Poznan University of Technology
Faculty of Chemical Technology
Physical Chemistry Division
Laboratory Exercises

TEMPERATURE DEPENDENCE OF REACTION RATE CONSTANT

INTRODUCTION

The rate of a second-order reaction:

$$A + B \rightarrow C \tag{1}$$

depends on the concentration of substrates A and B

$$v = k'[A][B] \tag{2}$$

When one of the reactants is a solvent (i.e., A), its concentration during the reaction practically does not change, so [A] = const. Therefore, $[A]$ can be incorporated into the reaction rate constant:

$$v = k[B] \qquad \text{where} \qquad k = k'[A] \tag{3}$$

Such reaction is called a **pseudo-first-order** reaction and its equation can be solved similarly as for the first-order reaction:

$$ln\frac{[B]_o}{[B]} = k \cdot t \tag{4}$$

where $[B]_o$ is the initial concentration of substrate B.

This type of reaction can be i.e. a reaction of acid chlorides with alcohol, where alcohol is the dissolving agent:

$$\text{RCOCl} + \text{ROH} \rightarrow \text{RCOOR} + \text{HCl} \tag{5}$$

Progress of this type of chemical reaction can be monitored by measuring the electrical conductivity G_{el} (or resistance R) of the solution during the process. The value of conductivity of the reaction mixture with a good approximation is proportional to the concentration of HCl:

$$G_{el} \approx [HCl] \tag{6}$$

Substrate concentration, $[B]$ = [RCOCl], during the process, can be expressed by the equation:

$$[B] = [HCl]_{\infty} - [HCl] \tag{7}$$

where $[HCl]_{\infty}$ is the total concentration of HCl when the whole amount of acid chloride is reacted.

Equations (6) and (7) lead to the relationship:

$$[B] \approx (G_{\infty} - G) \tag{8}$$

Therefore, the kinetic formula (4) can be described as follows:

$$ln\frac{G_{\infty}}{G_{\infty}-G}=k\cdot t \qquad (9)$$

Explanation of the experiment:
In the present measurement, ionic conductivity values are converted into potential signals measured by the METEX multimeter connected to the PC and recorded by the SCOPE VIEW application.

The change of conductivity (potential) with time is shown in Figure 1.

