

Reaction of malachite green with hydroxide ions: Influence of the concentration

Aims of the experiment

- To decolourise malachite green with sodium hydroxide solution.
- To follow and record the course of the reaction.
- To observe the rate of the reaction in dependency on the NaOH concentration.
- To determine the rate constant k_{eff} of the pseudo first-order reaction.
- To determine the rate constant k_2 of the second-order reaction.

Principles

The rate of a chemical reaction depends on the concentration of the substances involved. This changes during the course of the reaction, as the educt concentrations decrease and the product concentrations increase. How the reaction rate depends on these concentrations is described by the rate law. For the reaction



The rate law is as follows:

$$v = k \cdot c(A) \cdot c(B)$$

The reaction order provides information on the way in which the rate is dependent on the concentration. In the reaction quoted here, the rate over the course of the reaction depends on both reactants. Therefore, this is a case of a second-order reaction. The order is calculated formally from the exponents of the reactants involved, however, it must be determined experimentally.

In a first-order reaction, the rate only depends on the concentration of one reactant:

$$v = k \cdot c(A)$$

First-order reactions can therefore be easily investigated. If in a first-order reaction the logarithm of the concentration is plotted against time, this produces a straight line. In this case, the slope of the straight line corresponds to the rate constant k .

Reactions can be transformed into other (pseudo) orders by suitable reaction conditions. A second-order reaction can proceed as a pseudo first-order reaction. This becomes possible when one of the educts is present in such a large excess that its concentration remains practically constant during the course of the reaction.

The discolouration of malachite green (MG) by hydroxide ions, according to the reaction equation (see Fig. 2), is a second-order reaction. Malachite green is a triphenylmethane dye. It consists of a planar ring system which is responsible for the colour. Hydroxide ions attack the central C atom and destroy the colour. Here we are dealing with a bimolecular reaction in which a hydroxide molecule and a malachite green molecule meet.

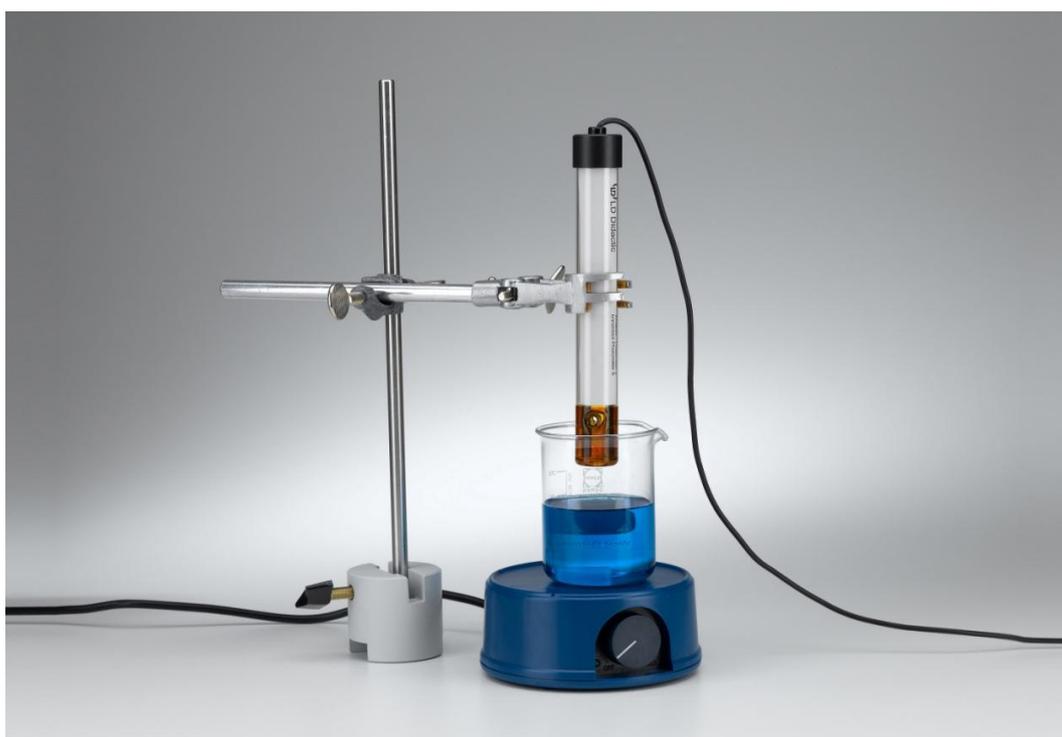


Fig. 1: Set-up of the experiment.

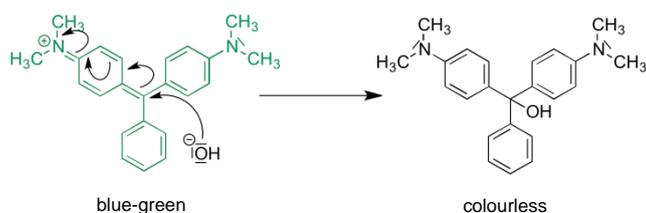


Fig. 2: Reaction of malachite green with hydroxide ions.

If the reaction conditions are chosen such that one component - here the sodium hydroxide solution - is present in a very great excess, this reaction can also proceed as a pseudo first-order reaction. The concentration of the sodium hydroxide solution can then be calculated into the rate constant k .

From

$$v = k_2 \cdot c(\text{MG}) \cdot c(\text{NaOH})$$

we obtain

$$v = k_{\text{eff}} \cdot c(\text{MG}), \text{ with } k_{\text{eff}} = k_2 \cdot c(\text{NaOH}).$$

The effective rate constant k_{eff} depends on the concentration of sodium hydroxide solution, because this is used in the calculation.

An understanding of this is to be provided in this experiment by using various concentrations of sodium hydroxide solution to decolourise the malachite green. The effective rate constants k_{eff} calculated from this can then be plotted against the concentration of hydroxide ions in another diagram. This produces a straight line whose slope represents the second-order rate constant.

Risk assessment

Malachite green is a hazardous substance. This primarily relates to the solid substance and its dust. It should therefore be weighed out very carefully.

When preparing the sodium hydroxide solution, a large amount of heat can be generated. Therefore, stir the solution vigorously.

Malachite green	
 	<p>Hazard statements</p> <p>H360d Suspected of damaging fertility or the unborn child.</p> <p>H318 Causes serious eye damage.</p> <p>Precautionary statements</p> <p>P280 Wear protective gloves.</p> <p>P281 Use personal protective equipment as required.</p> <p>P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.</p> <p>P308+P313 If exposed or concerned: Get medical advice/attention.</p> <p>Signal word: Hazard</p>

Sodium hydroxide pellets

 Signal word: Hazard	<p>Hazard statements</p> <p>H314 Causes severe skin burns and eye damage.</p> <p>Precautionary statements</p> <p>P280 Wear protective gloves/protective clothing/eye protection/face protection.</p> <p>P301+P330+P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.</p> <p>P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.</p>
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Ethanol

 Signal word: Hazard	<p>Hazard statements</p> <p>H225 Highly flammable liquid and vapour.</p> <p>Precautionary statements</p> <p>P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking.</p>
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Equipment and chemicals

1	Immersion photometer S	524 069
1	Pocket-CASSY 2 Bluetooth	524 018
1	CASSY Lab 2	524 220
1	Magnetic stirrer, mini	607 105
4	Stirring magnet, 25 mm x 6 mm diam.	666 851
4	Beaker, DURAN, 250 mL, squat	664 103
1	Measuring cylinder 500 mL	665 756
1	Measuring cylinder 250 mL	665 755
1	Measuring cylinder 50 mL	665 753
1	Analytical balance 83: 0.0001 g	667 7988
1	Spoon-ended spatula, nickel, 120 mm	604 5651
1	Volumetric flask, Boro 3.3, 100 mL	665 793
1	Graduated pipette, 10 mL	665 997
1	Pipetting ball (Peleus ball)	666 003
1	Laboratory bottle, 500 mL, GL 45	602 347
1	Saddle base	300 11
1	Stand rod, 25 cm, 12 mm diam.	300 41
1	Double, crossed nosshhead, 0...16 mm	666 543
1	Universal clamp, 0...80 mm	666 555
1	Wash bottle, PE, 500 mL	661 243
1	Malachite green, 25 g	673 1670
1	Ethanol, denatured, 1 L	671 9720
1	Sodium hydroxide, 100 g	673 6800
1	Water, pure, 1L	675 3400
Additionally required:		
1	PC with Windows XP, Vista, 7 or 8	
Also necessary for wireless measurement:		
1	Bluetooth dongle	524 0031
1	Battery for Pocket-CASSY 2 Bluetooth	524 019

Set-up and preparation of the experiment

Preparing the solutions

5 molar sodium hydroxide solution: For 100 mL of solution, weigh 20 g of sodium hydroxide into a beaker and add about 50 mL of distilled water. Stir well on the magnetic stirrer until the sodium hydroxide pellets have completely dissolved. Then transfer into a volumetric flask and fill to 100 mL with distilled water.

Caution: When preparing the sodium hydroxide solution, a large amount of heat can be generated. Therefore, stir the solution vigorously.

0.001% malachite green solution (c. 20 μ molar, 1 mg/L): For 500 mL of solution, weigh out 5 mg of malachite green and place it into the laboratory bottle. Malachite green does not dissolve well in water. Therefore 10 % ethanol must be added. For this, first place 50 mL of ethanol into the laboratory bottle. Then add 450 mL of distilled water. Shake well until the malachite green has completely dissolved.

Note: Due to its low water solubility, splashes and residues of malachite green can best be removed with ethanol.

Construction of the experiment

For the photometric measurement, set up an apparatus consisting of a magnetic stirrer, stand material and an immersion photometer (see Fig. 1). Prepare three beakers with a stirring magnet. Connect the Peleus ball to the graduated pipette. Using this, add the sodium hydroxide solution to the reaction mixture.

Note: Sometimes the graduated pipette does not fit into the volumetric flask. Then simply pour some sodium hydroxide solution back into the beaker and pipette out of this.

Connect the immersion photometer S to the Pocket-CASSY. Using a USB cable, connect this to a computer running the CASSY Lab software.

Note: Alternatively, the Pocket-CASSY can also be connected to the computer via Bluetooth. The rechargeable battery for the Pocket-CASSY and a Bluetooth dongle are required additionally for this.

Measuring with CASSY

1. Load CASSY Lab settings.

2. Calibrating the immersion photometer. For this, prepare a beaker with water and zero the measured absorbance value by pressing the button $\rightarrow 0 \leftarrow$. After this, the absorbance of the solvent (without dye) will be subtracted from all measured values.

3. In order to convert the absorbance of the solution into a concentration value of malachite green, the absorbance coefficient ϵ of malachite green is required. As this depends on the solvent and the wavelength, it should be determined before the experiment.

a. Place 150 mL of malachite green solution into a beaker. Switch on the magnetic stirrer. The solution must be stirred vigorously.

b. Immerse the immersion photometer S into the solution and fix it in place (see Fig. 1). A constant absorbance should be measured (c. 0.8).

Note: Ensure that no air bubbles gather in the immersion photometer S. This will considerably falsify the measured values. If necessary, remove them by shaking.

4. Record the measured value in the CASSY Lab parameter "Absorbance with 20 μ M malachite green". From this, CASSY Lab automatically calculates the absorbance coefficient ϵ and

the concentration c of malachite green at every stage during the measurement.

Note: The absorbance coefficient ϵ determined in this way is rather imprecise, as the method of production of the solution is flawed. A more precise determination of the absorbance coefficient should be done, it is therefore recommended to create a series of dilutions and measure several concentrations of malachite green. This is performed in the experiment C3.3.2.1 (Beer-Lambert law) on copper tetramine, by way of example.

Performing the experiment

1. The 150 mL of malachite green solution which was used for the determination of the absorbance coefficient can now also be used for the experiment.

2. Various quantities of sodium hydroxide solution are used for discolouration of the malachite green solution (see Tab. 1).

Tab. 1: Concentrations of NaOH used in the reaction and volumes of a 5 molar sodium hydroxide solution required for this.

c(NaOH) in the reaction	V(NaOH, 5mol/L)
0.20 mol/L	6.0 mL
0.10 mol/L	3.0 mL
0.05 mol/L	1.5 mL

Note: The increased volume due to the sodium hydroxide solution can be disregarded.

3. The sodium hydroxide solution is added at the same time as the start of the measurements.

4. First measure out 6 mL (to produce 0.2 mol/L) of the prepared sodium hydroxide solution using a graduated pipette.

5. Pipette the sodium hydroxide solution quickly into the malachite solution. When about half of the quantity is pipetted into the solution, start the measurement by pressing the button on the Pocket-CASSY.

Note: The measurement can also be started with the F9 key or by clicking on the  icon.

6. Follow the measurement. Continue measuring until the solution is colourless and the immersion photometer indicates an absorbance of $E = 0$ (c. 30 sec).

7. Repeat the experiment with a smaller quantity of sodium hydroxide solution (lower concentration) (see Tab. 1). Use one of the prepared beakers for each measurement. Clean the immersion photometer with water from the wash bottle between the measurements.

Note: The measurement series can be named directly in CASSY Lab. To do this, enter the concentrations used in the field next to the series.

Observation

With the addition of sodium hydroxide solution, the initially green-blue malachite solution quickly decolourises. This can be distinctly seen also in the CASSY Lab diagram. The lower the concentration of sodium hydroxide solution, the slower the decolouration takes place.

Evaluation

The evaluation is performed in CASSY Lab. For this, several diagrams have been prepared in the CASSY example.

The absorbance of the solution measured by the immersion photometer is converted into a malachite green concentration

by CASSY Lab using the measured absorbance coefficient. The diagram with the measurements of the three NaOH concentrations is shown in Figure 3. It can be seen in the diagram that by halving the concentration of sodium hydroxide solution, this leads to the reaction rate being halved.

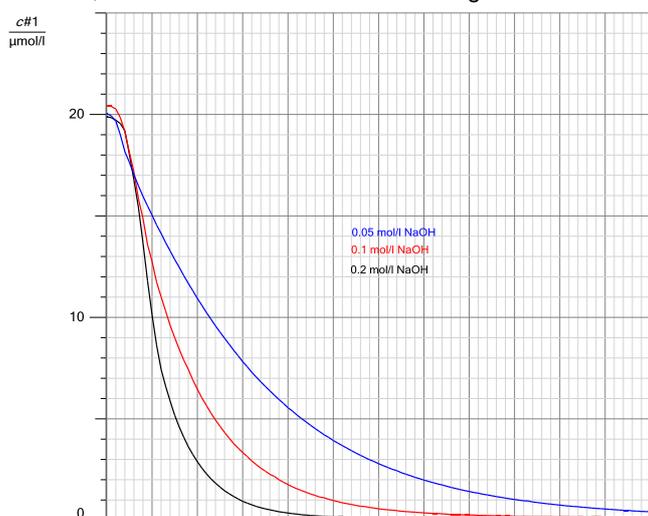


Fig. 3: Chronological course of the malachite green concentration with various NaOH concentrations (stated in each case).

Determining the effective rate constants k_{eff} of the pseudo first-order reaction

As the decolouration of malachite green is a case of a pseudo first-order reaction, the course of the reaction can be linearised by plotting the logarithm of the concentration against time. This is realised in the diagram "Linearised diagram" in CASSY Lab (see Fig. 4).

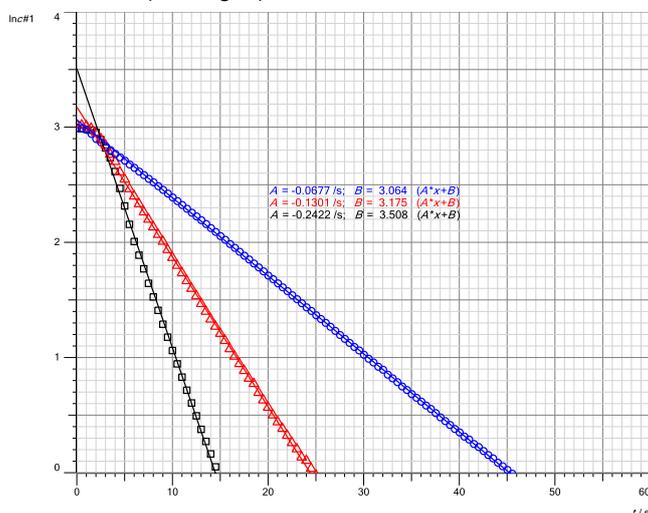


Fig. 4: Linearised diagram of the course of the reaction for determination of the effective rate constant.

The slope of the straight line is determined by placing a line of best fit ($f(x)$ Fit Function \rightarrow Best-fit Straight Line). The slope of this straight line is shown in the status line and can be "dragged" into the diagram by Drag & Drop. The effective rate constant for each concentration of sodium hydroxide solution can be determined from the slope of the straight line ("A") based on the following formula.

$$\ln c(\text{MG}) = -k \cdot t + \ln c_0(\text{MG})$$

The measured values from an example measurement are shown in Table 2.

Tab. 2: The effective rate constant k_{eff} is determined by reversing the sign of the slope of the straight line A in the linearised diagram.

c(NaOH)	Slope A	k_{eff}
0.20 mol/L	- 0.242	0.242 s ⁻¹
0.10 mol/L	- 0.130	0.130 s ⁻¹
0.05 mol/L	- 0.067	0.068 s ⁻¹

Determining the rate constants of the second-order reaction

Now the real rate constant of the reaction (in this case second order) can be determined from the effective rate constants. According to the formula:

$$k_{\text{eff}} = k_2 \cdot c(\text{NaOH})$$

the rate constant can be calculated. However, the graphical evaluation is more precise. For this, the measured rate constant k_{eff} is plotted against the NaOH concentration (see Fig. 5).

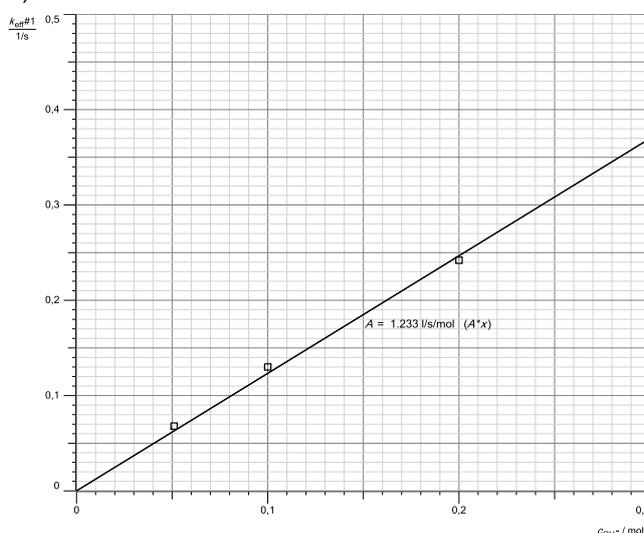


Fig. 5: Determination of the second-order rate constants. For this, the effective rate constant is plotted against the concentration of sodium hydroxide solution.

A diagram "Second-order rate constant" has been prepared in CASSY Lab for this. Here the table must be filled out manually. To do this, type in the NaOH concentrations used in the first column (c_{OH^-}). Enter the effective rate constants in the second column (k_{eff}). These can be entered into the table from the evaluation of the corresponding diagram (slope A) using Drag & Drop. Then reverse the sign manually.

Now draw a line of origin through the diagram to determine the second-order rate constant ($f(x)$ Fit Function \rightarrow Straight Line through Origin). A line of origin begins at the zero point. The reaction rate would also be zero without the addition of sodium hydroxide solution. The slope of this straight line A provides the rate constant k_2 in the second order integrated rate law for the reaction of malachite green and sodium hydroxide solution.

$$v = k_2 \cdot c(\text{MG}) \cdot c(\text{NaOH})$$

Result

The effective rate constants of the pseudo first-order reaction

When the change in concentration of malachite green is logarithmized and plotted against time, a straight line is produced. Therefore, this is in fact a case of a pseudo first-order reaction. The effective rate constants are summarised in Table 2.

The values show that by halving the concentration of sodium hydroxide solution, the effective rate constant is roughly halved as a result.

The rate constant k_2 of the second-order reaction

By plotting the effective rate constant against the concentration of sodium hydroxide solution, the rate constant of the second-order reaction can be determined.

The slope of this straight line A provides the rate constant k_2 in the second order integrated rate law for the reaction of malachite green and sodium hydroxide solution.

$$v = k_2 \cdot c(\text{MG}) \cdot c(\text{NaOH}) = k_{\text{eff}} \cdot c(\text{MG})$$

The slope and therefore the rate constant k_2 is $A = 1.233 \text{ L}/(\text{mol}\cdot\text{s})$.

Cleaning and disposal

Dispose of used solutions in the container for liquid organic waste (water-soluble). If required, first allow the solution to evaporate somewhat.

Note: The colourless solution also contains malachite green.

The prepared sodium hydroxide solution can be used for further experiments. If it is to be disposed of, neutralise the sodium hydroxide solution if necessary and pour it down the drain with plenty of water.