the formation of an unstable active complex made of nuclei and electrons of colliding particles. Each chemically effective collision proceeds through an intermediate stage lasting about 10–13 seconds, e.g. in a reaction:

A – B + C → A + B–C, a complex is formed temporarily A•••B•••C:
A – B + C → A•••B•••C → A + B – C

It is not necessary to completely break the bonds in the substrate molecules. This explains why in the given reaction the activation energy is lower than the sum of the bond energies in the substrate particles. There are old bonds in the complex, although weakened and new, but not yet fully durable.

Activation energy $E_1$ is the smallest energy that substrate molecules must have in order for a chemical reaction to occur as a result of the collision of these molecules.

2. The reaction rate depends on:

- the active complex concentration,
- the speed with which it breaks down into products.

Based on both kinetic theories, it is easier to understand the dependence of the reaction rate on various factors.

## 2.4. Factors affecting the rate of reaction

The most important factors determining the reaction rate are:

- type of reaction, properties of the reactants and their fragmentation;
- the concentration of the reacting substances or their pressure (if the reaction takes place in the gas phase);
- temperature;
- reaction environment;
- the presence of catalysts.

**a) Type of reaction, properties and fragmentation of the reactants**

Some processes, such as weathering rocks or corrosion of some metals, are slow, while others, such as burning coal – are very fast. The reaction rate depends on the properties of the reactants. If solids are used for the reaction, the rate of reaction can be increased by fragmenting them, increasing the surface of the reacting substrates and the possibility of contact with other substrates. We can achieve a significant increase in the reaction rate by mixing the reactants.

**b) Reactant's/Reactants' concentration**

The dependence of the reaction rate on the concentration is captured by the Guldberg and Waage law of mass action. This law says that the rate of reaction is directly proportional to the product of the activities or concentrations of the reactants. An increase in the concentration of reactants increases the reaction rate in accordance with the kinetic equation appropriate for a given order of a chemical reaction, e.g. for first order reactions: A → B

$$v = k \cdot c_A$$

and for the second order: A + B → C the rate depends on the concentrations of both reactants and is expressed as the relationship:

$$v = k \cdot c_A \cdot c_B$$

The experimental basis for determining the order of the reaction is the result of the reactant concentration analyses performed during the course of the reaction.

**c) Temperature**

The reaction rate is very significantly dependent on the temperature. An example is the reaction of oxygen with hydrogen, which is slow at 200°C, while at 600°C it is explosive, within a fraction of a second. Jacobus van't Hoff (1852 – 1911) was the first to give a general dependence on the influence of temperature on the reaction rate based on the results of his experiments. According to van't Hoff's rule, increasing the temperature by about 10 degrees causes a 2 – 4 fold increase in the reaction rate.

$$\frac{v_2}{v_1} = \frac{t_1}{t_2} = \gamma^{\frac{\Delta T}{10}}$$

where:

- $v_1$ – reaction rate at time $t_1$ at temperature $T_1$ ,
- $v_2$ – reaction rate at time $t_2$ at temperature $T_2$,
- $\gamma$ – temperature coefficient (for most chemical reactions $\gamma$ = 2, but for some reactions its value may be 3 or even 4) $\Delta T = T_2$ [K]– $T_1$ [K].

The strong influence of temperature on the rate of reaction explains why in practice heating is used to speed up the reaction, also in the case of exothermic reactions (proceeding with the release of heat). The increase in speed with temperature is exponential. In 1889, Svant Arrhenius formulated the dependence of changes in the reaction rate constant k on the change in temperature. This equation has the following form:

$$\mathrm{k} = Ae^{-\frac{E_a}{RT}}$$

or after logarithm:

$$\log k = \log A - \frac{E_a}{RT}$$

where:

$E_a$ – activation energy,
$A$ – pre-exponential factor,
$R$ – gas constant: 8.31 [J / mol · K]
$T$ – temperature [K].

The analysis of the equation shows that the increase in the constant k (determining the reaction rate) can be obtained thanks to the increase in temperature (heating the reactants), but also by lowering the activation energy (using a catalyst)

**d) Reaction environment**

Polar solvents facilitate the reactions between polar compounds, while nonpolar solvents can be used to increase the reaction rate of non-polar compounds. A properly selected solvent allows the reactant molecules to mix thoroughly, facilitating contact between them, and thus increasing the rate of reaction.

**e) Catalysts, inhibitors**

The rate of reaction and its mechanism depend on the catalysts. A properly selected catalyst can largely (many thousand times) change the reaction rate.

## 3. PERFORMING THE EXERCISE

### Experiment 1 – Effect of the concentration of reagents on the rate of reaction

**Materials and reagents:**

Rack with test tubes, sulphuric(VI) acid solution (0.1 M $H_2SO_4$), sodium thiosulphate solution (0.5 M $Na_2S_2O_3$); stopwatch, measuring cylinder.

**Performance:**

Prepare three identical test tubes: 1, 2, 3. Pour reagents to each of three test tubes according to the table: first make solutions of sodium thiosulfate and distilled water (test tubes 1, 2, 3) and then add sulfuric acid to the first test tube and start measuring the time, stop the stopwatch when the solution in the first test tube is turbid. Record the elapsed time – t[s], do the same thing with the test tube 2 and 3.

