Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Technical chemistry laboratory

Laboratory exercise

Catalysis and catalysts

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EXERCISE SHEET

1	**Relation to subjects**: ESO/26, DiRMiUO/26, EOUNIE/26		
	Specialty/Subject	**Learning outcomes for the subject**	**Detailed learning outcomes for the subject**
	ESO/25 Technical chemistry	EKP1 K_W01, K_W02, K_U05 EKP2 K_U08, K_U09	SEKP7 – Mastering the experimental knowledge in studying the rate of chemical reactions and drawing conclusions from the conducted experiments. Mastering the knowledge of the mechanism and type of catalysis as well as identifying catalysts and inhibitors. Expanding knowledge on the use of catalysts in technology and environmental protection.
	ESO/26 Chemistry of water, fuels and lubricants	EKP3 K_U014, K_U015, K_U016	SEKP6 – Determination of oxygen and ammoniacal nitrogen content in technical water. SEKP6 – Determination of corrosion inhibitors in technical water.
	DiRMiUO/26 Chemistry of water, fuels and lubricants	EKP3 K_U014, K_U015, K_U016	SEKP6 – Determination of oxygen and ammoniacal nitrogen content in technical water SEKP6 – Determination of corrosion inhibitors in technical water.
	EOUNIE/26 Chemistry of water, fuels and lubricants	EKP3 K_U014, K_U015, K_U016	SEKP6 – Determination of oxygen and ammoniacal nitrogen content in technical water SEKP6 – Determination of corrosion inhibitors in technical water
2	**Purpose of the exercise:** 1. Learning and consolidation of the basic concepts related to the rate of chemical reactions and catalysis. 2. Understanding the practical impact of selected factors on the rate of chemical reactions in laboratory conditions. 3. Analysing the theoretical way of influencing the acceleration or delay of chemical processes.		
3	**Prerequisites:** general chemical knowledge of the rate of chemical reactions, catalysis and catalysts		

4	**Description of the laboratory workplace:** Basic laboratory equipment – test tube rack, water baths, micro-spatula, stopwatch with a second hand, 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.
5	**Risk assessment:** chemical burns resulting from contact with 0.2 M sulphuric acid and caustic soda are very unlikely, the possible 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.
6	**The course of the exercise:** 1. Getting to know the workplace manual (appendix 1), 2. Performing individual exercises according to the instructions.
7	**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.
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 – control of the knowledge of basic chemical concepts regarding the rate of chemical reactions, catalysis, catalysts and inhibitors during the classes, 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: – 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; – 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; – 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; – 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:** 1. Stundis H., Trześniowski W., Żmijewska S.: *Ćwiczenia laboratoryjne z chemii nieorganicznej*. WSM, Szczecin 1995. 2. Kozłowski A., Gabriel-Półrolniczak U., Ćwirko K., *Instrukcja stanowiskowa do ćwiczeń laboratoryjnych: Szybkość reakcji chemicznych. Kataliza,* AM Szczecin, 2013. 3. Kozłowski A., *Materiały dydaktyczne z chemii technicznej*, prepared for auditorium classes (not published).

	4. Cox. P.A. translation of Z. Zawadzki: *Chemia nieorganiczna*. PWN. Warsaw 2006. 5. Drapała T.: *Chemia ogólna i nieorganiczna*. SGGW, Warsaw 1994. 6. Bielański A.: *Chemia ogólna i nieorganiczna*. PWN, Warsaw 1994. 7. Jones L., Atkins P., *Chemia ogólna. Cząsteczki, materia reakcje*, WN PWN, Warsaw 2004 8. Mastalerz P.: *Elementarna chemia nieorganiczna*. Wydawnictwo Chemiczne. Warsaw 2000. 9. Śliwa A.: *Obliczenia chemiczne. Zbiór zadań.* PWN. Warsaw 1994 10. Pazdro M. *Zbiór zadań z chemii dla szkół średnich*. 11. Resources Open AGH. http://open.agh.edu.pl/open2/ 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 related to catalysis;
- mechanism of catalysis;
- the concept of catalyst and inhibitor;
- practical use of catalysis, contacts, catalytic converters.

