The automated blue bottle experiment: a reversible redox reaction

Aims of the experiment

- To learn about organic redox reactions and the redox indicator methylene blue
- To perform the blue bottle experiment in a new, automated version
- To set up and use a two-point control system
- To perform photometry using an immersion photometer
- To use carbohydrates such as glucose as a reducing agent

Principles

The blue bottle experiment is a favourite demonstration experiment in practical lectures. In the classic version, the experimenter shakes a bottle filled with a clear liquid which then turns blue. After a while, the liquid becomes colourless, but then turns blue again through shaking.

The experiment is based on the redox indicator, methylene blue. Methylene blue is blue in its oxidised form, and in its reduced form, so-called leucomethylene blue, is colourless (see Fig. 2). The colour change is a reversible process. Methylene blue is reduced by reducing agents to leucomethylene blue. The reverse reaction occurs with oxidising agents: Leucomethylene blue is oxidised and becomes coloured once again.

In the blue bottle experiment, the reducing sugar glucose acts as the reducing agent. It reduces methylene blue to leucomethylene blue. By shaking, oxygen diffuses through the solution and re-oxidises the leucomethylene blue to methylene blue. This is then reduced again by the glucose. The reaction terminates when there is no more oxygen available in the air or the glucose reducing agent has been depleted.

This experiment is a modification of the classic blue bottle experiment. Instead of shaking, the air is pumped through the reaction mixture. This is done automatically as soon as the solution becomes colourless. Air is pumped through until the solution becomes deep blue again. The pump then switches off automatically. The solution slowly loses its colour and the process then begins anew.

Fig. 1: Set-up of the experiment.

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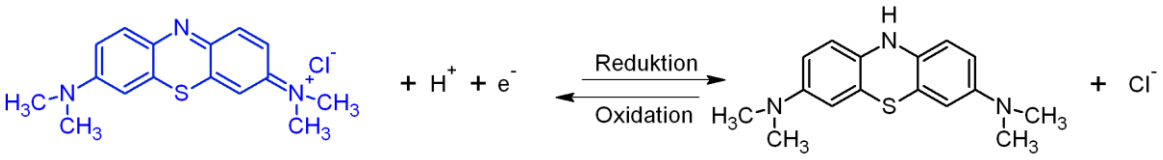

Methylene blue (blue) **Leukomethylene blue (colourless)**

Fig. 2: Reaction equation of the reversible reaction of methylene blue (blue) to leucomethylene blue (colourless).

In this automated version of the blue bottle experiment, a so-called "two-point control system" is used. Here, two states are defined in which the system automatically performs a change. State 1 is the colourless liquid, and when this occurs the pump is switched on to pump air into the solution. State 2 is the distinctly coloured solution. As soon as this state is entered, the pump ceases to operate.

The colour of the solution, and thus the point at which each of the two states is reached, is measured with an immersion photometer. It measures the light transmittance T of the solution. Thus the intensity I_0 of the incident radiation at a defined wavelength (here 612 nm) is compared with the intensity I of the light leaving the obstruction (the solution) according to the following formula:

$$T = \frac{I}{I_0}$$

The blue bottle solution still transmits light even in the completely coloured state. For this reason, point 1 of the two-point control system is set to about 35%. The solution in its colourless state is also not completely clear, therefore point 2 is set to 85%.

Risk assessment

Sodium hydroxide causes severe skin burns and eye damage.

Sodium hydroxide pellets

Signal word: Hazard

Hazard statements

H314 Causes severe skin burns and eye damage.

H290 May be corrosive to metals.

Precautionary statements

P280 Wear protective gloves/protective clothing/eye protection/face protection.

P301 + P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

P309 + P310 IF exposed or you feel unwell:: Immediately call a POISON CENTER or doctor/physician.

P305 + P351 + P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

Equipment and chemicals

1	Sensor-CASSY 2	524 013
1	CASSY Lab 2	524 220
1	Immersion photometer S	524 069
1	Panel frame C50, two-level, for CPS	666 425
1	Woulff's bottle with manometer, CPS	666 438
1	Screw cap, GL 45, mB	667 3095
1	Silicone gasket, GL 45/26, set of 10	667 3107
1	Aeration pump, variable, CPS	666 482
1	Connecting leads19 A, 25 cm, pair	501 44
1	Electronic balance 200 g: 0.01 g	667 7977
2	Watch glass dish, 125 mm diam.	664 157
2	Spoon-ended spatula, SS, 180 mm	666 966
1	Laboratory bottle, 500 mL	602 347
1	Pipetting ball (Peleus ball)	666 003
1	Graduated pipette, 5 mL	665 996
1	Measuring cylinder, 500 mL	665 756
1	PVC tubing 7 mm diam., 1 m	604 501
1	Hose clamp 8...12 mm	604 460
1	Methylene blue solution, 100 mL	673 2920
1	Sodium hydroxide, pellets, 100 g	673 6800
1	D(+) Glucose, 100 g	672 1100
1	Water, pure, 1l	675 3400

also required:
1 PC with Windows XP/Vista/7/8

Set-up and preparation of the experiment

Preparing the solutions

1. Dissolve 3 g of sodium hydroxide pellets in 300 mL of water in the laboratory bottle by shaking.
2. Add 4 mL of methylene blue solution to the solution.
3. Add 20 g of glucose and shake until completely dissolved.

Construction of the apparatus

1. Set up the CPS apparatus as shown in Fig. 1.
2. Remove the screw cap with the gasket off the Woulff's bottle and insert the immersion photometer S into the opening instead of the manometer.

Note: The immersion photometer can be easily moved if the screw cap is only screwed on loosely. When it is screwed up tight, it is fixed in this position.

3. Insert the Woulff's bottle in the CPS holder so that the variable pump and the long tube are on one side (left).
4. Connect the variable pump to the long glass tube in the Woulff's bottle using the PVC tubing. Fix the tube on the pump using a hose clamp.
5. Connect the immersion photometer to input A1 of the Sensor-CASSY.
6. Connect the variable pump to the power supply of the Sensor-CASSY using the connecting leads. Switch the pump control to "External" control. Provide both units with power.

Note: The pump power can be adjusted manually using the small knob in the centre of the power supply on the Sensor-CASSY.

7. Connect the Sensor-CASSY to the PC using a USB cable.

CASSY Lab settings

Load CASSY Lab settings.

or

1. Set the transmission on the immersion photometer to 612 nm.

2. Enter the following formula into the voltage source and activate "Switch on automatic recording":

TA1 > T2 or (TA1 > T1 and S).

3. Define the parameters T_1 and T_2. T_1 is the lower and T_2 the upper transmission limit. The following applies for both parameters:

- Name: Transmission 1 or Transmission 2
- Symbol: *T_1* or *T_2*
- Units: %
- From 0 to 100
- Decimals: 1
- Value *T1*: 35%, Value *T2*: 90%
- Type: Constant (no table column)

Note: The values for T1 and T2 must possibly be adjusted to the prevailing conditions. Particularly T2 should be adjusted downwards during the course of the experiment as the solution will become cloudy through secondary reactions.

4. Set the following measurement conditions:

- Recording: automatic
- Measurement time: leave empty
- Interval: 1 s

Performing the experiment

1. Remove the Woulff's bottle from the holder and fill it with the solution through the large opening.

2. Immerse the immersion photometer into the solution so that it is just clear of the base of the bottle (see Fig. 1).

3. Clip the Woulff's bottle back into its holder and fix it in place with the tensioning springs.

4. Wait until the solution becomes colourless. When the solution is completely colourless, calibrate the immersion photometer by clicking on the 100% button.

5. Switch on the variable aeration pump.

6. Start the measurement in CASSY Lab 2, and therefore the experiment.

Observation

The colourless sodium hydroxide solution is coloured deep blue after adding the methylene blue solution. After adding the glucose, the solution slowly becomes colourless. Every movement of the solution causes a return of the blue colour, which however quickly disappears again.

After starting the measurement, air is blown into the initially colourless solution. As soon as the reaction solution is coloured deep blue, the pump switches off automatically. The solution then becomes colourless again. This process can be repeated as often as desired.

In time, the solution in its colourless state becomes cloudy. It therefore takes an increasingly longer time until 90% transmission is reached. This is probably because the CO_2 contained in the air reacts with the basic sodium hydroxide solution to form a precipitate. To allow the experiment to run longer, it is therefore recommended to then lower the transmission to 85%.

If the solution is left to stand for a long time (e.g. overnight), it becomes yellow. This is due to decomposition products of glucose.

Evaluation

As soon as the experiment has been started, it will run on for as long as desired. A typical curve is shown in Fig. 3.

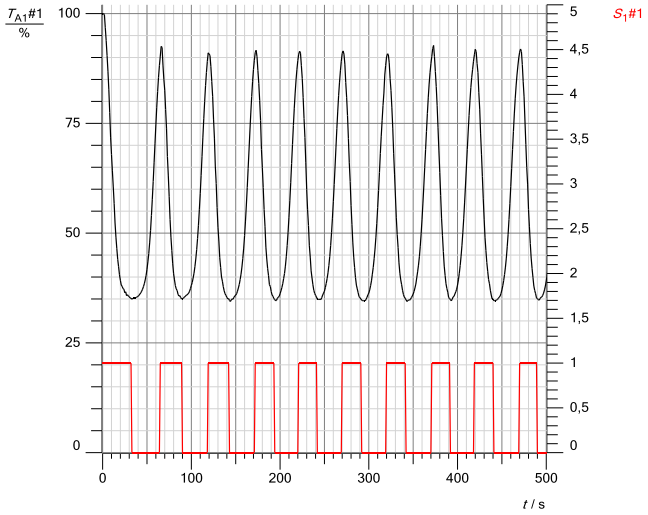

Fig. 4: The blue bottle experiment in CASSY Lab. Black: transmission measured with the immersion photometer, red: switching state of the power source (1: pump off, 0: pump off).

At the start of the measurement, a transmission of 100% is achieved (black line in Fig. 4). The pump is switched on at this value (red line in Fig. 4) and air is pumped into the solution. Because of this, the solution becomes darker with time. When the switching point of 35% is reached, then the pump switches off. The glucose in the solution then reduces the methylene blue dye and the solution becomes clear. At a transmission of 90%, the pump is switched on again. This can run on for several hours.

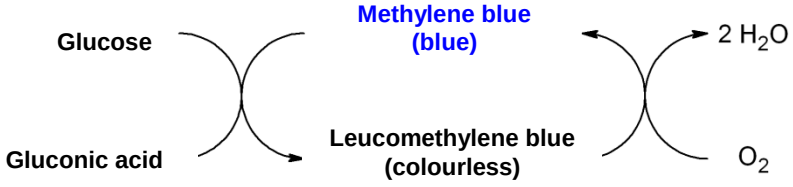

Fig. 3: Overall reaction in the blue bottle experiment. Glucose reduces methylene blue to leucomethylene blue and is thereby oxidised to gluconic acid. Leucomethylene blue is oxidised again to methylene blue by oxygen.

Results

In this experiment, the automated blue bottle experiment is constructed and presented. This makes use of the reversible process of reduction and oxidation of methylene blue. Methylene blue is colourless in its reduced state (leucomethylene blue) and deep blue in its oxidised state. In a basic solution with glucose, methylene blue becomes colourless because of the reducing properties of glucose. This is itself oxidised to gluconic acid (see Fig. 3)

This decolourisation is measured with the immersion photometer. When it is complete, the pump is switched on again automatically, which blows air through the solution. The oxygen contained in the air oxidises the methylene blue, which then achieves its deep blue colour again (see Fig. 3). This is registered by the immersion photometer, following which the pump is switched off again under the control of CASSY. This process can continue repeatedly until the glucose in the solution is depleted.

Disposal

The solutions can be disposed of in the laboratory drain. Rinse away with a large quantity of water.