DETERMINATION OF THE RATE CONSTANT AND REACTION ORDER

(Decomposition of manganese oxalate)

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Task 40a

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(Decomposition of manganese oxalate)

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 the decomposition of the oxalate manganese reaction.

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.

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III. Theory

III. 1. Chemical kinetics

Chemical kinetics is a branch of physical chemistry that studies the rate of a chemical reaction. Knowledge of reaction rate allows:

- to define how fast the reactants are consumed while being converted into products of chemical reaction,
- to define in what way we can influence the rate of chemical reaction using a variety of factors such as: temperature, pressure, concentration of reagent and presence of the catalyst,
- to define how fast the state equilibrium of the reaction in the reaction mixture is reached, which is of great practical importance,
- to understand the reaction mechanism – i.e. analysis into the sequence of elementary steps.

To study the rate and mechanism of a chemical reaction it is necessary to:

- define the stoichiometry of the reaction and identify any side reactions,
- analyse the relationship between the concentration of the products and the reaction time.

III. 2. The rate of chemical reaction

The rate of chemical reaction is defined as the change in the concentration of reactant in time. If the considered reagent is the reaction product, the reaction rate can be defined as:

$$v = \frac{dc}{dt} \tag{1}$$

where: c – the product concentration.

If the considered reagent is a reactant, the reaction rate can be defined as:

$$v = -\frac{dc}{dt} \tag{2}$$

where: c – the reactant concentration under consideration.

The sign (–) in equation 2 results from the fact that the reaction rate is always a positive value. During the reaction the reactant concentration decreases, therefore the dc value is negative.

If reagent concentration is expressed in [mole·dm^{-3}], the reaction rate can be expressed in [mole·dm^{-3}·s^{-1}]. If the stoichiometric equation, the stoichiometric parameters of reaction products and reactants are different, changes of concentration of particular reagents in time

are not the same (they are proportional to the value of reagent stoichiometric coefficient). In this case, if we define the reaction rate, it should be pointed out for which reagent the investigation is carried out or according to the thermodynamic considerations in the equation for the reaction rate, the so-called **algebraic stoichiometric coefficients** η_i, which are equal to the absolute value of stoichiometric coefficients, for products they are positive and for reactants are negative, should be taken into account.

$$v = \frac{dc_1}{\eta_1 dt} \tag{3}$$

The reaction rate can be related with the concentration of reacting reactants. The relationship between reaction rate, concentration of reacting substrates and reaction stoichiometry is called **the kinetic rate equation**.

$$v = k \, c_1^n c_2^m \tag{4}$$

where: *n* and *m* are the stoichiometric coefficients of the reaction under consideration.

The coefficient *k* is called **the rate constant for the reaction**. The rate constant for the reaction is the reaction rate if the reagent concentration is equal to one. The unit of the rate constant depends on stoichiometric coefficients of the reaction (after setting *k* value to the rate equation for a particular reaction, the reaction rate should have a unit [mole·dm^{-3}·s^{-1}].

As follows from the rate equation, the reaction rate at a given temperature is not constant, it decreases in time. Therefore from equations 1, 2 and 3 only the reaction rate at a specific time – so-called the **instantaneous reaction rate** can be calculated.

The instantaneous reaction rate can be calculated from the dependence of reactant (or products) concentration in time. The reaction rate can be determined from the tangent slope at a given point of the curve of the dependence of reagent concentration on time. At constant temperature the reaction rate decreases. When the reaction system reaches the equilibrium state, the resultant reaction rate is equal to zero.

The rate equation is of significant importance. On its basis one can predict:

- reaction rate in the reacting mixture of a specific composition,
- concentration of products and reactants at specific time,
- form of the rate equation gives important clues about the reaction mechanism.

The rate equation is found experimentally – not from the stoichiometric equation of reaction.

III. 3. Molecularity of chemical reaction

The molecularity of chemical reaction is a number of molecules participating in elementary reaction. From the kinetic point of view, the reactions can be divided into one and multimolecular. The concept of molecularity is associated with one stage of the reaction and not the whole reaction as a whole.

Unimolecular reaction – a disintegration of a single molecule into fragments or rearrangement of atoms that constitute the molecule. This type of reaction includes thermal dissociation reaction, radioactive decay, izomerization.

Bimolecular reaction – bonding between two molecules.

Clash of more than three molecules, is impossible from a practical point of view, therefore, so far known reactions are trimolecular at most.