2. THEORETICAL INTRODUCTION TO THE EXERCISE

2.1. Catalysis and catalysts

A catalyst is a substance whose presence in a mixture of reagents increases the rate of the reaction, and an inhibitor – a substance whose presence causes a reduction in the rate of the reaction. Fig. 1 shows the effect of the catalyst on the activation energies.

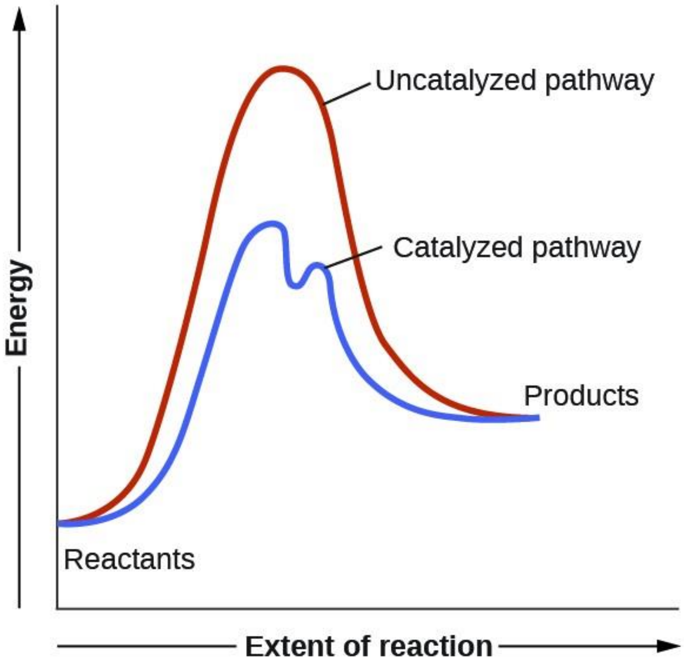

Fig. 1. Effect of the catalyst on the activation energy
source: https://courses.lumenlearning.com/suny-albany-chemistry/chapter/catalysis/)
(accessed October, 5, 2021)

The catalyst works by „converting” reactions with high activation energy Ea (without catalyst) into two or more reactions with lower activation energy (Fig. 2). In other words, the path from reactants to products is transformed into a series of elementary reactions with the participation of the catalyst, with low activation energies of individual stages.

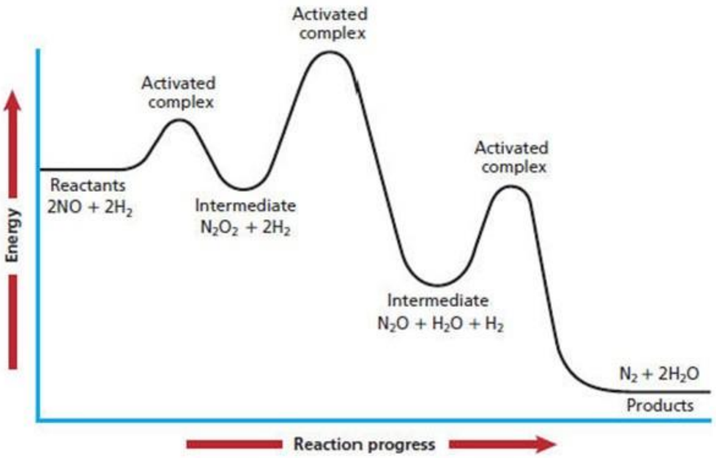

Fig. 2. The path from reactants to products with low activation energies of individual stages with the catalyst source: https://slideplayer.com/slide/3860981/)
(accessed October, 5, 2021)

Sometimes, when certain processes (e.g.: corrosion, decomposition of substances) are too fast and we want to slow them down or control their rate, inhibitors (sometimes called „negative" catalysts) are used. Both the catalyst and the inhibitor are practically not consumed during the reaction, after its completion they remain unchanged compared to their state before the reaction.

