RATE OF DECOMPOSITION OF AN OXALO-MANGANIC COMPLEX (spectrophotometric method)

1. PURPOSE OF THE WORK

Determination of the rate constant and the order of reaction of the decomposition of the oxalo-manganese (III) complex ($[Mn(C_2O_4)_3^{3-}]$).

2. THEORETICAL NOTIONS

Methods for determining reaction order and rate constant

The variation of the concentration in the unit of time of the components of a reaction, by definition, is called the reaction rate and is expressed in relation to one or the other of the components. For the reaction

$\nu_A A + \nu_B B + \ldots \rightarrow \nu_L L + \ldots$

reaction rate is

$$v_A = -\frac{1}{\nu_A}\cdot\frac{dc_A}{dt} \; ; \; v_B = -\frac{1}{\nu_B}\cdot\frac{dc_B}{dt} \; ; \; v_L = -\frac{1}{\nu_L}\cdot\frac{dc_L}{dt} \qquad (1)$$

where c_A, c_B, $.c_L$ - concentration; t - time.

The rate of chemical reactions depends on the concentration of the substances entering the reaction, temperature, pressure, catalysts, etc.

The expression of the reaction rate, in general, can be written:

$$v_A = -\frac{1}{\nu_A}\cdot\frac{dc_A}{dt} = k\cdot c_A^{n_A}\cdot c_B^{n_B} \qquad (2)$$

where n_A, n_B represent the partial reaction orders with respect to components A and B and can be equal to the stoichiometric coefficients. The coefficient k, called the rate constant, is independent of concentration, but depends on all other factors that influence the reaction rate. From a numerical point of view (but not in terms of dimensions), the reaction rate constant is equal to the reaction rate when the concentrations of all the substances entering the reaction are equal to unity. The dimensions of the rate constant depend on the expression of the reaction rate and result from the relation:

$$k = -\frac{dc}{dt}\cdot\frac{1}{\prod c_i^n}, (mol/L)^{(1-\sum n_i)} min^{-1} \quad , \qquad (3)$$

The sum of the partial reaction orders (exponents of the concentrations in the velocity equation) represents the reaction order.

The number of molecules that react in an elementary step is called **molecularity**. The order of the reaction is defined in relation to one of the components of the reaction. Unlike molecularity, which refers to the intimate process of the chemical reaction and always has a well-defined physical meaning and is expressed by an integer, the reaction order has an empirical character, it can be whole or fractional, positive or negative, or zero, as evidenced by the data provided by experiment.

From the value of the reaction order it can be deduced, to a certain extent, whether the mechanism of a reaction is simple or complex. In elementary reactions, the partial reaction orders are identical with the respective stoichiometric coefficients, and the total reaction order always has an integer and positive value. In this case, the order of reaction is equal to the molecularity. The change in the concentration of the components of a reaction during the chemical process can be traced by physical or chemical methods, determining the variation over time of the concentration or a property proportional to it.

If the curve c = f(t) is drawn, the reaction rate at a given moment will be tangent to the curve at that point. At the beginning of the reaction the speed has high values, and as the reaction advances the value of the speed decreases towards zero:

$$tg\,\alpha = v = -\frac{dc}{dt} \tag{4}$$

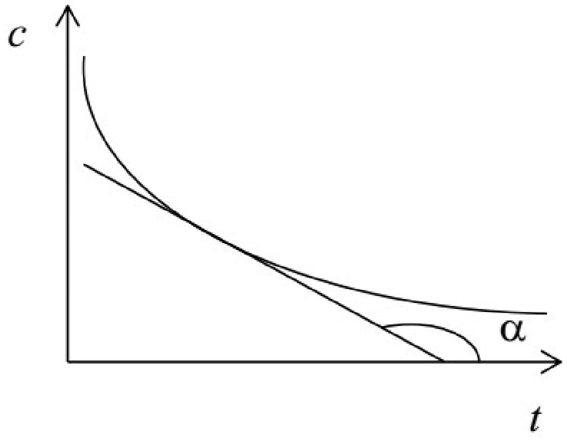

Fig. 1. Determination of the reaction rate by the tangent method

The reaction order can be calculated by:

