DETERMINATION OF THE RATE CONSTANT AND REACTION ORDER

(Oxidation of Fe^{2+} ions by ClO_4^- ions in acid environment)

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Task 40b

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I. Aim of the task

The aim of the task is determination of the order of reaction, rate constant for the reaction and half-life of reaction oxidation of Fe^{2+} ions by ClO_4^- ions in acid environment.

II. Introduction

1. Optical properties of substances.
2. Absorption of electromagnetic radiation.
3. Impact of electromagnetic radiation with matter.
4. Beer-Lambert law.
5. Deviations from the Beer-Lambert law.
6. Molecularity and chemical reaction order.
7. Rate and half-life of chemical reaction.
8. Rate constant for chemical reaction.
9. Rate equations of first - order and second – order reactions.

Knowledge of the theoretical part from task 40a is required

References:

1. P. Atkins, J. de Paula, „ *Atkins' Physical Chemistry*", Oxford, 2006. Points 6-9: chapters 22-23, points 2-4: pp. 431-432.
2. P. Atkins, J. de Paula, „ *Elements of Physical Chemistry*", Oxford, 2009. Points 6-9: chapters 10-11, points 2-4: pp. 220-221.
3. A.M. Azzan, J.A.W. Shimi "*Z. Phys. Chem. NeueFolge*", 33 (1962) 190.
4. K.A. Connors, *"Chemical kinetics-the study of reaction rates in solution"*, VCH, New York, 1990. Points 6-9: chapters 1-2.

5. G.L. David Krupadanam, „*Analytical Chemistry*”*,* Universities Press, Hyderabat, 2001. Points 1-5: chapter 4.
6. K. Gumiński, „*Wykłady z chemii fizycznej"*,Warszawa, PWN, 1973.
7. K. Pigoń, Z. Ruziewicz, „*Chemia fizyczna T.1 Podstawy fenomenologiczne*”, PWN, Warszawa, 2005. chapter 7.
8. E. Szymański, „*Ćwiczenia laboratoryjne z chemii fizycznej - Aparatura pomiarowa, Część 1*”*,* UMCS, Lublin 1991, chapter 4.5.1.
9. www.camlab.co.uk.

IV. Experimental

A. Devices and materials

1. **Devices:**
   - Spectrophotometer Cecil 1011,
   - cuvette ofthe thickness d = 1 cm,
   - measuring flask: 25 cm^3 – 6 u,
   - measuring flask: 50 cm^3 – 1 u,
   - graduated pipette: 5 cm^3 – 1 u,
   - graduated pipette: 2 cm^3 – 3 u,
   - graduated pipette: 20 cm^3 – 1 u,
   - erlenmeyer flask or beaker: 100 cm^3 – 2 u.
2. **Materials:**
   - 0.1M solution of salt Fe^{2+} (Mohr's salt),
   - 0.01M solution of salt Fe^{3+} in 0.01 M HCl,
   - 0.1 M solution of salt ClO_3^- in 0.01 M HCl,
   - 0.01 M HCl,
   - 25% solution of KSCN in 0.01 M HCl.

B. Preparation of the spectrophotometer for measurements

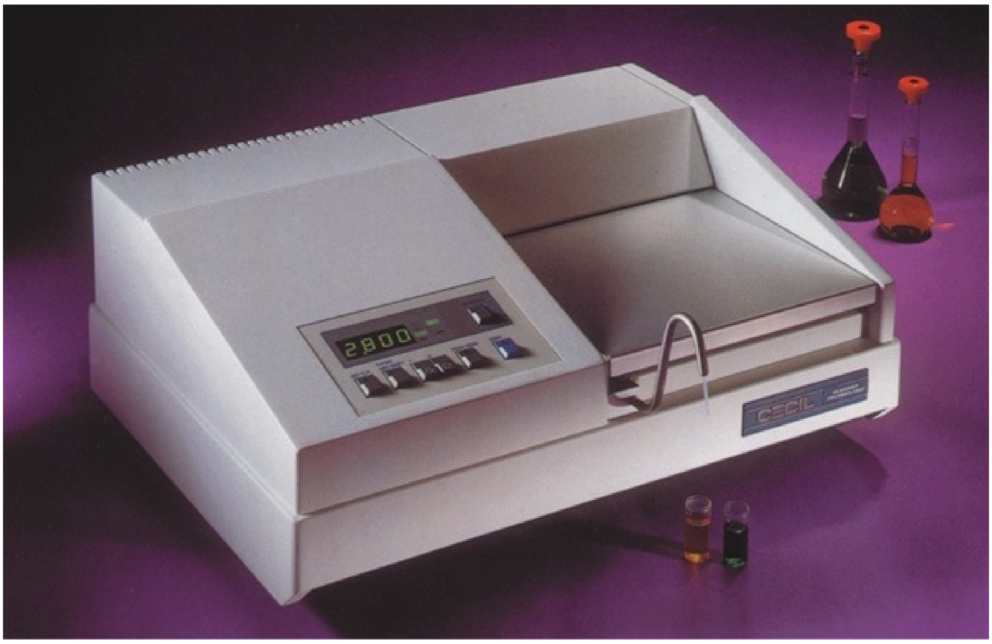

Fig. 1. Spectrophotometer Cecil 1011 [9].

Instructions for the Spectrophotometer Cecil 1011

- Plug in the apparatus pressing the button (left side) for 10 minutes before measurements. There will appear the inscription **CAL**, next **AUTO** on the display – the apparatus is zeroed automatically. If figures appear on the display before measurements, zero the apparatus pressing the button **ZERO**.
- Set up the wavelength pressing the button **READOUT**, light the inscription *nm* on the right side and then set up the wavelength by means of the key button -/+ (wait 15 seconds till the apparatus gets steady). Set up the wavelength at $\lambda = 450$ nm.
- Put the cuvette with the standard liquid into the measurement chamber under the metal lid, light ***A*** or ***T*** with the key button **READOUT** and press the key **ZERO** – the apparatus will set up zero of absorbance or 100% ***T*.**
- Take out the cuvette with standard liquid and in this place put next cuvettes with the measurement liquid.
- Light the required measurement quantity (***A*** or ***T***) with the key **READOUT** (*A* for colourless or coloured solutions, *T* for opaque solutions).
- With each change of wavelength, zero the apparatus on standard liquid pressing the key **ZERO.**
- During long-lasting measurements, at the same wavelength, zero for the standard liquid must be checked from time to time.
- When the measurements are over, take out the cuvette from the chamber and rinse it thoroughly with distilled water.
- Switch off the apparatus.

C. Preparation of reagents solutions and reading the changed values of absorbance during the reaction

To determine the order of the reaction by the integral method, reaction rate (or concentration change of one of the products) for different reagents concentrations in the reaction mixture should be defined.

If room temperature is higher than 20°C the measurements are made for the reaction mixture where the reactants concentrations are:

- $c\ (Fe^{2+}) = 2.5\cdot10^{-3}$ M/dm^3, $c\ (ClO_3^-) = 2.5\cdot10^{-3}$ M/dm^3
- $c\ (Fe^{2+}) = 1.5\cdot10^{-3}$ M/dm^3, $c\ (ClO_3^-) = 1.5\cdot10^{-3}$ M/dm^3

If the temperature in room is lower than 20°C the measurements are made for the reaction mixture where the reactants concentrations are:

- $c\ (Fe^{2+}) = 2.5\cdot10^{-3}$ M/dm^3, $c\ (ClO_3^-) = 2.5\cdot10^{-3}$ M/dm^3
- $c\ (Fe^{2+}) = 4.0\cdot10^{-3}$ M/dm^3, $c\ (ClO_3^-) = 4.0\cdot10^{-3}$ M/dm^3

Before preparation of the reaction mixture, the spectrophotometer should be ready to work!

To prepare 20 cm^{3}of the reaction mixture where the concentration of Fe^{2+} and ClO_3^- ions is $2.5\cdot10^{-3}$ M/dm^3 to a clean and dry beaker (erlenmeyer flask) there should be pipette **respectively**:

- 17 cm^{3}of 0.1 M HCl,
- 2 cm^3 of 25% solution of KSCN in 0.01 M HCl,
- 0.5 cm^{3}of 0.1 M solution ClO_3^-,
- 0.5 cm^{3}of 0.1 M solution Fe^{2+}.

The moment of adding the Fe^{2+} salt solution is assumed to be t=0 [s].

The solution prepared in this way is poured into cuvette and absorbance is measured every minute (or every 2 minutes – it depends on the laboratory demonstrator) to the absorbance value A = 1 or about 40 minutes (if absorbance changes very slowly – the measurements are made every 5 minutes).

To prepare 20 cm^{3}of the reaction mixture where the concentration of Fe^{2+} and ClO_3^- ions is $1.5\cdot10^{-3}$ M/dm^3 to the clean and dry beaker (erlenmeyer flask) pipette **respectively**:

- 17.4 cm^{3}of 0.1 M HCl,
- 2 cm^3 of 25% solution of KSCN in 0.01 M HCl,
- 0.3 cm^{3}of 0.1 M solution ClO_3^-,
- 0.3 cm^{3}of 0.1 M solution Fe^{2+}.

To prepare 20 cm^{3}of the reaction mixture where the concentration of Fe^{2+} and ClO_3^- ions is $4\cdot10^{-3}$ M/dm^3 to clean and dry beaker (erlenmeyer flask) pipette **respectively**:

- 16.4 cm^3 0.1 of M HCl,
- 2 cm^3 of 25% solution of KSCN in 0.01 M HCl,
- 0.8 cm^{3}of 0.1 M solution ClO_3^-,
- 0.8 cm^{3}of 0.1 M solution Fe^{2+}.

t = 0 [s] is assumed to be the moment of adding the Fe^{2+} salt solution.

Pour the prepared solutions into the cuvette and measure absorbance every minute up to the absorbance value A = 1.

D. Preparing calibration curve

For the wavelength λ = 450 nm prepare calibration curve of absorbance dependence on concentration of Fe^{3+} ions, A = f(c). Fe^{3+} ions occur in the firmly coloured thiocyanate complex. The reaction of Fe^{3+} ions with thiocyanate ions is reversible, so that thiocyanate ions should be added in excess to form the $Fe(SCN)_3$ complex of all Fe^{3+} ions.

Solutions for the calibration curve should be prepared using the 0.001 M solution of Fe^{3+} ions. For this purpose from 0.01 M solution of Fe^{3+} ions prepare 50 cm^3 0.001 M solution of Fe^{3+}ions.

The solutions of iron thiocyanate for the calibration curve are prepared in the measuring flask (25 cm^3) as follows:

- add a fixed volume of 0.001 M solution of Fe^{3+} ions ,
- add 2 cm^3 25% solution of KSCN to 0.01 M HCl,
- the whole content should reach the mark of 0.1 M HCl

The solutions for the calibration curve should have the following concentrations – **Table 1.**

Table 1.

Number of measuring flask	**c (Fe^{3+}) [mol/dm^3]**	**0.001 M Fe^{3+} V[cm^3]**	**A**
1	$2\cdot10^{-5}$		
2	$4\cdot10^{-5}$		
3	$6\cdot10^{-5}$		
4	$8\cdot10^{-5}$		
5	$10\cdot10^{-5}$		
6	$12\cdot10^{-5}$		
a =	*b* =		

Next check 0 on the spectrophotometer, and measure the absorbance of the prepared solutions with different Fe^{3+} concentrations.

E. Results and conclusions

The oxidation reaction of Fe^{2+} ions by ClO_4^- ions in the acid environment proceeds according to the reaction:

$$ClO_3^- + 6H^+ + 6Fe^{2+} \leftrightarrow Cl^- + 3H_2O + 6Fe^{3+} \quad (1)$$

From literature [3] it is known that the determining step in kinetics is the reaction:

$$Fe^{2+} + ClO_3^- + H^+ \leftrightarrow Fe^{3+} + HClO_3^- \quad (2)$$

On the basis of equation (2) we can assume that the oxidation reaction of Fe^{2+} ions with ClO_4^- ions is the second – order reaction. The reaction is followed by equation (1) described above. The decisive step of kinetics is reaction (2) [3].

The progress of the reaction is controlled by measuring the increase in the concentration of Fe^{3+} thiocyanate complex using a spectrophotometric method.The concentration of iron (III) ions during the reaction is obtained from the earlier made absorbance calibration curve A = f ($x_{Fe(SCN)3}$). Dependence of the value of $Fe(SCN)_3$ on the concentration of the thiocyanate complex for diluted solutions is a straight line. The parameters of this line can be found by the least squares method substituting for x = c_{Fe3+}, for y = A (The explanation of the method of least squares can be found in Appendix).

The results of the calibration curve measurements are presented as a graph and in Table 1. The results of the reaction progress measurements are presented as a graph and in Table 2.

Table 2.

t [s]	**A**	**c (Fe^{3+}) [mol/dm^3]**	**c (Fe^{2+}) [mol/dm^3]**	**1/c**

The concentration of Fe^{3+} ions obtained in reactions 1 and 2 can be determined using the calibration curve in two ways:

- substituting a measured value of *A* after time *t* of the reaction to the linear equation obtained by the method of least squares presenting calibration curve,
- by the graphical method by reading the value of concentration of iron ions directly from the plot of the obtained values of *A* as a function of the concentration of Fe^{3+}, ions remembering that this method is much less accurate than that presented above.

From the obtained results a graph of the $1/c$ from time reaction *t* [s] is made, according to the second-order reaction when the reactants concentrations are equal. The graphs do not need to have all obtained points, but there should be chosen such the time intervals that include the minimum 8-10 points.

$$\frac{1}{c} = \frac{1}{c_0} + k_2 t \tag{3}$$

where: c_o– the initial concentration of reactant, c – the concentration of reactant after time t [s], $c=c_o - Fe^{3+}$

For the second – order reaction equation (3) is satisfied and in the coordinate system $y = 1/c$, $x = t$ [s] there is obtained a straight line graph, whose slope is equal to k. The k value is obtained using the method of least squares. Despite the linear dependence of the inverse of the reactant concentration on the time of the reaction, the order of reaction must be checked using the integral method of Ostwald-Zawidzki. This method covers the measurement of time at which a specified fraction of the reactant is reacted. For this purpose is made a graph of the dependence of the number of progress reaction *x’* on time *t* [s]. The number of progress reaction *x’* is the ratio of the concentration of unreacted Fe^{2+} ions (*x* - in our case it is equal to the concentration of received Fe^{3+} ions) and the initial reactant concentration (c_o):

$$x' = \frac{x}{c_0} \tag{4}$$

The concentration of reacted Fe^{2+} ions is equal to the obtained concentration of Fe^{3+} ions, which we be determined the calibration curve. From the graph of x′ = f*(t)* for both initial concentrations (Figures are placed on one coordinate system) we read the value of t_1 and t_2 for any value of the number of progress reaction and put them into the equation defining the order of the reaction:

$$n = 1 + \frac{log\ (t_1/t_2)}{\log(c_{02}/c_{01})} \tag{5}$$

where: c_{o1}, c_{o2} – the initial concentration of reactants for 1 and 2 series of measurements, t_1, t_2 – the time for the specific number of progress reaction for 1 and 2 series of measurements.

Write the following conclusions:

1. Have you achieved the aim of the task?
2. Compare the obtained results with the literature data.
3. In the case of large results discrepancies explain the cause of them.