The catalyst/inhibitor alters the rate of the reaction going to the right and the reverse to the same degree. Catalysts do not affect the position of the equilibrium state, they only accelerate the time after which this equilibrium is achieved.

A special type of chemical catalysis is enzymatic biocatalysis. Enzymes are protein substances containing hydrophilic and hydrophobic groups that determine, through various types of interactions, the spatial structure of the enzyme protein. Due to their proteinaceous nature, enzymes are very sensitive to the pH value of the reaction medium and temperature.

Important features of catalysts/inhibitors are their selectivity and specificity. Catalyst selectivity is the ability to accelerate/delay only some of the processes possible in a given environment.

The specificity of the catalyst means that the performance of each of the catalysts/inhibitors is limited to at most a few different reactions.

Depending on whether the catalyst and reactants are in the same phase or the catalyst is in a different phase, **catalysis** is defined as **homogeneous** and **heterogeneous**, respectively. An example of homogeneous catalysis can be the esterification of acetic acid with methanol in the presence of sulphuric acid (VI) as a catalyst. The reactants and the catalyst are in the liquid phase. Other examples may be sucrose hydrolysis catalysed by H+ ions, or oxidation of SO_2 catalysed by vanadium oxide and platinum (as an example of gas phase catalysis).

In the case of heterogeneous catalysis, we most often deal with a catalyst in the solid phase (so-called contact) and reactants that are in the gas or liquid phase.

An example of heterogeneous catalysis can be the synthesis of ammonia from nitrogen and hydrogen on an iron catalyst or decomposition of hydrogen peroxide catalysed by manganese (IV) oxide.

There are also known reactions in which one of the reaction products acts as the catalyst. This type of catalysis is called **autocatalysis**. An example of this kind of catalysis is the reduction of potassium manganate (VII) by oxalic acid in an acid medium:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

In this reaction, the catalyst is the Mn^{2+} ions formed during the reaction.

2.2. Application of selected catalysts in practice

The correct scientific name for a car catalyst is a catalytic converter. The catalytic converter is an indispensable element of the exhaust system so that the newly produced car meets the applicable exhaust gas purity standards. Harmful substances are emitted in the exhaust gases during the operation of spark ignition engines. The most dangerous of them are carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x). Catalysts in spark ignition engines should be able to reduce nitrogen oxides and oxidize carbon monoxide (to carbon dioxide) and hydrocarbons (which produces water and carbon dioxide).

The exhaust gas purity standards force the reduction of the content of harmful substances in fumes, and one of the methods is to clean them by appropriately selected chemical oxidation and reduction reactions.

$$2CO + O_2 \longrightarrow 2CO_2$$
$$2C_6H_{14} + 19O_2 \longrightarrow 12CO_2 + 14H_2O$$
$$2NO + 2CO \longrightarrow N_2 + 2CO_2$$

The active mass in catalytic converters is usually platinum, palladium and rhodium. The appropriate selection of catalytic substances causes that as a result of such reactions, forced by catalysts, chemical compounds are produced that are less (or not at all) harmful to the environment (e.g. carbon dioxide is produced from carbon monoxide). Although the catalysts (as chemical substances) do not use up, the life of the catalytic converter is estimated at approx. 80 – 100 thousand. km, although they can serve up to twice as long. The catalytic converter is placed in close proximity to the engine. Thanks to this arrangement, the reactor can heat up faster to its proper operating temperature (usually above 300 – 400^{o}C). It can also be heated by additional processes (such as extra fuel injection, ignition retardation) or supported by a small start-up converter, operating immediately after starting the engine.

Three-way converters are used in gasoline engines. This means that they play three roles: oxidation of carbon monoxide (to carbon dioxide, which is not harmful to humans, but has a negative impact on the greenhouse effect), oxidation of hydrocarbons (resulting in the formation of water and carbon dioxide) and reduction of nitrogen oxides. In order for these three processes to run properly, an appropriate composition of the fuel-air mixture is required, therefore it is necessary to control the excess air with the so-called lambda probes.

In diesel engines, due to the specificity of their operation (on a lean mixture), it is impossible to reduce nitrogen oxides from exhaust gases at the same time. Therefore, additional converters are used, in which the catalytic substance is e.g. urea, which, however, is consumed.

The catalytic converter (Fig. 3) consists of a core made of a ceramic or metal honeycomb monolith, an intermediate layer, an active layer, a sealing and heat-insulating layer in the form of mats and a heat-resistant casing made of corrosion-resistant steel.

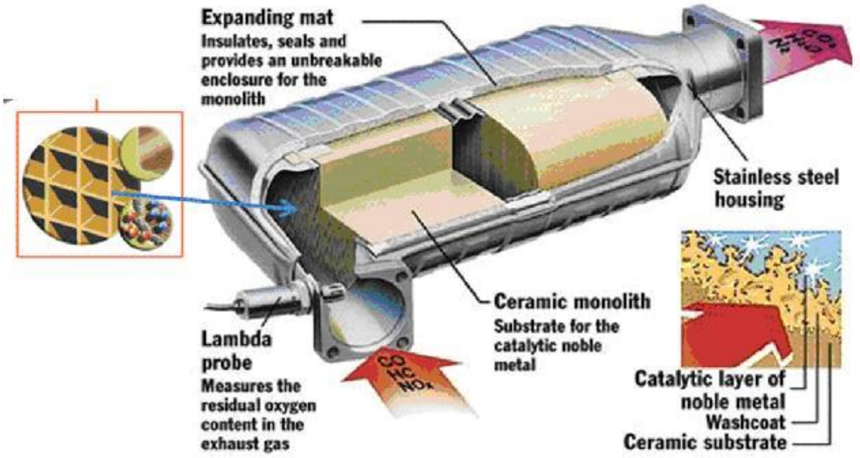

Fig. 3. Three-way catalytic converter
source: http://www.cchem.berkeley.edu/molsim/teaching/fall2009/catalytic_converter/bkgcatcon.html)
(accessed October, 5, 2021)

The monolith is made of a large number of channels arranged transversely in the direction of the exhaust gas flow. They are separated from each other by thin walls, and in the cross-section the monolith forms a honeycomb-like structure.

Ceramic monoliths have square-shaped channels, but can also be rectangular, triangular or hexagonal, which is less common. Their wall thickness is about 0.05 – 0.15 mm. Metal monoliths are made of very thin corrosion-resistant steel foil. They are formed by rolling two sheets of different structure, which are then soldered or welded. The wall thickness is about 0.03 – 0.07 mm.

Catalytic decomposition of nitrogen oxides is a simple method of removing them from an industrial gas stream. Catalytic reduction used in the processes of nitrogen oxides removal from exhaust gases consists in the reduction of nitrogen oxides with ammonia, carbon monoxide or hydrocarbons in the presence of catalysts. The catalysts for this reaction are noble metals such as platinum, palladium, rhodium deposited on ceramic supports. The reactions take place according to the scheme:

$$2NO_2 + 4NH_3 + O_2 \longrightarrow 3N_2 + 6H_2O$$
$$2NO_2 + CH_4 \longrightarrow N_2 + CO_2 + 2H_2O$$
$$2NO_2 + 4CO \longrightarrow N_2 + 4CO_2$$

Corrosion inhibitors. The name of corrosion inhibitors covers substances which, when added in a small concentration to an aggressive environment, significantly reduce the corrosion rate of the metal in contact with this environment.

