HOMOGENEOUS CATALYSIS

INTRODUCTION

Catalysis: It is the process of accelerating the rate of a reaction in the presence of a catalyst. A **catalyst** is a substance, which - although it participates in the chemical reaction - remains unchanged after its completion. It accelerates the chemical reaction as a result of reducing the activation energy. If a substrate bonds with a catalyst very strongly, the energy barrier is increased. In such a situation we deal with negative catalysis (inhibition) and such a catalyst is referred to as an **inhibitor.** Depending on the state of aggregation of the reacting substances and catalysts the processes of catalysis are divided into **homogeneous** and **heterogeneous**.

A catalyst may be a component of the homogeneous phase (gaseous or liquid), in which the reaction takes place - in such a case we deal with homogeneous catalysis.
An example of a homogeneous catalytic reaction may be the oxidation of SO_2 to SO_3 in the lead chamber process of sulfuric acid production with nitrogen oxide as a catalyst:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$
$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

Summary reaction: $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

All the reactants – the substrates (SO_2, O_2), the catalyst (NO_2) and the product, SO_3, are gaseous substances and they constitute a one-phase, i.e. homogeneous system.

Acceleration of the rate of the reaction by the catalyst consists in a reduction of the activation energy in comparison to the non-catalytic reaction. For the reaction occurring without the presence of a catalyst:

$$A + B \rightarrow AB$$

We have activation energy $\boldsymbol{E_A}$. The same reaction proceeding with the participation of catalyst **K** may be described by the following equations:

$A + K \rightarrow AK$ activation energy E_A^1

$AK + B \rightarrow AB + K$ activation energy E_A^2

If a reaction without a catalyst requires activation energy $\boldsymbol{E_A}$, then in the presence of catalyst $\boldsymbol{K}$ the two reactions have activation energies $\boldsymbol{E_1}$ and $\boldsymbol{E_2}$, while each of them is lower than $\boldsymbol{E_A}$ **(Fig. 1)**.

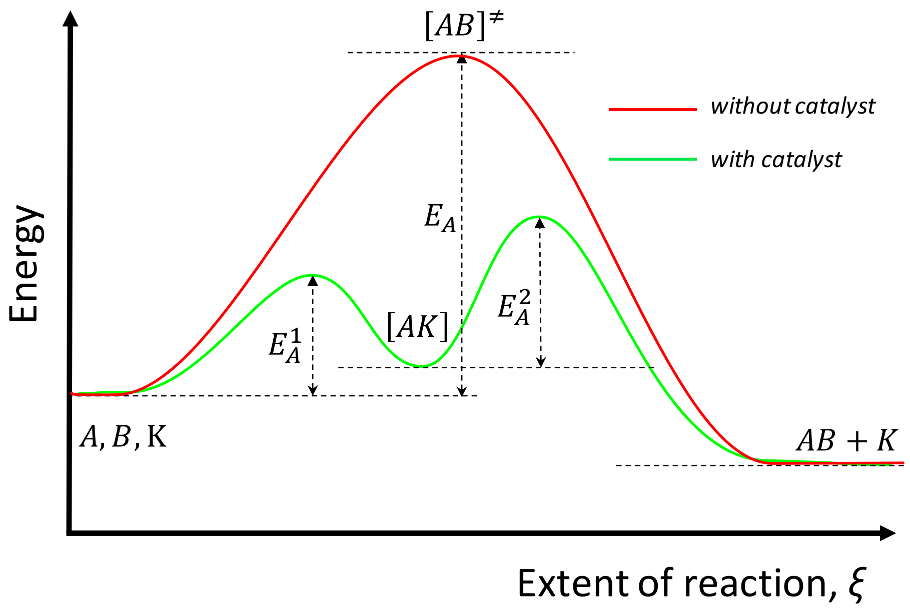

Fig.1. The effect of a catalyst on the energy profile of the reaction.

An increase in the rate of a reaction results from a lower activation energy of the successive stages in comparison to the activation energy of a single-step conversion with no catalyst.