III. 4. Reaction order

Chemical reactions can be divided according to their kinetics. The basis of this classification is the nature of the change in concentration in time. Such a division of the reaction is based on the concept of the reaction order. There can be considered:

– partial reaction order with respect to a selected reagent,
– total reaction order.

Partial reaction order with respect to a selected reagent is an exponent, in which there occurs a reactant in the kinetic equation of reaction. **Total reaction order** is the sum of all orders of the particular reagents – the sum of the exponents occurring in the concentrations in the reaction kinetic equation. The reaction order does not have to be the integer value. The stoichiometric equation can give only preliminary information regarding the reaction order. The reaction kinetic equation can be presented also in the integral form. This form of equation is very useful, because on its basis, the concentration of the reagents can be determined at any time of the reaction. The integral form of equation can be obtained combining the reaction rate equation and kinetic equation:

$$v = -\frac{dc}{dt} \text{ and } v = kc_1^n c_2^m \ldots \Rightarrow -\frac{dc}{dt} = kc_1^n c_2^m \ldots \tag{5}$$

For the zero-order reaction:

$$-\frac{dc}{dt} = k \Rightarrow -dc = ktd \implies -\int_{c_0}^{c} dc = \int_{t=0}^{t} ktd \Rightarrow c = c_0 - kt \tag{6}$$

The zero-order reactions are such reactions, whose rate of reaction does not depend on the concentration. They include photochemical, polymerization and isomerization reactions. The concentration of reactant is proportional to the reaction time and rate constant.

For the first-order reaction:

$$-\frac{dc}{dt} = kc \tag{7}$$

$$-\frac{dc}{c} = kdt \Rightarrow -\int_{c_0}^{c} \frac{dc}{c} = \int_{t=0}^{t} kdt \tag{8}$$

$$lnc - lnc_0 = -kt \tag{9}$$

$$lnc = -kt + lnc_0 \tag{10}$$

The equation allows to determine concentration of reactant in the first-order reaction. If the reaction is first-order, according to equation (10), the natural logarithm from the concentration of reactant is a linear function of time $lnc = f(t)$. Knowing the concentration of reactants and products at specific time, using mathematical methods or graphically from the slope of the linear relations, the rate constant of reaction can be determined.
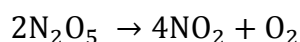
The first-order kinetic equation reaction is:

– decomposition into ethane radicals

$$C_2H_6 \rightarrow 2CH_3^*$$
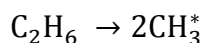
– isomerization of cyclopropane
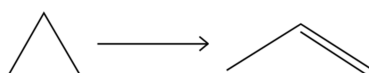
– decomposition of dinitrogen pentoxide propene

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

For the second-order reaction:

$$-\frac{dc}{dt} = kc_1c_2 \tag{11}$$

Assuming that the initial concentrations of reactants are equal $c_1 = c_2 = c$ equation (11) is:
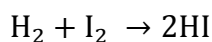
$$-\frac{dc}{dt} = kc^2 \tag{12}$$

$$-\int_{c_0}^{c} \frac{dc}{c^2} = \int_{0}^{t} kdt \tag{13}$$

$$\frac{1}{c} - \frac{1}{c_0} = kt \ \Rightarrow \ \frac{1}{c} = kt + \frac{1}{c_0} \tag{14}$$
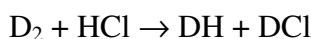
If the initial concentrations are not the same then the equation is more complicated. If it is the second-order reaction then $1/c$ is directly proportional to the reaction time.

The reactions that satisfy the second-order kinetic equation:

– hydrogen iodide synthesis

$$H_2 + I_2 \rightarrow 2HI$$

– deuterium from HCl

$$D_2 + HCl \rightarrow DH + DCl$$

– formation of iodine molecule

$$2I \rightarrow I_2$$

For the third-order reaction:

$$-\frac{dc}{dt} = kc_1 c_2 c_3 \tag{15}$$

Assuming that the initial concentrations of reactants are equal $c_1 = c_2 = c_3 = c$, equation (15) is:

$$-\int_{c_0}^{c} \frac{dc}{c^3} = \int_{0}^{t} kdt \tag{16}$$

$$\frac{1}{2c^2} - \frac{1}{2c_0^2} = kt \;\Rightarrow\; \frac{1}{c^2} = 2kt + \frac{1}{c_0^2} \tag{17}$$

For the *n*-order equation, assuming that the initial concentrations of reagents are the same $c_1 = c_2 = \dots = c_n$:

$$-\frac{dc}{dt} = kc^n \;\Rightarrow\; \frac{1}{(n-1)c^{n-1}} = kt + \frac{1}{(n-1)c_0^{n-1}} \tag{18}$$