If the metal is in contact with the gas phase (exhaust gases, other aggressive gases or humid air) – volatile or contact inhibitors are used. When the phase is electrolyte solution – inhibitors are used for acidic, alkaline or neutral environments.

There are a number of different classifications of inhibitors, depending on their chemical composition (organic or inorganic inhibitors), corrosive environment, or their mechanism of action. However, none of these divisions is completely unambiguous.

In the present description, the division of inhibitors has been adopted due to the electrochemical mechanism of their action, which separates the following three groups:

- cathode inhibitors,
- anodic inhibitors,
- mixed action inhibitors.

Anodic inhibitors, for example, increase the anodic polarization of the metal and thus shift the corrosion potential in the positive direction. This group includes chemical compounds with an oxidizing (passivators) or opaque effect. Anions, which usually constitute a group of active compounds, migrate to the metal surface and passivate the metal under favourable conditions, often with the participation of oxygen.

Passivators are oxidizing inhibitors introduced into an aggressive environment, which prevent the dissolution of the metal, as they cause the formation of metal oxides on the surface of the metal. As a result of this reaction, a dense oxide film is formed on the surface of the metal, which prevents hydration and the transfer of metal ions into solution. The most important passivators are nitrates(III) and chromates(VI).

Covering inhibitors are alkaline substances with a buffer action, e.g. NaOH, Na_2CO_3, phosphates, silicates, benzoates and volatile amines. They are used to protect iron and steel in water systems at a pH close to neutral, and the effective operation is ensured by a concentration of 10 mol/dm^3. Due to their non-toxicity, silicates have been used as inhibitors in drinking water circuits.

The protective effect of an inhibitor depends on many factors, the most important of which are: the concentration of the inhibitor, pH and the type and concentration of aggressive ions in the environment, temperature and flow rate of the environment. The influence of the above-mentioned factors depends on their influence on the kinetics and the mechanism of the reactions taking place on the metal surface in a given corrosive environment.

3. PERFORMING THE EXERCISE

Experiment 1 – Catalysis

Materials and reagents:

Sulphuric acid(VI) solution (H_2SO_4, 1 : 3), potassium manganate(VII) (0.1 M $KMnO_4$), potassium nitrate(V) (1 M KNO_3), metallic zinc (Zn) in granules

Performance:

Pour 2 cm^3 of sulphuric acid(VI) solution (H_2SO_4, 1 : 3) into two test tubes, add a few drops of potassium manganate(VII) solution (0.1 M $KMnO_4$) and shake. To one of the test tubes, add two drops of potassium nitrate(V) (1 M KNO_3), then add the zinc (Zn) granule to both test tubes simultaneously. Observe the rate of discoloration of the solution in both cases.

Elaboration of the results:

1. Describe the course of the experiment, bearing in mind that the reaction between potassium nitrate(V) and potassium manganate(VII) does not take place.
2. What kind of catalysis occurs in the performed experiment?

Experiment 2 – Influence of the presence of a catalyst on the reaction rate

Materials and reagents:

Potassium manganate(VII) solution (0.1 M $KMnO_4$), sulphuric(VI) acid (0.1 M H_2SO_4), oxalic acid (0.1 M $H_2C_2O_4$), manganese(II) sulphate(VI) ($MnSO_4$), measuring cylinder.

Performance:

Pour 4 cm^3 of potassium manganate(VII) (0.1 M $KMnO_4$) and 4 cm^3 of oxalic acid (0.1 M $H_2C_2O_4$) and into the second test tube the same: 4 cm^3 of potassium manganate(VII) (0.1 M $KMnO_4$) and 4 cm^3 of oxalic acid (0.1 M $H_2C_2O_4$). Acidify the obtained solutions with 2 – 3 drops of sulphuric(VI) acid (0.1 M H_2SO_4). To the second test tube, add a crystal of manganese(II) sulphate(VI) ($MnSO_4$) and observe the colour change of the solution.