The integral method, which consists in integrating the reaction rate expression and introducing the experimental data in the reaction rate relations. The expression for which the values of k remain constant decides the order of reaction. The most common integrated reaction rate expressions are:

a) for first order reactions: A → products $$k = \frac{1}{t}\ln\frac{a}{a-x}$$

where a -initial reactant concentration; x-conversion.

b) for second order reactions: A + B → products

For A ≡ B or cA = cB: $$k=\frac{1}{t}[\frac{1}{a-x}-\frac{1}{a}]$$

For different molecules and different concentrations: $$k=\frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}$$

c) for order III reactions with identical molecules or concentrations:

3A → products $$k=\frac{1}{2t}[\frac{1}{(a-x)^2}-\frac{1}{a^2}]$$

More used lately is the graphical variant of this method, which consists in bringing the equation $c = f(t)$ to a linear form $y = a + bt$, in which the rate constant is calculated from the slope of the line (b), and the function y is given by the following expressions for each of the cases presented above:

a) Order I: $\ln(a-x)=\ln a-kt$

b) Order II: $\frac{1}{a-x}=\frac{1}{a}+kt$

and $\ln\frac{a-x}{b-x}=\ln\frac{a}{b}+k(a-b)t$

c) Order III: $\frac{1}{(a-x)^2}=\frac{1}{a^2}+2kt$

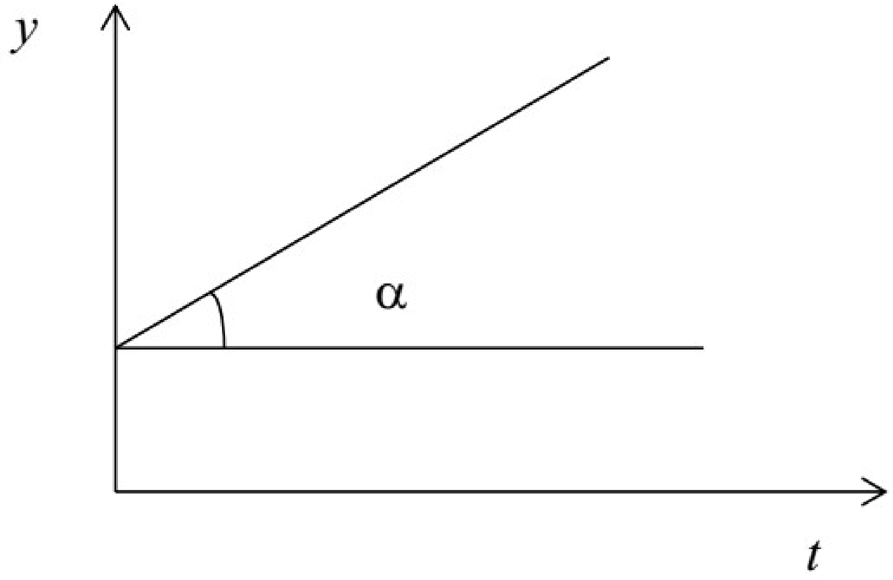

Fig. 2. Determination of the reaction rate by the integral method

The differential method or the initial velocities (or the tangent) method consists in the graphical representation of the logarithmic expression of the reaction rate:

$$\ln\left(-\frac{dc}{dt}\right)=\ln k+n\ln c$$

The slope of the line (n) represents the reaction order, and the initial velocities for samples with different initial concentrations of reactants are determined from the slopes of the tangents to the curves $c = f(t)$ at times $t = 0$.

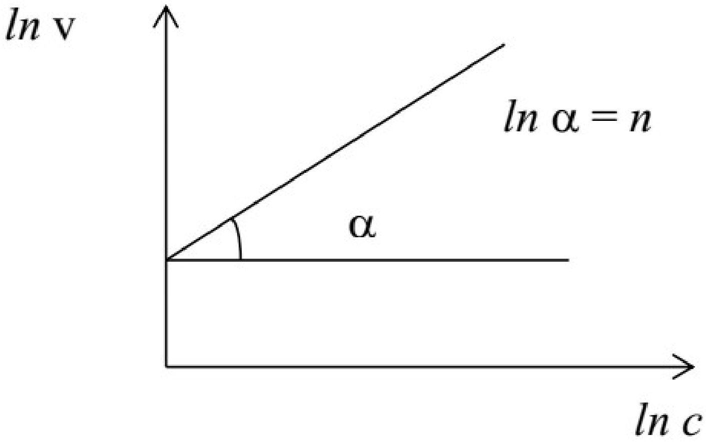

Fig. 3. Determination of the reaction rate by the differential method

The **fractionation time method** allows the calculation of the reaction order when only one species of molecules participates in the chemical process; if several species are involved in the process, then their concentrations must be equal.

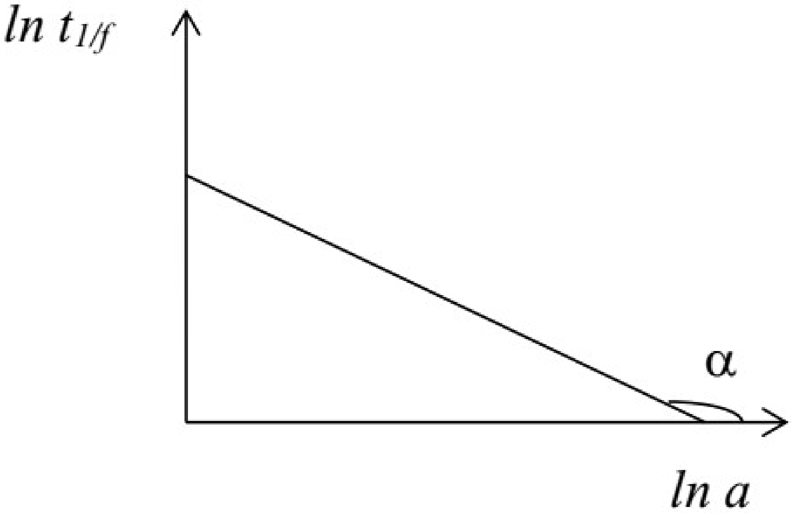

Fig. 4. Determination of the reaction rate by the fractionation time method

By logarithmizing the expression of the fractionation time $t_{1/f}=\frac{const}{a^{n-1}}$, the relation is obtained:

$$\ln t_{1/f} = \ln const - (n-1)\ln a \quad ,$$

which is solved graphically and leads to the value of slope 1-*n*, or analytically, for two different initial concentrations, reaching the expression:

$$n = 1 + \frac{\ln \frac{t_{1/f}}{t'_{1/f}}}{\ln \frac{a'}{a}}$$

First order reactions are recognized immediately, because the fractionation time does not depend on the initial concentration, and for the particular case of the half-life, the rate constant can be calculated from the expression:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \tag{5}$$

The principle of the method

The decomposition of the oxalo-manganic complex ion takes place after the reaction

$Mn(C_2O_4)_3^{3-} \rightarrow Mn^{2+} + 5/2\ C_2O_4^{2-} + CO_2$

and can be monitored with the SP-830 spectrophotometer, as during the reaction the color changes from brown-violet characteristic of Mn^{3+} , to pale pink (practically colorless in dilute solution) characteristic of Mn^{2+}.

Due to the complex that decomposes through an oxidation-reduction reaction, the intensity of the brown color decreases during the process. Instead of concentration, the variation of a property proportional to it will be measured, the extinction, which according to Lambert-Beer's law is

$$E = \varepsilon \cdot c \cdot l = \ln \frac{I_0}{I} \tag{6}$$

where: ε - is the molar extinction coefficient, ($L \cdot mol^{-1} \cdot cm^{-1}$);

l - length of the optical path (solution layer), cm;

c - concentration of the solution to be analyzed, (mol / L).

The determinations are made at the wavelength λ = 450 nm, using the filter 2 and a cuvette with a thickness of 1 cm, and as a control sample the distilled water is used.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- spectrophotometer, 250 mL Erlenmeyer flask, 3 100 mL Berzelius beakers, 4 x 1 cm diameter test tubes or measuring cuvettes, 2 x 5 mL pipettes, one 1 mL pipette, one 25 mL pipette, rubber pump, 0.01 M $KMnO_4$ solution, 0.1 M $MnSO_4$ solution, 0.1 M oxalic acid solution, distilled water.

3.2. PROCEDURE

3.2.1. Connect the spectrophotometer to the mains via the power cord and press the button on the back;

3.2.2. Allow the spectrophotometer to warm up for at least 20 minutes for the electronic components to enter the steady mode;

3.2.3. Adjust the working wavelength with the drum and then the corresponding filter (λ = 450 nm, filter 2);

3.2.4. The apparatus is calibrated by inserting a test tube or cuvette of distilled water into the sample chamber. Close the sample chamber and select the **absorbance** mode by pressing the **[A]** button and then calibrate pressing the **[100% T]** button. The electronic display will show 0.000 in absorbance mode. Insert the sample cuvette and read the absorbance (extinction) value on the electronic display.

3.2.5. After completing the measurements, turn off the spectrophotometer from back button and unplug it.

Sample preparation

To prepare the $Mn(C_2O_4)_3^{3-}$ oxalo-manganese complex, mix 2 mL of 10^{-1} M manganese sulfate solution with 14 mL of 10^{-1} M oxalic acid solution in an Erlenmayer beaker. From this mixture take 2 mL in 3 Berzelius beakers and prepare samples of different concentrations of the complex, adding 2 mL, 2.5 mL and respectively 2.75 mL of distilled water and 1 mL, 0.5 mL, respectively 0.25 mL of 10^{-2} M potassium permanganate so that the total volume is 5 mL (**the volume of water will be added before the permanganate**). The moment of addition of the permanganate solution represents the initial moment, t_0, when the stopwatch for the respective sample starts. Shake, pour into the measuring cuvette and read as soon as possible the extinction corresponding to the value of the moment t indicated by the stopwatch. The initial extinction A_0 is obtained by extrapolating the curve $A = f(t)$ at time $t = 0$. The samples are performed in parallel at a time difference of about one minute between samples, practically the time required to read the first extinction for a sample and pipette the volume of permanganate for the next sample.

Extinction readings are then continued every 3 minutes for half an hour, until an extinction value of less than 0.05, which means that the decomposition of the complex is almost complete (at low extinction values, the reading error of about +/- 0.01 becomes comparable to the extinction of the solution, which can lead to the observation of an oscillation of values). During the measurements, the samples are not held in the hand to avoid heating the solutions, accelerating the reaction and thereby obtaining inadequate results.

4. PROCESSING OF EXPERIMENTAL DATA

4.1. The experimental results are listed in a table of the form:

Nr. crt.	**Absorbance solution 1** **(A_1)** **(1 mL $KMnO_4$)**	**Absorbance solution 2** **(A_2)** **(0,5 mL $KMnO_4$)**	**Absorbance solution 3** **(A_3)** **(0,25 mL $KMnO_4$)**	**ln A_1**	**ln A_2**	**ln A_3**
1						
2						
…						

4.2. The values A = f (t) for the 3 samples, with different complex concentrations, are represented on the same graph and the respective half-lives are calculated. Calculate the reaction order and rate constant;

4.3. Using the same graph, check the reaction order obtained in point 1, using the initial velocity method;

4.4. The average value of the velocity constant is calculated by the graphical variant of the integral method, ie from the graphs ln A = f (t).

5. QUESTIONS

5.1. What are the values of the velocity constant for the 3 complex concentrations? What is the order of this reaction?

5.2. Find five other examples of reactions with this reaction order in the literature.

5.3. Propose the reaction by which the oxalo-manganic complex is formed.