Main properties of catalysts:

- Activity (a measure of the rate of a reaction)
- Selectivity (preference for one direction of the process)
- Stability (catalyst viability during its lifetime)
- The temperature range of effective catalyst activity

A solid-phase catalyst is composed of several elements:
1. the **carrier** – its role is to increase the active surface and enhance the mechanical strength and heat resistance of the catalyst. It may be a source of other types of active centres than the active phase or it may modify its electron structure. Examples of carriers include SiO_2, γ-Al_2O_3, α-Al_2O_3, Cr_2O_3, MgO and CaO.
2. the **active phase** – it is a source of active centres of one or various types, on which transitional complexes are formed. Examples of the active phase include Fe, Ni, Pt, Cu Pd, Ag, Ni O and ZnO.
3. **promoters** – they modify the physical and electron structure of the active substance, inhibit its adverse phase transitions and promote regeneration. Examples of promoters include ZrO_2, HCl, MgO, K_2O and rare earth elements.

The more active the catalysts, the more effectively they reduce activation energy. Selectivity consists of the ability of the catalyst to lower the activation energy of only one reaction out of several thermodynamically possible. The phenomenon of catalyst ageing is connected with a change in its crystalline structure. Transformation into a more stable crystal lattice leads to a considerable decrease in the number of active centres (i.e. sites in the catalyst participating in the catalytic process) and a loss of catalytic activity. Poison resistance is the ability to retain activity in the presence of small amounts of catalyst poisons.
The catalyst capacity to direct chemical reactions is of paramount importance in industrial applications. The most commonly used catalysts are solid-phase:

- Nickel (Ni) – nickel catalysts are commonly used in two processes of hydrogen production: methane steam reforming and purification of produced hydrogen to remove traces of carbon oxides.

- Platinum (Pt) - platinum is used as a catalyst in the form of platinum black, sponge and gauze, e.g. in the production of ammonia, hydrocyanic acid, and during crude oil storage.
- Palladium (Pd) – the most important reactions in organic synthesis are the reactions forming new C-C bonds. Among the many transition metals for many years palladium compounds have been considered particularly interesting thanks to their extensive and multiple applications in organic synthesis, both on the bench scale and commercial scale of industrial production. At present over 90 organic reactions are catalysed by palladium compounds; however, not all of them have found applications in industrial practice. The most important reactions include reactions of aryl halides leading to the formation of carboxylic acids, esters, amides, biphenyl compounds, new olefins, etc.

While the mode of action of a catalyst is generally the same, the kinetics of the reaction differ depending on the catalyst phase - either identical to the substrates or different.
The rate of the homogenous catalytic reaction may be described by the equation:

$$-\frac{dc}{dt} = (k + k_K \cdot c_K) \cdot c^n \tag{1}$$

i.e.:

$$-\frac{dc}{dt} = k \cdot c^n + k_K \cdot c_K \cdot c^n \tag{2}$$

where:
c – concentration of the substrate in the solution
c_k – concentration of the catalyst
k – rate constant for the reaction proceeding with no catalyst
k_K – rate constant for the reaction proceeding in the presence of the catalyst
n – reaction order, which for catalytic reactions takes values of 0-2 (including also fractional values).

The rate of a catalytic reaction is thus equal to the sum of two independent processes: one involving the catalyst and the other with no participation of a catalyst. Equation 1 indicates that the rate of a homogeneous reaction depends on the concentration of the catalyst and temperature. The latter parameter affects the value of the reaction rate constant:

$$k = z \cdot e^{-\frac{E_A}{RT}} \tag{3}$$

$E^{\#}$ – activation energy
R – gas constant
T – temperature
z – constant
If the diffusion of reagents to the surface of the solid phase is the slow stage, then the kinetic equation describing the catalytic process may be described as:

$$-\frac{dc}{dt} = \left(k + \frac{DS_K}{V\delta}\right) \cdot c^n \tag{4}$$

where:
V – volume of the solution
D – diffusion coefficient of a reagent
S_K – the surface area of the catalyst
δ – thickness of the diffusion layer
k – rate constant of the reaction proceeding within the solution with no catalyst present.

In such a case the rate of the reaction depends not only on the concentrations of the substrates and the temperature but also on the surface of the solid phase (catalyst) and the solution mixing rate.
If the reaction on the surface of the catalyst is the slow stage, the kinetic equation describing the catalytic process may be described as:

$$-\frac{dc}{dt} = (k + k_K \cdot S_K) \cdot c^n \tag{5}$$

where: k_K – rate constant for the reaction proceeding on the surface of the catalyst.

