A34   Beer-Lambert law – Decomposition of the manganese oxalate ion

Task:

1. Determine the wavelength of maximal absorbance λ_{max} of a hydrated $Cu(NH_3)_4{}^{2+}$ complex in the wavelength region of 400 to 800 nm. Afterwards, quantify the molar decadic exctinction coefficient ε at λ_{max} by a concentration series.
2. Track the absorbance A(t) during the decomposition of the manganese oxalate complex and determine the rate constant k in s^{-1}.

Basics:

Beer-Lambert law:

Irradiation with monochromatic light at a given intensity I_0 of an absorbing solution leads to a differential intensity loss dI within a path length dx at the corresponding intensity I. Using k as proportionality factor one has

$$dI = -k\,I\,dx. \tag{1}$$

Integration in the limits x = 0 and x = d gives

$$I = I_0 e^{-kd}. \tag{2}$$

I: light intensity at location d (unit?)
I_0: light intensity at location x = 0
d: path length of the irradiated layer

Beer found that for diluted solutions the proportionality factor k is also proportional to the concentration c of the absorbing solute, i.e.

$$k = \alpha \cdot c. \tag{3}$$

α: molar absorption or extinction coefficient

From (2) and (3) it follows

$$ln\left(\frac{I}{I_0}\right) = -\alpha c d. \tag{4}$$

In this experiment, the absorbance A will be recorded which is defined as

$$A = log\left(\frac{I_0}{I}\right). \tag{5}$$

As

$$log\left(\frac{I_0}{I}\right) = 0.43ln\left(\frac{I_0}{I}\right) \qquad (6)$$

it follows using equation (5)

$$A = 0.43\alpha cd \qquad (7)$$

and finally

$$\varepsilon = 0.43\alpha. \qquad (8)$$

ε: molar decadic extinction coefficient

$$A = log\left(\frac{I_0}{I}\right) = \varepsilon cd \qquad (9)$$

The absorbance is sometimes confused with absorption with is defined by 1-T where T is the transmission

$$T = \frac{I}{I_0} \qquad (10)$$

Furthermore, absorbance and extinction are not identical. Extinction considers the overall attenuation of light, which is caused by absorption, scattering and reflection. Absorbance is attenuation of light by absorption only.

Decomposition of manganese oxalate ions:
The decomposition of manganese oxalate ions according to the equation

$$Mn(C_2O_4)_3^{3-} \rightarrow Mn^{2+} + \frac{5}{2}(C_2O_4)^{2-} + CO_2 \qquad (11)$$
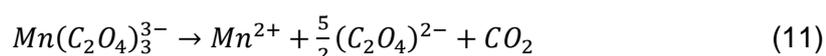
can be considered as a 1. order reaction with the differential rate equation

$$\frac{dc}{dt} = -kc. \qquad (12)$$

Integration in the limits to $t_0 = 0$ and t gives

$$c = c_0 e^{-kt} \qquad (13)$$

k: rate constant
c: concentration of $Mn(C_2O_4)_3^{3-}$ at time t
c_0: initial concentration of the complex (t = 0)

The time-dependent change of the concentration c can be followed by the time-dependent change of the absorbance A(t).
Using

$$A(t) = \varepsilon c d \tag{9}$$

and equation (13) it follows

$$\frac{c}{c_0} = \frac{A(t)}{A_0} = e^{-kt} \tag{14}$$

and hence

$$ln\left(\frac{A(t)}{A_0}\right) = -kt. \tag{15}$$

Experimental procedure:
Measurements will be performed with the spectral photometer "GENESYS 20". The device needs 20 minutes warm-up time prior to the experiments. At all measurements, the absorbance has to be determined.
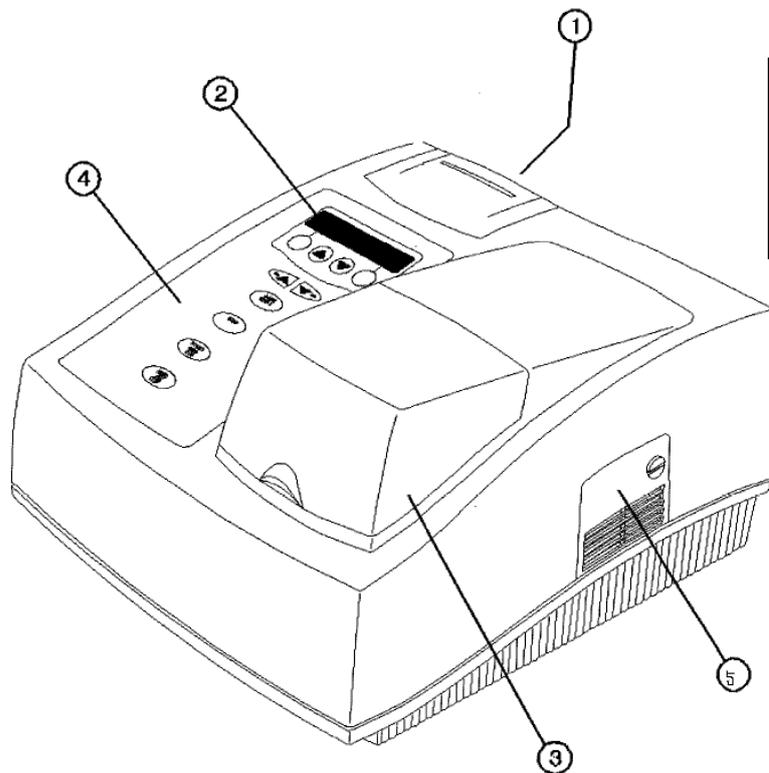
1) On/off
2) LCD-display
3) Sample opening
4) Keyboard
5) Lamp

Spectral photometer
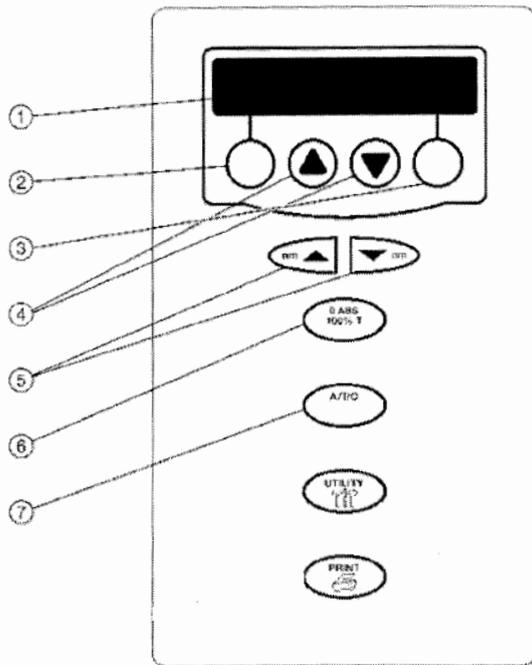
1) Display
2) 1. key: Function depends on screen, usually exit or clear
3) 2. key: usually enter, accept or continue
4) Up/Down
5) Wavelength setting
6) 0 ABS/100%T
7) A/T/C: Choice between measurements of absorbance, transmission and concentration

Keyboard

Clean the cuvettes prior to each measurement. Use only deionized water for cleaning plastic cuvettes, never acetone or ethanol.

ad task 1:
Pipette 0.5, 1, 2, 4, 6 and 8 ml of a 0.03 m $CuSO_4$ stock solution in the corresponding 25 ml volumetric flasks. Add 5 ml NH_4OH solution to each flask and fill up with deionized water. The NH_4OH solution has the right concentration to quantitatively form the desired complex.
Determination of λ_{max}:
In order to correct the spectrum of the Cu-complex from influences of the cuvette, the solvent and the spectrometer, record a background spectrum first. For this purpose, fill a cuvette with deionized water and place it in the cuvette holder inside the spectrometer. Then, adjust the absorbance at a wavelength of 656 nm to 0 using the key "0 ABS". Finally, start the measurement at 400 nm in steps of 20 nm. After recording all values up to 800 nm replace the content of deionized water in the cuvette with that of the highest concentration of the $Cu(NH_3)_4^{2+}$ complex. Again, the wavelength will be varied in steps of 20 nm between 400 and 800 nm and the absorbance will be read off. In order to obtain the spectrum of the Cu complex, the background has to be subtracted. The maximum is located between the two highest values of the absorbance. To determine λ_{max} more exactly measure in this range in steps of 2 nm. Do not forget to subtract the background absorbance again.
Measurement of the absorbance of the concentration series at λ_{max}: Set the photometer at the determined wavelength λ_{max} and measure at this wavelength the absorbance of the different concentrated solutions.

ad task 2:
Prior to the measurement, the photometer must be set to 0 absorbance at a wavelength of 405 nm with a cuvette filled with deionized water. The preparation of the manganese oxalate solution is to be done by mixing the following solutions:

17.5 ml   0.25 m oxalic acid
2.5 ml   0.2 m $MnSO_4$ solution
5 ml   0.02 m $KMnO_4$ solution

Pour the manganese solution into a cuvette and place it inside the spectrometer. Read off the absorbance A(t) every 30 s for a period of 15 minutes. Repeat the measurement with a freshly prepared solution.

Data analysis:
ad task 1:
1. Plot the absorbance of the solution with the highest concentration of the Cu complexes versus wavelength after subtracting the background and identify λ_{max}.
2. Plot the measured absorbance A at λ_{max} versus concentration c of the $Cu(NH_3)_4^{2+}$ complex and determine of the molar decadic extinction coefficient in $cm^2 \cdot mol^{-1}$ from the slope of the best-fit line. Path length d = 1 cm.
3. Estimate the errors of the concentration c (estimated maximum error). The error of the apparatus is 0.003 for absorbance between 0 and 0.3 and 1 % of the measured value for higher absorbance. Determine graphically the error of the identified extinction coefficient ε.

ad task 2:
1. Plot $\ln(A(t)/A_0)$ versus time and determine from the slope of the best-fit line the rate constant k in s^{-1} of the decomposition of the manganese oxalate complex.
2. Determine graphically the error of k and discuss the error.

ad tasks 1 and 2:
Compare the obtained results with literature data.

What one should know:
Absorbance, extinction, absorption and transmission, Beer-Lambert law, prerequisite for validity of Beer-Lambert's law; rate laws for reactions of 0., 1. and 2. order, half-time, order and molecularity of reaction.

Mandatory supplementary question:
Which possible interactions do exist between electromagnetic radiation and molecules (excitation of degrees of freedom)?