Summary of results for experiment 1

Table 1

<table>
<tr><th>Test tube</th><th>Quantities of reagents (sodium thiosulphate / water + acid) [$cm^3$]</th><th>Concentration $C_m$ [$mol/dm^3$]</th><th>Balanced chemical reaction (from the experiment)</th><th>Elapsed time [s]</th><th>Conclusions</th></tr>
<tr><td>1.</td><td>3 /6 +1</td><td></td><td rowspan="3"></td><td></td><td rowspan="3"></td></tr>
<tr><td>2.</td><td>6/3 + 1</td><td></td><td></td></tr>
<tr><td>3.</td><td>9/0 + 1</td><td></td><td></td></tr>
</table>

**Elaboration of the results**

1. Write down the chemical reaction of the decomposition of $S_2O_3^{2-}$ thiosulphate ions in an acidic environment.
2. Fill in the Table 1.
3. Draw a graph of elapsed time versus reactant's ($Na_2S_2O_3$) concentration.
4. Explain why and how the rate of the reaction depends on the concentration of the reactants.

### Experiment 2 – Influence of temperature on the reaction rate

**Materials and reagents:**

Rack with test tubes, potassium manganate(VII) solution (0.1 M $KMnO_4$), sulphuric acid(VI) solution (0.1 M $H_2SO_4$), oxalic acid solution (0.1 M $H_2C_2O_4$), stopwatch, measuring cylinder.

**Performance:**

Pour 4 $cm^3$ of potassium manganate(VII) solution (0.1 M $KMnO_4$) into three test tubes: 1, 2, 3 and acidify the contents of the test tube with 5 drops of sulfuric acid(VI) (0.1 M $H_2SO_4$)

and add 2 $cm^3$ of oxalic acid (0.1 M $H_2C_2O_4$). Then heat the first test tube in a water bath at 353K (80$^oC$) until complete discoloration, noting the time of the course of the reaction measured with a stopwatch. Heat the second test tube at 363K (90$^oC$), also noting the reaction time. Leave the test tube number 3 unheated and treat it as a reference test tube.

Analysis of the results for experiment 2

Table 2

| Test tube | Heating temperature, K | Time of discoloration, s | Balanced chemical reaction – ionic form | Calculated temperature coefficient $\gamma$ | Conclusions |
|---|---|---|---|---|---|
| 1 | 353 | | | | |
| 2 | 363 | | | | |
| 3 | 293 (without heating) | | | | |

**Elaboration of the results**

1. Record the times needed for complete decolorization of the solutions in individual test tubes and, knowing the temperature difference $\Delta T$ in the test tubes, calculate the experimentally obtained temperature coefficient $\gamma$ (based on the Van't Hoff equation).
2. Fill in the Table 2.
3. Explain why and how the reaction rate is temperature dependent.

## Experiment 3 – Influence of the properties of reactive substances on the rate of chemical reactions

**Materials and reagents**:

Beakers, glass rod, potassium manganate(VII) solution (0.1 M $KMnO_4$), sulphuric acid(VI) solution (0.1 M $H_2SO_4$), iron(II) sulphate(VI) solution (5% $FeSO_4$)

**Performance:**

Pour equal amounts (5 $cm^3$) of potassium manganate(VII) (0.1 M $KMnO_4$) into two beakers then add 2 – 3 drops of sulphuric acid(VI) (0.1 M $H_2SO_4$) into both of them. To the first beaker, add a drop of iron(II) sulphate(VI) (5% $FeSO_4$), every 2 seconds until complete discoloration, note the time of this change. To the second beaker, also add iron(II) sulphate(VI) (5% $FeSO_4$) every 2 seconds but stir it (mix it) using the glass rod while adding the solution. Keep adding the solution until a complete discoloration, note the time of this change.

**Elaboration of the results:**

The rate of chemical reactions depends, among other things, on the properties of the reacting substances. Explain this phenomenon on the basis of the obtained results of the conducted experiment.

## 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 task with a solution

**Task**

How will the reaction rate of $N_2 + 3H_2 \rightarrow 2NH_3$ change if the pressure of the reacting gases is doubled?

**Solution:**

At the initial pressure, the reaction rate is as follows:

$$v_1 = k \cdot c_{N_2} \cdot c_{H_2}^3$$

If the pressure is doubled, the volume will be doubled and therefore the concentrations will be doubled. We calculate the reaction rate according to the formula:

$$v_2 = k \cdot 2c_{N_2} \cdot \left(2c_{H_2}\right)^3 = 16k \cdot c_{N_2} \cdot c_{H_2}^3$$

Answer: The reaction rate will increase 16 times.

## II. Tasks and questions to be completed by the student

1. How many times will the reaction rate constant meeting the van't Hoff rule increase as a result of heating the system by 100°C, if the temperature reaction coefficient γ is equal to: a) 2, b) 4?
2. How will the reaction rate change which proceeds according to the following kinetic equation:

$$v = k \cdot c_A^2 \cdot c_B$$

when the concentrations $c_A$ i $c_B$ increase 3-fold?

3. When heating $NO_2$ in a closed vessel at a certain temperature, the chemical equilibrium for the reaction:

$$2NO_2 \rightleftharpoons 2NO + O_2$$

   is determined when the following concentrations are reached: $c_{NO2} = 0.06$ mol/dm$^3$; $c_{NO} = 0.24$ mol/dm$^3$; $c_{O2} = 0.12$ mol/dm$^3$. Calculate the chemical equilibrium constant at this temperature.
4. At the initial moment of the third-order reaction: 2A + B → C + … the concentration of substance A is $c_A = 4$ mol/dm$^3$, of substance B is $c_B = 2$ mol/dm$^3$, and the reaction rate constant (at the measured temperature) $k = 0.8$.
   a) What is the reaction rate in the initial moment?
   b) What is the reaction rate when the concentration of $c_A$ decreases by 1 mol/dm$^3$?
5. Explain what it means that a chemical reaction is irreversible or reversible?