

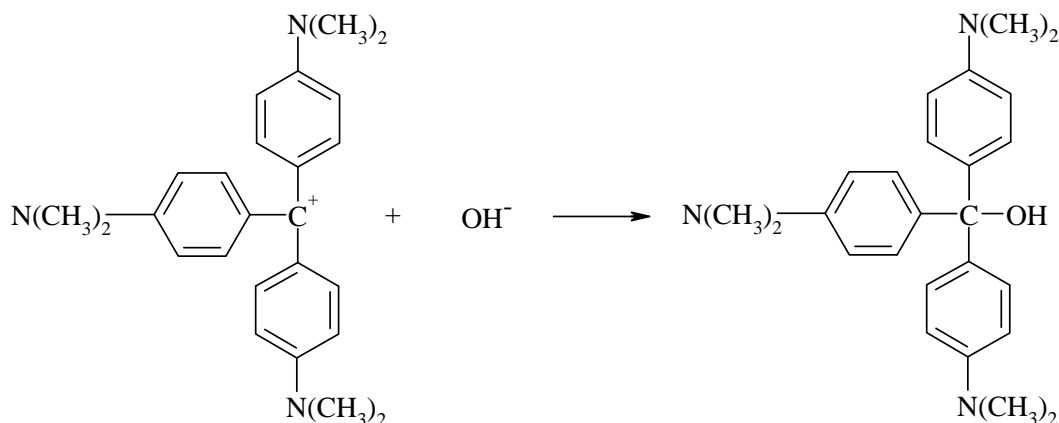
LABORATORY EXERCISE NO. 2

DETERMINATION OF RATE CONSTANT FOR REACTION OF CRYSTAL VIOLET DYE AND HYDROXIDE ION

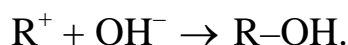
Objective: Determination of rate constant for the reaction of crystal violet and hydroxide ion reaction by colorimetric method.

Theoretical background

In this experimental exercise you will determine the rate constant for a chemical reaction of crystal violet dye and hydroxide ion. This reaction proceeds according to scheme



or in a brief form



Cation R^+ is characterized by intensive color with absorption maxima at 590 nm and molar absorption coefficient is about $1 \cdot 10^5$ L/(mol·cm), while $R-OH$ does not absorb in visible spectra region. So, if reaction proceeds, the disappearance of the solution color intensity is observed. This fact can be registered by colorimeter.

Colorimetry is a technique based on the determination of concentration of colored compounds in solution. This experimental method uses the Beer–Lambert–Bouguer law of light absorption

$$A = \epsilon cl, \tag{1}$$

where A – absorbance, ϵ – molar absorption coefficient, l – distance of the light path. *Colorimeter* is a device used in colorimetry, it measures the absorbance of particular wavelengths of light by a specific solution.

Reaction of crystal violet dye and hydroxide ion has a first order with respect to each reacting substances and overall second order. So, the rate law for this reaction can be written in form

$$v = k \cdot c_{R^+} \cdot c_{OH^-}, \quad (2)$$

where k – rate constant, c_{R^+} and c_{OH^-} – concentrations of colored dye cation and hydroxide ion in solution. If during the experiment the initial concentration of OH^- will be much more than initial concentration of the dye the change in c_{OH^-} at reaction proceeding will be insignificant, therefore, the product $k \cdot c_{OH^-}$ will be constant. Designating this product as k' , we can then simplify equation (2) to form

$$v = k' \cdot c_{R^+}. \quad (3)$$

Equation (3) shows that under conditions of high and constant concentration of the OH^- ion the rate of given reaction is determined only by c_{R^+} , in other words the reaction is characterized by *pseudofirst order*. According to general conception of the first-order reactions the value of k' can be calculated by equation

$$k' = \frac{1}{t} \ln \frac{c_{o,R^+}}{c_{R^+}}, \quad (4)$$

where c_{o,R^+} and c_{R^+} – initial concentration of dye cation and its value at moment of time t . Equation (4) can be written in form

$$\ln \frac{c_{o,R^+}}{c_{R^+}} = k't. \quad (5)$$

According to Beer–Lambert–Bouguer law the concentration of colored cation at moment of time t and its initial concentration are determined by expressions

$$c_{R^+} = A_t / \varepsilon l, \quad c_{o,R^+} = A_o / \varepsilon l, \quad (6)$$

where A_o and A_t – initial solution absorbance and absorbance at time t . Substituting equations (6) to equation (5) one obtains

$$\ln \frac{A_o}{A_t} = k't, \quad (7)$$

and in linearized form

$$\ln A_t = \ln A_o - k't, \quad (8)$$

According to equation (8) the graph of $\ln A_t$ as a function of time will give a straight line (Fig. 1). The plot of $\ln A_t$ as a function of t gives k' as the line slope. Second-order rate constant of the reaction can be calculated as a ratio of k' value and hydroxide ion concentration

$$k = k' / c_{\text{OH}^-}. \quad (9)$$

Experiment and calculations

1. Turn on colorimeter and switch on 590 nm color filter.
2. Prepare working solution containing crystal violet ($c = 1 \cdot 10^{-5}$ mol/L) and NaOH ($c = 5 \cdot 10^{-3}$ mol/L) in 50 mL volumetric flask using burette and stock solutions of crystal violet ($c = 2.5 \cdot 10^{-4}$ mol/L) and NaOH ($c = 0.1$ mol/L). Stir the flask content.
3. Pour prepared solution to colorimeter cuvette and place it into colorimeter.
4. Measure absorbance of the solution during 15 minutes, write absorbance value each minute.
5. Draw the plot of dependence of $\ln A_t$ versus time as a straight line.
6. Calculate the k' value using plot $\ln A_t$ vs t . According to equation (8) the k' value is equal to the slope of the straight line. The slope can be calculated as a ratio of $\Delta \ln A_t$ and corresponding Δt value

$$k' = -slope = \frac{\Delta \ln A}{\Delta t}. \quad (10)$$

For this calculation the right-angled triangle with the graph as hypotenuse must be drawn (Fig. 1), the values of $\Delta \ln A_t$ and Δt are equal the lengths of the cathetuses of the triangle. In case, when all experimental points lie on the straight line, for the calculation of the k' value by equation (10) one can use the coordinates of the first and the final points of dependence.

7. Calculate the k value using equation (9).

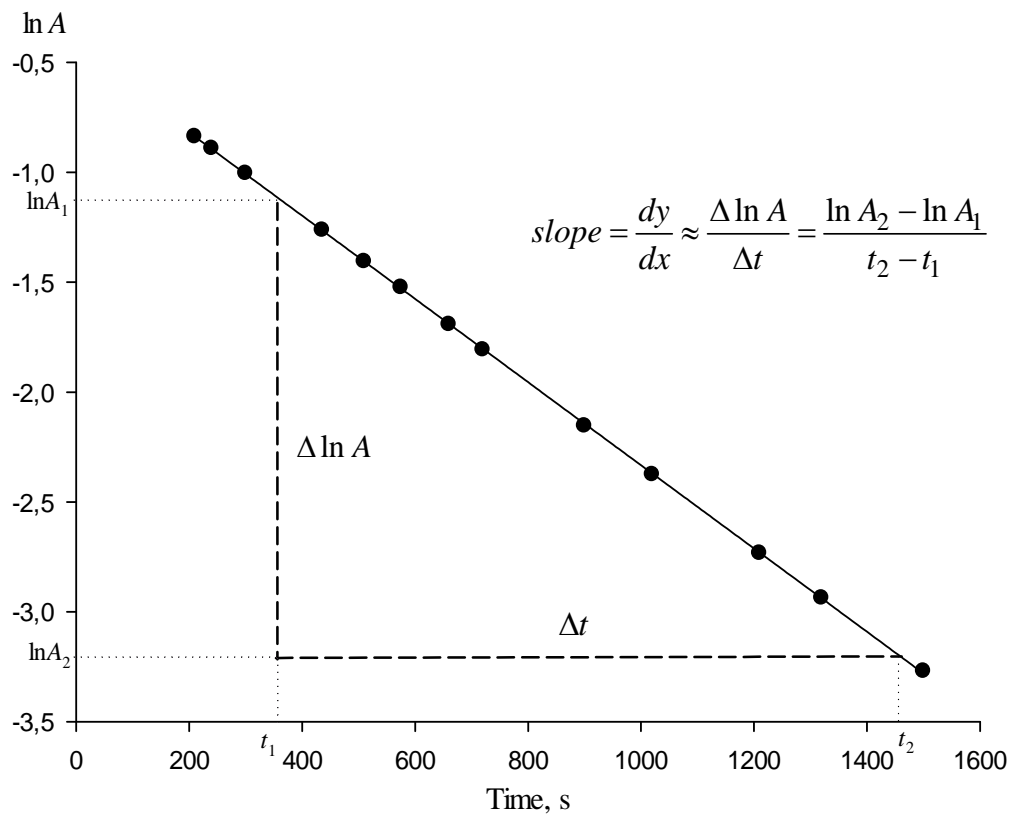


Fig. 1. Plot of logarithm of absorbance versus time