In this case, the rate of the reaction depends on the concentrations of the substrates, temperature and the surface area of the solid phase, while a change in the circulation rate does not influence the rate of the process.
An example illustrating the presented dependencies may be the decomposition of hydrogen peroxide H_2O_2 (hydrogen peroxide solution) in the presence and absence of a catalyst. H_2O_2 is decomposed according to the reaction:

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \tag{6}$$

The reaction of decomposition of a hydrogen peroxide solution is a first-order reaction, i.e. it proceeds according to the kinetic equation:

$$-\frac{dc_{H_2O_2}}{dt} = k \cdot c_{H_2O_2} \tag{7}$$

After integration, equation 7 takes the form:

$$ln\, c_{H_2O_2} = ln\, c^o_{H_2O_2} - kt \tag{8}$$

$c^o_{H_2O_2}$ – initial concentration of H_2O_2 in the solution
$c_{H_2O_2}$ – concentration of H_2O_2 in the solution after time t

Plotting a graph in the coordinate system $\ln c_{H_2O_2} = f(t)$ provides a graphic presentation of constant k

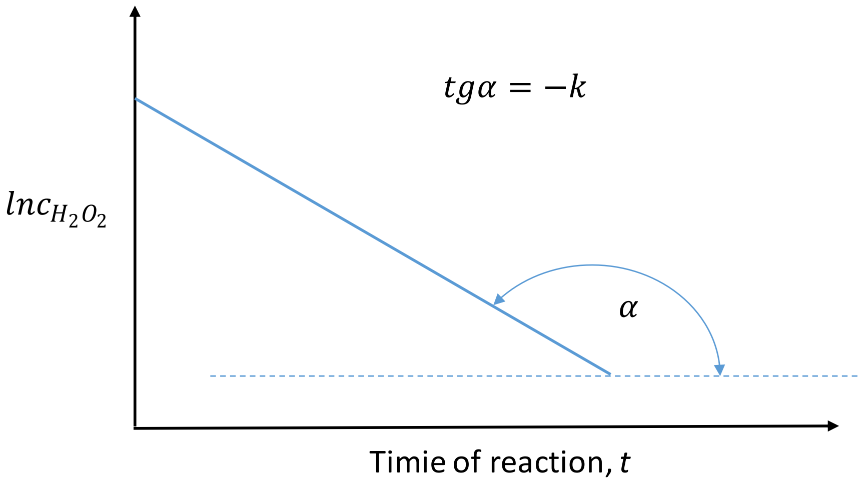

Fig. 2. Graphic determination of reaction rate constant.

The rate of decomposition of the hydrogen peroxide solution increases in the presence of some metal compounds. The decomposition of H_2O_2 in an aqueous solution is accelerated by many ions, e.g. $Fe^{3+,}$ Fe^{2+}, MoO^{2-}, WO_4^{2-} and $Cr_2O_7^{2-}$. In the case of homogeneous catalysis, the rate of the reaction may be described by the formula:

$$-\frac{dc_{H_2O_2}}{dt} = (k + k_K \cdot c_K) \cdot c_{H_2O_2} \tag{9}$$

After integration, it takes the form:

$$ln\, c_{H_2O_2} = \ ln\, c_{H_2O_2^o} - k't \tag{10}$$

where:
$k' = k + k_k \cdot c_K$

If a reaction with no addition of the catalyst proceeds very slowly (k is by 1-2 orders of magnitude lower than k_K), then $k' \approx k_K \cdot c_K$. The rate constant for reaction k_K does not depend on the concentration of the catalyst, thus it may be expected that the effect of the concentration of the catalyst on the rate of this reaction may be followed based on the changes in k values.

PURPOSE OF EXERCISE

The objective of the task is to determine the rate of hydrogen peroxide decomposition in the process of homogeneous catalysis in the presence of various amounts of the catalyst $Fe_2(SO_4)_3$.

LAB GLASS

- 50 cm^3 burette - 1 piece
- a funnel - 1 piece
- 250 cm^3 volumetric flask - 1 piece
- 100 cm^3 Erlenmeyer flask- 4 pieces

- 50 cm^3 pipette - 1 piece
- 10 cm^3 pipette - 1 piece
- 5 cm^3 pipette - 4 pieces
- Conical flasks for titration - 3 pieces

CHEMICALS

- 3 % H_2O_2
- 0.02 M $KMnO_4$
- 2 M H_2SO_4
- Solution of 0.05 M $Fe_2(SO_4)_3$ in 0.1 M H_2SO_4

EXPERIMENT PROCEDURE

The process of hydrogen peroxide decomposition may be investigated by titration of H_2O_2 with the solution of potassium permanganate $KMnO_4$ in an acidic medium or by measuring the volume of released oxygen at specific time intervals. The first method will be used in this task.