Elaboration of the results:

1. Present the ongoing reaction with an appropriate equation, knowing that one of the products, apart from the evolved gas, are Mn^{2+}ions.
2. Explain the influence of the addition of manganese(II) sulphate(VI) crystal on the reaction rate.

Experiment 3 – Effect of catalyst/inhibitor presence on reaction rate

Materials and reagents:

Hydrogen peroxide solution (3% H_2O_2); manganese(IV) oxide (MnO_2), lead(IV) oxide (PbO_2), orthophosphoric(V) acid solution (0.1 M H_3PO_4), measuring cylinder.

Performance:

Pour 4 cm^3 of hydrogen peroxide (H_2O_2) solution into two test tubes. Leave the first test tube as a standard. Add a half of manganese(IV) oxide (MnO_2) micro-spatula to the second test tube. Compare the changes in the rate of decomposition of hydrogen peroxide in both test tubes. Insert a glowing torch into the outlets of both test tubes. Repeat the experiment with lead(IV) oxide (PbO_2).

Table 1

Summary of results for experiment 3

Test tube	Substance added	Change in reaction rate*	Type of catalyst**	Reactions taking place	Conclusions, type of catalysis
1	MnO_2				
2	PbO_2				
3	Orthophosphoric acid (V)				
4	no substance added				

* + small; ++ medium; +++ big,

** no catalyst, good, weak, inhibitor

Elaboration of the results:

Evaluate the rate of decomposition of hydrogen peroxide observing the rate of combustion of the torch in the emitted oxygen.

1. Identify the nature of the added substances (catalyst, inhibitor) in terms of their influence on the rate of decomposition; the fourth test tube containing only the hydrogen peroxide solution acts as a reference.
2. Write the reaction of spontaneous decomposition of hydrogen peroxide and the reactions taking place in the presence of the catalyst.
3. Summarize the experience with conclusions.

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. P 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

Example

The reaction takes place in two stages:

$$H_2O_2 + I^- \rightarrow H_2O + IO^-$$

$$H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$$

a) write the summary equation for this reaction,
b) indicate the intermediate product,
c) indicate the catalyst.

Solution:

The summary reaction equation is as follows:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The intermediate product of the reaction is: IO^-, while the catalyst for the reaction is: I^-

II. Tasks and questions to be completed by the student

1. The chemical reaction takes place in two stages:

$$F_2 + 2NO_2 \rightarrow NO_2F + F + NO_2 \text{ (stage I free)}$$
$$F + NO_2 \rightarrow NO_2F \text{ (stage II fast)}$$

   a) write a summary equation for this reaction,
   b) determine which step determines the overall rate of the reaction,
   c) determine the intermediate reagent.

2. Determine from the reaction given below:

$$2NO + Br_2 \rightarrow 2NOBr \text{ (stage I)}$$
$$NOBr + Cl_2 \rightarrow 2NOCl + Br_2 \text{ (stage II)}$$

   a) catalyst formula,
   b) transitional product formula,
   c) reaction equation without catalyst.

3. Determine whether the listed catalysts are homogeneous or heterogeneous:
   a) Fe in the benzene bromination reaction,
   b) MnO_2 in the decomposition of an aqueous $KMnO_4$ solution,
   c) H_2SO_4 in the reaction of formic acid with methanol,
   d) H_2O in the synthesis of aluminium iodide from the elements.

4. As a result of catalytic decomposition of 30 g H_2O_2, 988 cm^3 of oxygen was obtained (normal conditions). Calculate the percentage of the solution.

5. Explain the action of a catalyst in catalytic reactions.
6. Explain why a finely divided solid catalyst is more effective at speeding up the reaction than a catalyst of the same mass but in the form of large lozenges.
7. Look for a few examples of the use of catalysts or inhibitors in technology or environmental protection.
8. What type of catalysts are nickel catalysing the synthesis of ammonia (gas), hydrogen and nitrogen?