III. 5. Determination of the reaction order

The reaction order is determined experimentally. Stoichiometric equation of reaction can give only a clue about the reaction order. Determining the reaction order is equivalent to determining the kinetic equation of reaction. There are many methods allowing to determine the reaction order:

1. From the integral form of the reaction kinetic equation (method of substitution to formula)
2. Ostwald isolation method
3. Method of inital rate- van't Hoff's differential method
4. Integral method
5. Half-life method

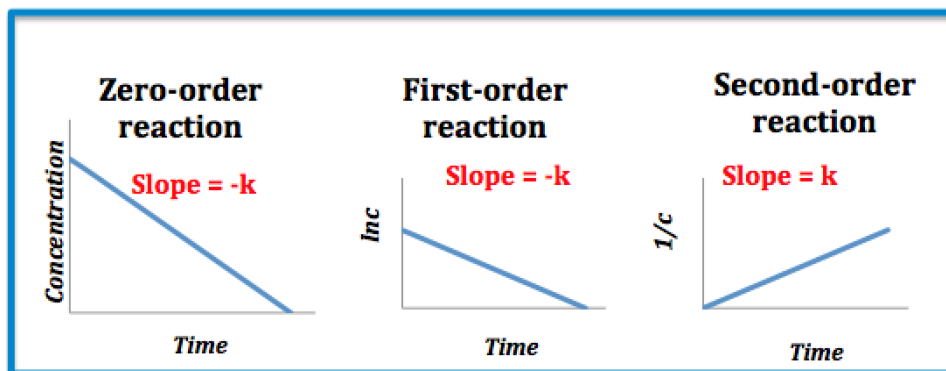## III. 5.1 From the integral form of the reaction kinetic equation

The integral form of the kinetic equation allows to determine, not only concentration of a particular product or a reactant at any time from the beginning of the reaction, but also it is helpful in determination of the reaction order. This method consists in analyzing the concentration of a particular product or reactant in the reaction time. Next, the obtained results are substituted successively in the integral form of the reaction kinetic equation for different reaction orders.

Table 1.

Reaction order	Kinetic equation	Linear dependence	Geometric interpretation
0	$v = -k$	$c = -kt + c_0$	$c = f(t)$
I	$v = -kc$	$lnc = -kt + lnc_0$	$lnc = f(t)$
II	$v = -kc^2$	$\dfrac{1}{c} = kt + \dfrac{1}{c_0}$	$\dfrac{1}{c} = f(t)$
III	$v = -kc^3$	$\dfrac{1}{c^2} = 2kt + \dfrac{1}{c_0^2}$	$\dfrac{1}{c^2} = f(t)$
n	$v = -kc^n$	$\dfrac{1}{(n-1)c^{n-1}} = kt + \dfrac{1}{(n-1)c_0^{n-1}}$	$\dfrac{1}{(n-1)c^{n-1}} = f(t)$

If, for example: the reaction is first-order, the linear dependence lnc is obtained from the reaction time; if the reaction is second-order, the linear dependence of inverse concentration on the reaction time is maintained (**Fig.1**). Linear dependences of reactant concentration change in the reaction time for reactions of different order, assuming that the initial reactants concentrations are equal.

Fig. 1. Schematic graphs illustrating determination of the reaction order from the integral form of the reaction kinetic equation.

III. 5.2 Ostwald isolation method

In the Ostwald isolation method the reaction proceeds with considerable excess of all reactants besides one. If the kinetic equation has a form:

$$v = kc_1^m c_2^n c_3^p \ldots \tag{19}$$

then during the reaction, the reagents concentrations which are in large excess are practically constant. Thus the kinetic equation for this reaction can be written (so-called pseudo-order form):

$$v = k'c_1^m \tag{20}$$

where $k' = kc_2^n c_3^p \ldots$

Thus the reduction of order reaction takes place. It is much easier to define a reaction order for the reduced equation than for its full form. Using for example, the integral form of the reaction kinetic equation a reaction order of specified substance can be determined. There should be repeated all the procedure determining the order of reaction as regards each reactant. The total order of the reaction is the sum of orders of pseudo-order reactions.

## III. 5.3 Method of initial rate - van't Hoff's differential method

This method is often used in conjunction with the isolation method of Ostwald. In this method the rate at the beginning of the reaction for the several different initial concentrations of reactants is measured. If e.g. selected reactant is denoted as A, then with a large excess of the remaining reactants the kinetic equation has the form of equation (20). The initial rate of the reaction is defined by the formula:

$$v_0 = k'c_{A0}^n \tag{21}$$

Taking logarithms of equation (21) gives:

$$log v_0 = log k' + n\, log c_{A0} \tag{22}$$

Dependence (22) is the equation of plot which relates the logarithm of initial reaction rates with the logarithm of initial concentrations of a selected reactant. The slope of this plot defines an order of the reaction (Fig.2).
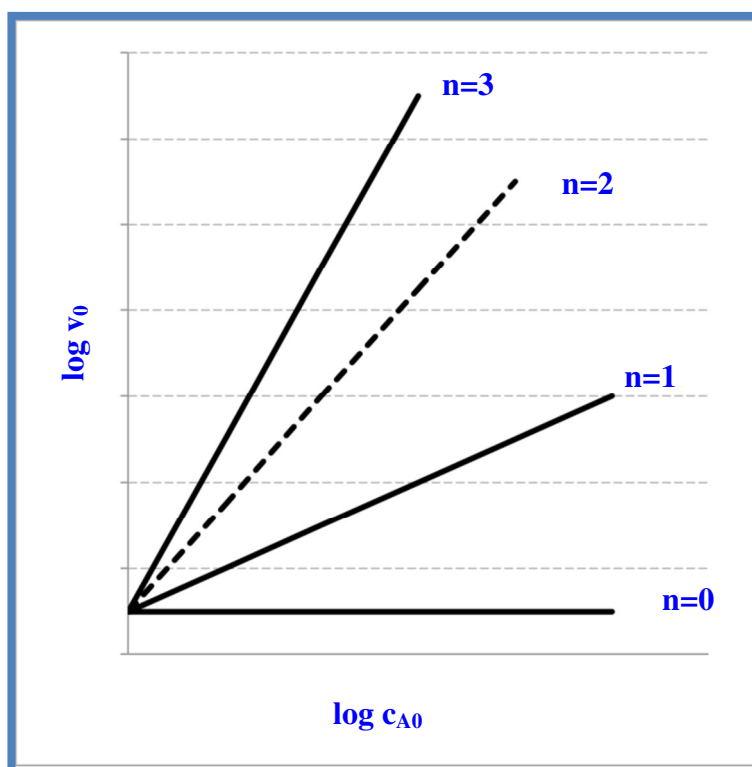
Fig. 2. Determination of the reaction order by the initial rate method based on the linear dependence between $log\, c_{A_0}$ and $log v_0$.

If the measurements are made only for two initial concentrations (however on the basis of this experiment, we can get the result saddled with a big mistake), then n can be expressed by the equation:

$$n = \frac{log \frac{v_1}{v_2}}{log \frac{c_{A01}}{c_{A02}}} \tag{23}$$

Determination of the rate reaction for $t = 0$ is not easy. For this purpose it is necessary to extrapolate the slope of the tangent to the concentration of the reagent in time zero (therefore the other name of this method is van't Hoff differential method).

III. 5.4 Integral Ostwald-Zawidzki method

This method includes measurement of time at which a specified fraction of the reactant is reacted. For this purpose a graph of the dependence progress number of reaction x' on time t [s] is made. The progress number of reaction x' is the ratio of the concentration of unreacted Fe^{2+} ions (x - in our case it is equal to the concentration of the obtained Fe^{3+} ions) to the initial reactant concentration (c_o):

$$x' = \frac{x}{c_0} \tag{24}$$

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 progress number of the reaction and put them into the equation defining the order of the reaction:

$$n = 1 + \frac{log\ (t_1/t_2)}{log(c_{02}/c_{01})} \tag{25}$$

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

III. 5.5 Half-life method

Half-life is the time after which the concentration of the reactants decreases to half the initial value. Half-life for the reaction which involves more than one reactant, can be determined only when the ratio of the concentrations of individual reactants corresponds to their stoichiometric relations. In this case, the half-life is the same for all reactants. To determine the half-life time also the rate reaction equation is useful. If in the integral equations for the reaction order the value c is substituted by the value 0.5 c_o, so depending on the order reaction, the equations that allow to calculate the half-life time are obtained (Table 2).

Table 2. Half-life equations for different order of reactions.

Reaction order	Kinetic equation	Half-life equation
I	$v = -kc$	$\tau = ln2/k$
II	$v = -kc^2$	$\tau = 1/(kc_o)$
III	$v = -kc^3$	$\tau = 3/(2kc_o^2)$

The equations presented in Table 2, show that:

– for the first-order reaction, the half-life of substance is independent of its initial concentration (Fig. 3.). It is dependent only on the rate constant. Therefore, for many first-order reactions, half-life can be given as a characteristic value for this reaction (e.g. decay reaction of radioactive elements),

– the half-life for the second-order reaction depends on the initial concentrations of reactants, so that it is not a characteristic value for this reaction. However, if we prove that the half-life is inversely proportional to the initial concentration, then we have the information that the reaction is the first-order,

– the half-life for the third-order reaction is inversely proportional to the square of the initial concentration.
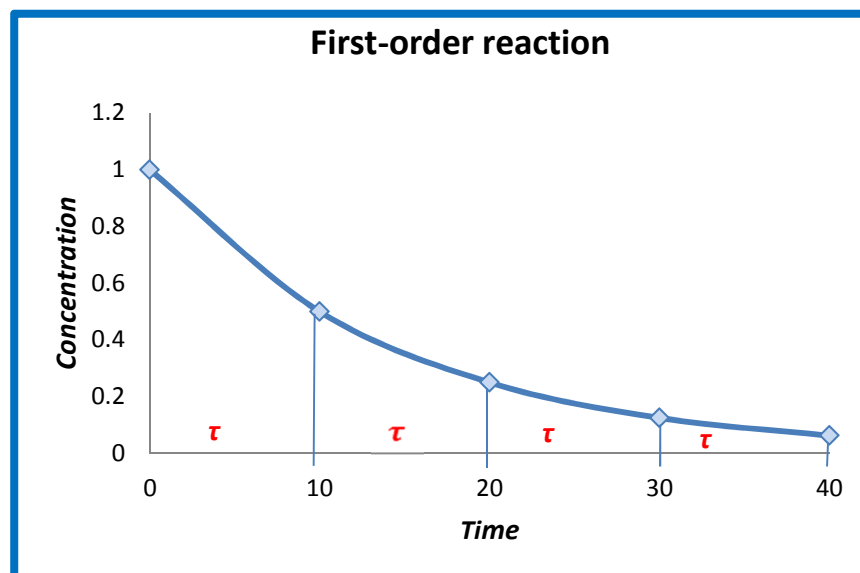
Fig. 3. Schematic graph illustrating the half-life of substance (τ) independent of its initial concentration for the first-order reaction.

IV. Experimental

A. Devices and materials

1. **Device:**
   – Spectrophotometer Cecil 1011,
   – cuvette of the thickness d = 1 cm,
   – glassware.
2. **Materials:**
   – 0.01 M $KMnO_4$ solution,
   – 0.1 M $MnSO_4$ solution,
   – 0.1 M $H_2C_2O_4$ solution.

B. Preparation of the spectrophotometer for measurements

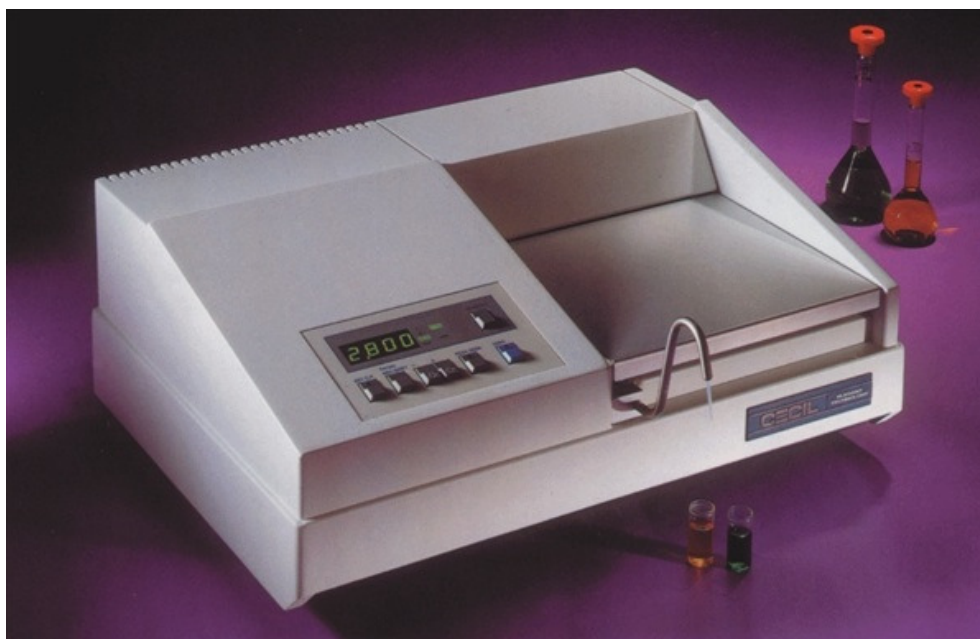**Fig. 4.** Spectrophotometer Cecil 1011 [8].

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 $\lambda = 440$ 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

To prepare the reaction mixture mix 2 cm^3 of 0.1 M MnSO$_4$ with 14 cm^3 of 0.1 M H$_2$C$_2$O$_4$ solution (solution I). Mix the prepared 8 cm^3 of solution with 2 cm^3 of 0.01M KMnO$_4$. Changing of the solution colour is due to manganese oxalate anion complex formation $[Mn(C_2O_4)_3]^{3-}$.

$$4 \, Mn^{2+} + MnO_4^- + 15 \, C_2O_4^{2-} + 8 \, H^+ \Leftrightarrow 5 \, [Mn(C_2O_4)_3]^{3-} + 4 \, H_2O \qquad (26)$$
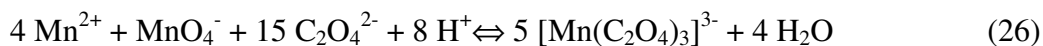
After mixing 2 cm^3 of solution I with 0.01 M KMnO$_4$ (t = 0), pour the obtained solution quickly into a ready cuvette and measure absorbance, initially every minute, next every two minutes. Absorbance measurements should be stopped when its value falls under 0.1. The first measure is made for t = 1min (ie. one minute after the solution (I) was mixed with 0.01 M KMnO$_4$).

Note: During measurements, control 0 (blind sample), using a cuvette (d = 1cm) with distilled water as the reference sample.

Series of measurement is repeated for twice smaller reagents concentration. Therefore mix 8 cm^3 of solution (I), remaining after the first part of measurements, with 1 cm^3 of KMnO$_4$ solution.

D. Results and conclusions

Decomposition of manganese oxalate anion complex proceeds according to the reaction:

$$2 \, [Mn(C_2O_4)_3]^{3-} \rightarrow 2 \, Mn^{2+} + 5C_2O_4^{2-} + 2 \, CO_2 \qquad (27)$$
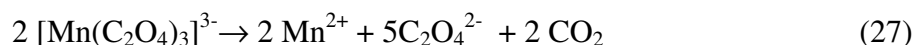
From the stoichiometric equation it could be assumed that decomposition of manganese oxalate is the first order reaction, thus check if the kinetic equation is fulfilled for the first order reaction:

$$ln\frac{c_0}{c} = k_1 c \tag{28}$$

where: c_o – the initial concentration of complex, c – the concentration of complex after time t, t – the reaction time [s].

Kinetics of the decomposition of coloured anion into colourless products can be followed using the spectrophotometric method by measuring extinction in time. Because absorbance A is proportional to the concentration of colour ions in the solution:

$$A = \varepsilon\, c\, d \tag{29}$$

where: ε – the molar absorption coefficient, d – the solution absorbing layer thickness

In equation (28) concentration can be replaced by directly measured value A and the equation takes the form:

$$ln\frac{A_0}{A} = kt \tag{30}$$

where: A_o – the absorbance value for solution for $t = 0$, A – the absorbance value after time t [s].

Equation (30) can be represented in the exponential form:

$$logA = logA_0 - \frac{k}{2.303}t \tag{31}$$

or

$$lnA = lnA_0 - kt \tag{31a}$$

From equations (31) and (31a), the expression for half-time reaction can be found, i.e. time taken for the concentration of a reactant to fall to half its initial value.

$$\tau = \frac{\ln 2}{k} \tag{32}$$

Using equation (30) it can be checked if decomposition of manganese oxalate is the first order reaction as suggested by the stoichiometric equation. For this purpose present a graph of the dependence $logA = f(t)$ (or $lnA = f(t)$ [s]) for all series and using the least squares method (where $x = t[s]$, $y = log\,A$ (or $ln\,A$), look Appendix) define parameters of equation (31). Value k can be calculated from the slope $log\,A = f(t)$ $(ln\,A = f(t))$ for all series, next determine the average value k and reaction half-time τ according to equation (32).

Put the obtained values into **Table 3:**

Table 3.

t [s]	A	log A (ln A)

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.