Manganometric determination of H_2O_2 concentration
Manganometric determination of H_2O_2 is based on the reaction:

$$5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O \qquad (11)$$

During titration in a strongly acidic solution, MnO_4^- ions of intensive purple colour are reduced with the formation of Mn^{2+} ions, which are pale pink (diluted solutions are practically colourless). Upon reaching the end point of titration the sample takes a pale pink colour coming from one drop of excess $KMnO_4$ (thus no indicators are required).

The concentration of H_2O_2 is calculated from the formula:

$$c_{H_2O_2} = \frac{2.5 \cdot c_{KMnO_4} \cdot v_{KMnO_4}}{v_p} \qquad (12)$$

$c_{H_2O_2}$ – concentration of H_2O_2, $mol \cdot dm^{-3}$
c_{KMnO_4} – concentration of $KMnO_4$, 0.02 M
v_{KMnO_4} – volume of $KMnO_4$ solution used in titration, cm^3
v_p – volume of titrated sample (5 cm^3)

1. Prepare H_2O_2 solution according to the teacher's instructions (to a 250cm^3 volumetric flask measure 50 cm^3 of 3% H_2O_2 solution and fill it with the distilled water).
2. To 4 numbered conical flasks add 50 cm^3 H_2O_2 solution prepared in step 1, followed by the catalyst in amounts given in the table below:

FLASK NO.	**AMOUNT OF DISTILLED WATER [cm^3]**	**AMOUNT OF CATALYST 0.05 M $Fe_2(SO_4)_3$ [cm^3]**
1	10	0
2	7.5	2.5
3	5	5
4	0	10

CAUTION! Do not add the catalyst to all flasks at the same time, since it is necessary to promptly collect and titrate samples at specific time intervals. Sufficient intervals need to be kept between adding the catalyst to individual flasks. See step 3.

3. After adding the catalyst $Fe_2(SO_4)_3$, the solution is mixed and a $5cm^3$ titration sample is collected. The following samples are collected and titrated following the scheme below:
   from flask 1, collect a titration sample after 10, 70 and 90 min from catalyst addition, while from flasks 2, 3 and 4 the first sample is collected after 5 min, followed by samples collected every 15 min, and the next two samples at every 20 min, i.e. from each flask six samples are collected, except for flask 1 – with three samples collected.

Solution samples are tested as follows:
To a $100cm^3$ conical flask add 5 cm^3 2 M H_2SO_4 and 5 cm^3 of the tested sample. Mix the flask contents and titrate with 0.02 M $KMnO_4$ solution until a pale pink colour is obtained.

PREPARATION OF RESULTS:

1. Based on titration results calculate the amount of substance concentration *c* (from equation (12)) in solutions during the reaction in four different systems.

FLASK NO.	**REACTION TIME, [min]**	**AMOUNT OF $KMNO_4$, [ml]**	**CONCENTRATION OF H_2O_2 c, [mol/dm^3]**	**ln c**
1	10 70 90			
2	5 20 35			

	50 70 90			
3	5 20 35 50 70 90			
4	5 20 35 50 70 90			

Plot graphs for dependence ln *c* = *f(t)* for all four systems to confirm that it is a first-order reaction. Next, for each mixture determine rate constant k using the linear regression method.

2. Plot graphs for the dependence of the reaction rate constant on the amount of added catalyst:

$$k = f\left(V_{Fe_2(SO_4)_3}\right)$$

Conclude the effect of the catalyst and its concentration on the rate of the reaction of H_2O_2 decomposition.

Template of the table and draft of the study

…………………………….. *Faculty* ……………………………….. *Field of study* *Full-time/ part-time studies*	……………………………………………… *Name and surname*	…………………………………... *Date:*
Group no.: ………………… *Team no.:* …………………	………..…………… *Exercise no.:*	…………………………………….. *Instructor:*

…………………………….. *Wydział* ……………………………….. *Kierunek* *Studia stacjonarne/niestacjonarne*	……………………………………………… *Imię i Nazwisko studenta*	…………………………………... *Data wykonywania ćwiczenia:*
Nr grupy: …………………... *Nr zespołu:* …………………..	………..…………… *Nr ćwiczenia:*	…………………………………….. *Nazwisko Prowadzącego:*

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: