

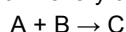
## Determination of the order of reaction of malachite green with hydroxide ions

### Aims of the experiment

- To follow the course of the reaction of malachite green with hydroxide ions
- To measure and record the course of the reaction
- To determine the half-life of the reaction
- To determine the order of the reaction graphically
- To calculate the rate constant of the reaction

### Principles

A chemical reaction proceeds at a certain rate. The reaction rate is stated as the decline in the concentrations of educts or the increase in the concentrations of the products. The rate changes over the course of the reaction, as it mostly depends on the concentration of the reaction partners. In order to state the reaction rate, information about the reaction concerned is needed in every case. For the reaction



the rate  $v$  is defined as follows:

$$v = -d[A]/dt = -d[B]/dt = +d[C]/dt.$$

The concentrations of A and B decrease and are therefore given a negative sign. The concentration of C increases. The rate with regard to C is therefore positive. It can be seen here that the rate of a reaction is always given with reference to one of the substances involved.

Although the reaction rate  $v$  can be easily measured, it is not really meaningful, as it depends on the concentrations of the components involved. The reaction rate is estab-

lished in dependence upon the concentration of the reactants with the help of the rate equation. The proportionality factor is the so-called rate constant  $k$ . The way in which the rate and the concentration are associated in a reaction is expressed through the reaction order. The order of a reaction is the sum of the exponents of the concentrations in the rate equation. Reactions are often of zero, first or second order. However, there are also reaction orders which are not whole numbers.

The rate equation, the reaction order and the rate constant must be determined experimentally. This is to be carried out in this experiment. For this purpose, the change in the concentration of a reactant over the time will be recorded. The concentration dependency of the reaction rate can be determined from these values. With this information, the reaction order and the rate equation will be constructed.

In order to follow a reaction, the concentration of at least one reactant at each stage of the reaction is measured. Colour reactions have proved to be successful for this. A reaction in which a participant changes colour can be followed precisely to the second using a photometer. There-

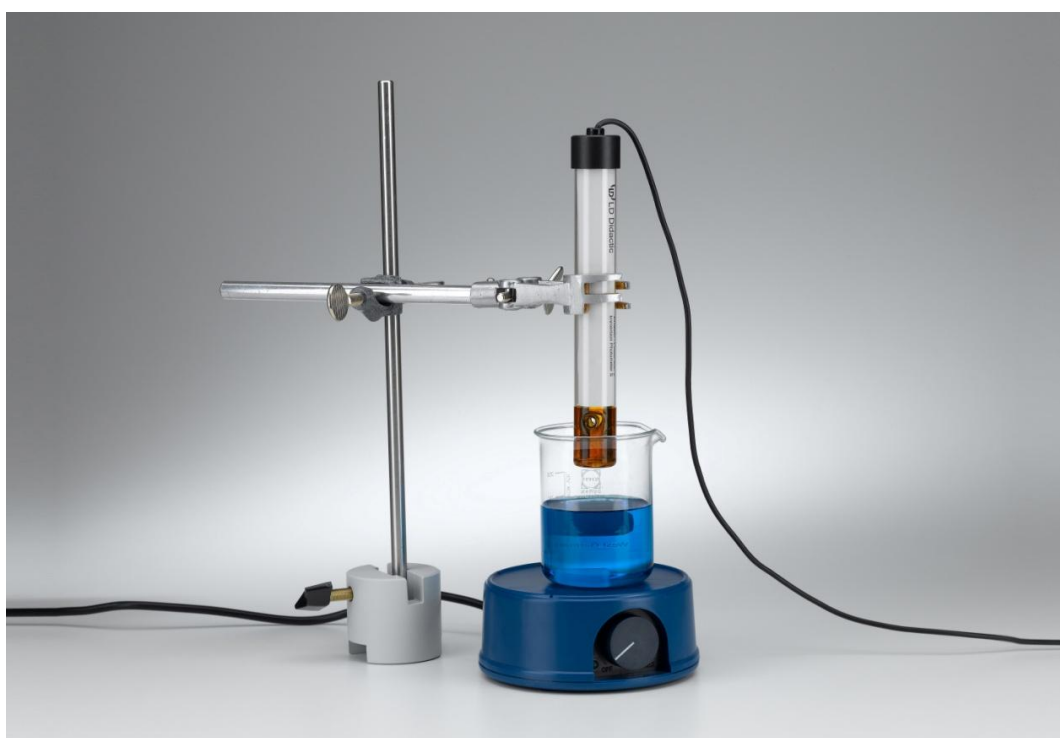


Fig. 1: Set-up of the experiment.

fore, the reaction of malachite green with sodium hydroxide solution will be investigated in this experiment (see Fig. 2).

Malachite green is a triphenylmethane dye, and is therefore related to crystal violet. Both dyes consist of a planar ring system which is responsible for the colour. Hydroxide ions then attack the central C atom. Hence, the planarity is destroyed and the substance appears colourless.

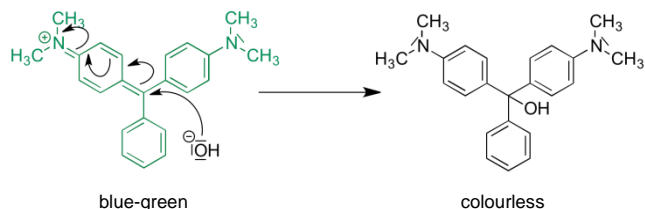


Fig. 2: Reaction of malachite green with hydroxide ions.

In this experiment, the reaction of malachite green with sodium hydroxide solution is followed using an immersion photometer. The reaction course measured in this way is used for further evaluations. Initially, the half-life of the reaction can be easily determined. This serves as a first estimation of the rate constant  $k$ . The order of the reaction is determined using various plots of the reaction course against time. The rate constant  $k$  can also be determined here. Then both values are compared.

### 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><b>Hazard statements</b></p> <p>H360d Suspected of damaging fertility or the unborn child.</p> <p>H318 Causes serious eye damage.</p> <p><b>Precautionary statements</b></p> <p>P280 Wear protective gloves/protective clothing/eye protection/face protection.</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><b>Signal word:</b> Hazard</p>	

Sodium hydroxide pellets	
	<p><b>Hazard statements</b></p> <p>H314 Causes severe skin burns and eye damage.</p> <p><b>Precautionary statements</b></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>
<p><b>Signal word:</b> Hazard</p>	
Ethanol	
	<p><b>Hazard statements</b></p> <p>H225 Highly flammable liquid and vapour.</p> <p><b>Precautionary statements</b></p> <p>P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking.</p>
<p><b>Signal word:</b> Hazard</p>	

### 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
1 Stirring magnet, 25 mm x 6 mm diam.....	666 851
3 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, 220:0.0001 g.....	667 7990
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 boss head, 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  $\mu\text{molar}$ , 1 mg/L):** For 500 mL of solution, weigh out 5 mg of malachite green and place it into the laboratory bottle. Malachite green is not very soluble 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 the beaker 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. Start 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  $\epsilon$  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  $\mu\text{M}$  malachite green". From this, CASSY Lab automatically calculates the absorbance coefficient

$\epsilon$  and the concentration  $c$  of malachite green at every stage during the measurement.

**Note:** The absorbance coefficient  $\epsilon$  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. The sodium hydroxide solution is added at the same time as the start of the measurements.

3. Measure out 6 mL (to produce 0.2 mol/l) of the prepared sodium hydroxide solution using a graduated pipette.

4. 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.

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

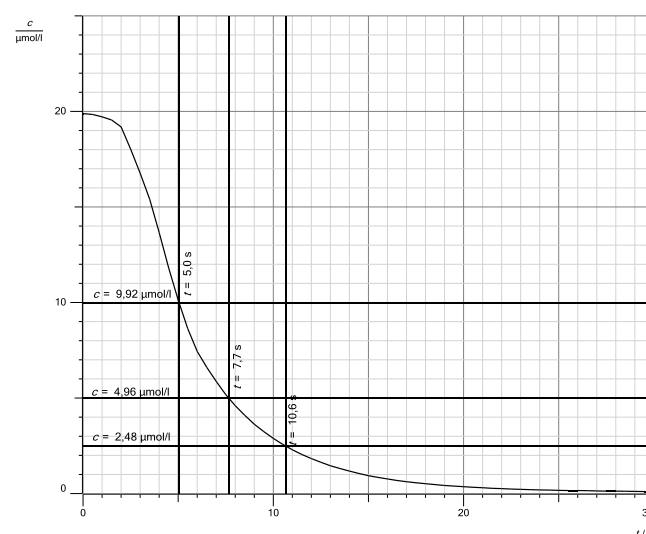
## Observation

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.

## 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 concentration by CASSY Lab using the measured absorbance coefficient. This diagram is illustrated in Figure 3.



**Fig. 3:** Chronological course of the malachite green concentration. Each vertical line marks a half-life.

### Determination of the half-life

The half-life of the reaction can be determined using this diagram. For this, calculate half the concentration and then half the concentration again (here:  $19.88 \mu\text{mol/l} / 2 = 9.97 \mu\text{mol/l}$  and  $9.97 \mu\text{mol/l} / 2 = 4.99 \mu\text{mol/l}$ ). With horizontal lines (⊕ Set Marker → — Horizontal Line) mark the concentration, and with vertical lines (⊕ Set Marker → | Vertical Line) read off the time. The start of the reaction is not easy to determine because addition of the sodium hydroxide solution and mixing also take time. It is therefore better to determine the half-life from the second half-life. The difference in time between one half and one quarter of the concentration gives the half-life (here: 2.9 s). Further half-lives can also be plotted here.

The half-life remains constant for this reaction. This is only the case with first-order reactions. The half-life of the reaction is c. 2.9 s. During this time, half of the malachite green molecules have reacted. The rate constant  $k$  can be determined directly from the half-life in first order reactions. The following applies:

$$t_{1/2} = \frac{1}{k} \cdot \ln 2 = \frac{0,693}{k}$$

In this way,  $k$  can be calculated in this reaction as:

$$k = \frac{0,693}{t_{1/2}} = \frac{0,693}{2,9 \text{ s}} = 0,24 \text{ s}^{-1}$$

### Determination of the reaction order

The reaction order is also determined graphically. The course of the reaction is presented in such a way that it forms a straight line. A first-order reaction can be linearised by plotting the natural logarithm of  $c$  ( $\ln c$ ) against the time. A diagram "Test for first order" has been prepared in CASSY Lab for this (see Fig. 4).

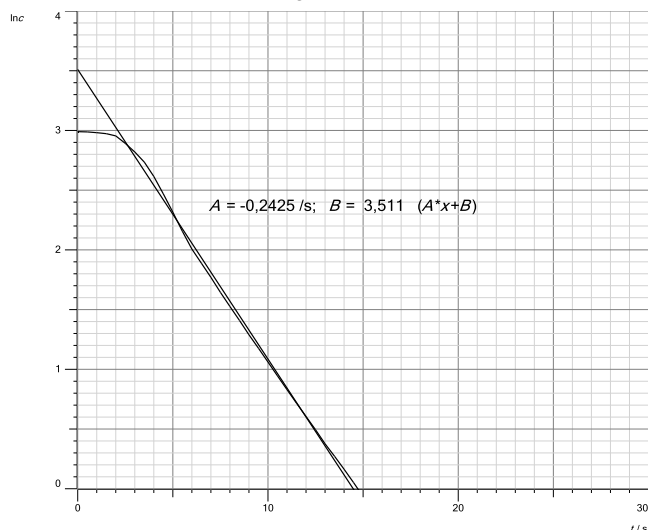


Fig. 4: Test for first order. Plot of the logarithm of  $c$  ( $\ln c$ ) against time.

A second-order reaction can be linearized by plotting the reciprocal of the concentration ( $1/c$ ) against time ( $t$ ). The diagram "Test for second order" has been prepared in CASSY Lab for this (see Fig. 5). In this way, the order can be determined at a glance.

The reaction of malachite green (MG) and sodium hydroxide solution follows first-order kinetics. Only a linear course is shown here (see Fig. 4). The slope of the straight line is determined by placing a line of best fit (f(x) Fit Function → Best-fit Straight Line). The rate constant can be deter-

mined from the slope of this straight line using the following formula.

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

The slope is:  $A = -0,242$ . The effective rate constant is therefore  $k_{\text{MG}} = 0,24 \text{ s}^{-1}$ .

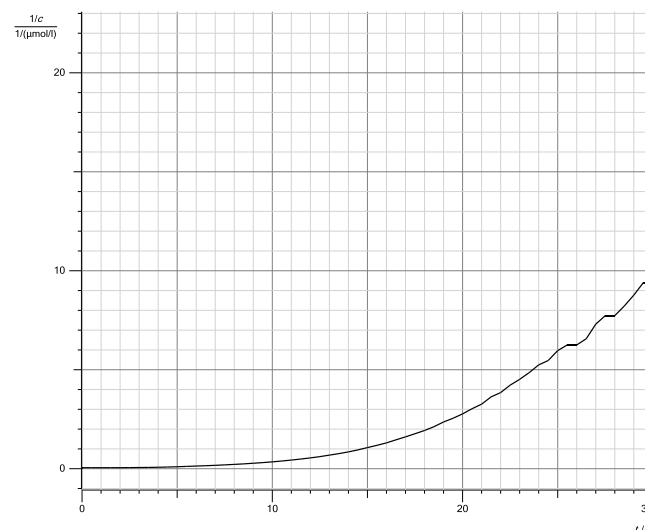


Fig. 5: Test for second order. Plot of the reciprocal of concentration ( $1/c$ ) against time.

The initial concentration of malachite green  $c_0$  is the point of intersection with the Y axis. This is shown distinctly too high. The reason is the slow pipetting of sodium hydroxide solution at the beginning of the measurement.

## Result

### Results from analysis of the half-life

On the addition of sodium hydroxide solution to the malachite green solution, the latter decolourises quickly. This can easily be seen in the diagram "Absorbance" in CASSY Lab. In the diagram "Concentration", the concentration of malachite green in the solution falls analogously very quickly.

### Reaction order

In this case, we are dealing with a reaction of the first order. The reaction rate is dependent on the concentration of a reaction partner. This is shown by two evaluations:

1. The half-lives are always of equal length.
2. The plot of  $\ln c$  against time is linear.

However, the reaction follows a pseudo first-order rate equation. The measured data show that the reaction depends on the concentration of only one of the reaction partners. The concentration of hydroxide ions is very much greater than the malachite green concentration (factor c. 10,000, 0.2 M to 20  $\mu\text{M}$ ). It stays virtually the same during the course of the reaction and can be regarded as constant. This is the way that a pseudo first-order reaction originates.

### Rate constant $k$

The rate constant  $k$  is calculated in two ways. Calculation by means of the half-life and calculation by means of the slope of the straight lines both produce a rate constant of

$$k = 2,4 \text{ s}^{-1}$$

This is the rate constant for the pseudo first-order reaction. If the concentration of sodium hydroxide solution were to be varied, different rate constants would be measured each time. The rate constant of the pseudo-first order reaction

measured here contains the concentration of sodium hydroxide solution as a constant.

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

Included in the rate constant is the sodium hydroxide solution concentration, which stays virtually the same during the course of the reaction.

A determination of the rate constant  $k$  which does not depend on the sodium hydroxide solution concentration is performed in experiment C4.1.3.1.

### 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.