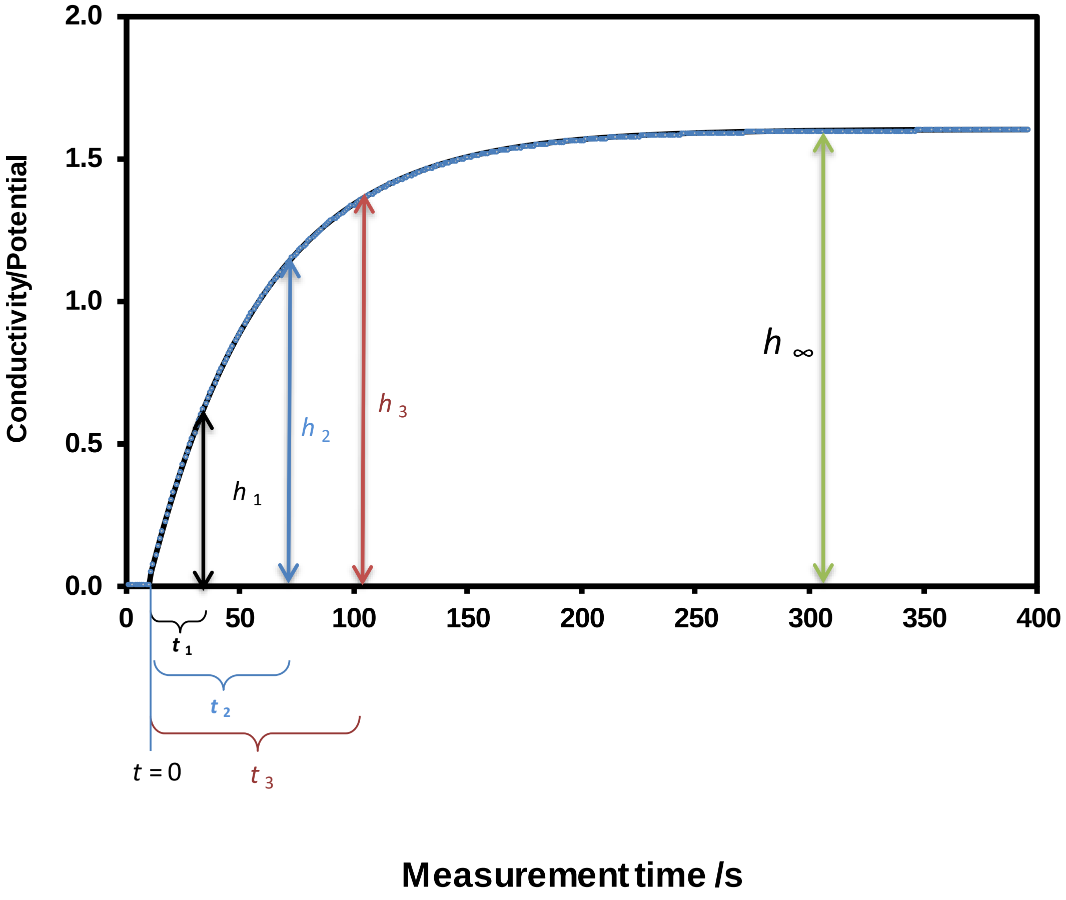

Figure 1. Changes of the potential during reaction time of the chemical reaction of benzoyl chloride methanolysis.

Potential values (height *h*) are proportional to the ionic conductivity, so that equation (9) can be expressed as:

$$ln\frac{h_{\infty}}{h_{\infty}-h}=k\cdot t \qquad (10)$$

Temperature dependence of the rate constant k follows the Arrhenius equation:

$$k = z \cdot e^{-\frac{E^{\neq}}{RT}} \tag{11}$$

where:

$E^{\neq}$ – activation energy
z – pre-exponential factor.

This equation can be written as:

$$lnk = a - \frac{b}{T} \tag{12}$$

where:

$$b = \frac{E^{\neq}}{R} \tag{13}$$

OBJECTIVE OF THE TASK

The aim of the exercise is to describe the temperature dependence of the rate constant of the reaction of benzoyl chloride with methanol.

APPARATUS

- computer
- multimeter - METEX.
- conductometer (i.e. OH-102/1 or CP-501).
- ultrathermostat (i.e. U-1)
- magnetic stirrer and a stirring bar
- electronic thermometer
- copper electrodes
- automatic pipette
- tweezers

GLASSWARE

- thermostatic reaction vessel
- 50 cm^3 beakers – 2 pcs
- Syringe with a needle (10 cm^3)

CHEMICALS
- Methanol
- 5M solution of benzoyl chloride (C_6H_5COCl) in acetone

EXPERIMENTAL PROCEDURES

Conductivity dependence on the reaction time is measured using copper electrodes attached to the conductometer. The analog output is connected to the multimeter METEX. The measured values of potential are proportional to the ionic conductivity of the system. The potential is recorded using the ScopeView application. The cell with the reaction mixture is thermostatted and the temperature is read by a thermometer immersed in the reaction vessel.

1. Start the computer.
2. Start the METEX SCOPE VIEW on the desktop and turn on the multimeter METEX.
3. In the program METEX SCOPE VIEW
    - Press the POWER button to verify communication with the meter (the program should begin to record the multimeter reading).
    - Press SCOPE to run the system control panel.
    - Set the range of potentials 0 to 2 V (values of vertical axis: start: 0 units/div: 0.25).
    - Press the RECORD button to save the name of the file before starting.
    - Press the SCOPE to open the recording panel.
    - Start recording by pressing the RUN, and at the end press STOP.
    - **Follow the operation manual on the program in the exercise and the teacher's guidelines.**

4. Set the required temperature on the thermostat.
5. Perform measurements at temperatures close to 25, 30, 35, 40, 45°C. (Conductometer OH 102/1 should work in the position "Range" 15 mS.).
6. Using a syringe with a needle pour 10 cm^3 of methanol into the thermostatic vessel and turn on the mixing (c.a. 50 rpm).
7. After fixing the temperature in the reaction vessel, wait about half a minute and start recording by pressing the RUN.
8. Using an automatic pipette introduce 0.2 cm^3 of benzoyl chloride (5M) into the reaction vessel. Record the curve of potential=f(time).
9. After receiving approximately constant potential (c.a. 2.0 V), finish by pressing STOP.
10. Prepare a system for carrying out the next reaction by **washing the vessel, electrodes, and stirring bar with methanol.**

Warnings!

- Do not use the water during this exercise
- Do not pour the solution into the sink under the hood
- Before pouring the solution out of the vessel, remove the stirring bar with the tweezers
- Detailed instructions will be given by the teacher.

CALCULATIONS

1. Draw the dependence of the potential/conductivity on the reaction time.
2. Determine from the curves G = f(t) values of h and t for several (at least three) points in a fragment selected from the rising part of the curve of the potential/conductivity over time.
3. Calculate the rate constant for each temperature and determine the mean values.
4. Plot a graph of the natural logarithm of the rate constant versus inverse temperature.
5. Based on the Arrhenius equation, use a linear regression equation to determine the coefficients describing the Arrhenius temperature dependence of the reaction rate constant (12).
6. From equation (13) determine the activation energy of the reaction.

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: