Equilibrium constant determination: planning, execution and analysis of a spectrophotometric experiment

Literature background: P.W. Atkins: *Physical Chemistry*.
Type of experiment: Performed in pairs.
Goal of the experiment: To demonstrate a possible experiment for the determination of an equilibrium constant. To teach students some key ideas for planning precise experiments.

1 Introduction

In chemistry it is often needed to know the exact concentration distribution of different compounds in equilibrium systems. Some examples are the acid–base indicators and different physiological processes, where the concentration of the different species should be precisely known under precisely defined experimental conditions.

Concentrations and concentration distribution curves can be easily calculated if the equilibrium constant under the given conditions and the chemical composition of the reaction system is known (i.e., all the possibly forming compounds are known). Th equilibrium constants can only be found in the literature very seldom, and the precision of the reported data are also questionable in some cases. A reason behind this is that some constants were determined using methods that are not any more accepted to be precise enough by the scientific community. In some cases a given equilibrium constant has been determined by independent researchers, and notable deviation can be seen between the values. In some cases it might be important to reproduce fully reliable data for the calibration of a new instrument.

This is one of the most suitable methods for checking a newly purchased instrument. Of course, accurate equilibrium constants can only be determined through well-defined, accurately performed and analysed measurements.

1.1 Theoretical background

Take a general equilibrium reaction:

$$\nu_1 X_1 + \nu_2 X_2 + \ldots + \nu_n X_n \rightleftharpoons 0\,,$$

where *n* is the total number of the different compounds participating in the reaction, X_i is the i-th compound, and ν_i is the stoichiometric number of the i-th compound, which is negative for reactants and positive for products. The thermodynamic equilibrium constant of the above reaction (K_a) is the product of the activities (a_i) of the reactants and products, all on the power of their respective stoichiometric number:

$$K_a = \prod_{i=1}^{n} a_i^{\nu_i}\,.$$

The activities are seldom known in real systems. In practice, the equilibrium constant is often calculated with the help of concentrations (c_i) and the unit concentration (c^0):

$$K_c = \prod_{i=1}^{n} \left(\frac{c_i}{c^0}\right)^{\nu_i}\,.$$

The activity is the product of the concentration and the activity coefficient (γ):

$$a_i = \gamma_i \cdot \frac{c_i}{c^0}\,,\ \text{hence}\ K_a = \prod_{i=1}^{n} \left(\gamma_i \cdot \frac{c_i}{c^0}\right)^{\nu_i} = K_c \cdot \prod_{i=1}^{n} \gamma_i^{\nu_i}\,.$$

The value of K_a in a given reaction, based on theoretical considerations, is constant at a given temperature and pressure. The activity coefficient is however highly dependent on the reaction conditions (ionic

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Figure 1: Some values for the equilibrium constant of the iodine–triiodide equilibrium system, from various literature references.

strength, chemical properties of the present compounds, etc.) These parameters therefore affect K_c. In general laboratory practice most often the concentration can be directly measured (and not the activity). The determination of the activity coefficient is typically complicated, it can often be performed only based on approximate models (e.g., Debye-Hückel), applying several simplifications.

While K_a is used in thermodynamic calculations, K_c is more of practical relevance due to the considerations detailed above. During the experiment, the students will determine the K_c value of a solution equilibrium system under the experimental conditions defined by the Instructor.

1.2 Determination of the equilibrium constant of the iodine–triiodide equilibrium system

1.2.1 Previous results from the scientific literature

The equilibrium constant of the iodine–triiodide equilibrium system was determined by many researchers, using many different methods, as summarized in Figure 1 (from R.W. Ramette et al., J. Am. Chem. Soc., 87, 5001 (1965)). The experimental results follow an almost linear trend. This is expected based on the van't Hoff equation:

$$\frac{\partial \ln K_a}{\partial T} = \frac{\Delta H_r^0}{R\,T^2},$$

where ΔH_r^0 is the standard reaction enthalpy at T temperature (in K), while R is the gas constant. If ΔH_r^0 is independent on the temperature (in the investigated temperature range), the above equation can be easily integrated:

$$\ln\frac{K_{a_2}}{K_{a_1}} = \frac{-\Delta H_r^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

By plotting the logarithm of the equilibrium constant as function of the reciprocal of the thermodynamic temperature, a linear is obtained from which the equilibrium constant can be calculated, theoretically, at any temperature. This however is not always the case, as a notable deviation from the linear trend can often be witnessed (see Figure 1). One of the reasons behind this deviation is the possible temperature dependence of the standard reaction enthalpy in the given temperature range. A more important observation on the figure is that different methods lead to different results at the same temperature. This is probably caused by the different concentration ranges that are optimal for and applied during the different experimental methods. A higher iodine concentration favors the formation of polyiodides. The following two parasitic reactions are considered most often in the literature:

$$2I_2 + I^- \rightleftharpoons I_5^- \quad \text{and} \quad 5I_2 + I^- \rightleftharpoons I_{11}^-.$$

These equilibrium reactions alter the concentration ratio of I_2 and I^- in the solutions, and the forming polyiodide ions might also contribute to the visible light absorption of the solution during spectrophotometric measurements. These reactions are negligible in case of dilute solutions, therefore low concentrations should be applied during the experiments to get precise and reliable results. The most suitable methods for this are *p*H-potentiometry and spectrophotometry, allowing to study the reaction even at a concentration of 10^{-4} M .

At higher *p*H, the disproportion of I_2 can also disturb the equilibrium:

$$3I_2 + 3H_2O \rightleftharpoons 5I^- + IO_3^- + 6H^+.$$

In acidic solutions (pH<6) the disproportion is almost completely suppressed, hence the measurements should be performed in solution of pH<6.

The ionic strength also affects the equilibrium constant, hence it must be kept constant during the experiments.

1.2.2 Mathematical description of the equilibrium system

The used experimental and evaluation method should be chosen before planning the experiments. For this, we must have preliminary knowledge on the mathematical description of the studied system, meaning the correlation between the experimentally variable parameters (total concentrations in this case) and the measured values (e.g., absorbance values).

The equilibrium constant of the $I_2 + I^- \rightleftharpoons I_3^-$ association reaction is:

$$K_c = \frac{[I_3^-] \cdot c^0}{[I_2] \cdot [I^-]},$$

from which the triiodide concentration can be derived as:

$$[I_3^-] = \frac{K_c \cdot [I_2][I^-]}{c^0}$$

The total concentration of iodine and iodide set during the solution preparation can be expressed as:

$$\begin{aligned} T_{I_2} &= [I_2] + [I_3^-] = [I_2]\left(1 + \frac{K_c \cdot [I^-]}{c^0}\right) \\ T_{I^-} &= [I^-] + [I_3^-] = [I^-]\left(1 + \frac{K_c \cdot [I_2]}{c^0}\right) \end{aligned}$$

Based on these, the equilibrium concentration of each equilibrium species can be expressed with the total concentrations:

$$[I_3^-] = \left(\frac{c^0}{K_c} + T_{I_2} + T_{I^-} - \sqrt{\left(\frac{c^0}{K_c} + T_{I_2} + T_{I^-}\right)^2 - 4 \cdot T_{I_2} \cdot T_{I^-}}\right) \Big/ 2 \quad (1)$$

$$[I_2] = T_{I_2} - [I_3^-] \quad (2)$$

$$[I^-] = T_{I^-} - [I_3^-] \quad (3)$$

Equations (1)–(3) show, that in case of a known K_c value the equilibrium concentrations can be calculated for any solution compositions with known total concentrations.

Iodine and triiodide both absorb light in the visible range. The correlation between the concentration of these colored species and the measured absorbance is given by the Beer-Lambert law. Note, that the absorbance (A) is additive, hence at a given wavelength (λ_i) it can be calculated as the sum of the individual absorbance of the species present:

$$A_{\lambda_i} = \left(\varepsilon_{\lambda_i}^{I_3^-} \cdot [I_3^-] + \varepsilon_{\lambda_i}^{I_2} \cdot [I_2]\right) \cdot \ell, \quad (4)$$

where ε_{λ_i} is the molar absorption coefficient at the given wavelength, and ℓ is the path length of the light through the cuvette (i.e., the thickness of the solution the light must pass through).

As seen from equations (1)–(4), 3 parameters connect the total concentrations and the measured absorbance at a given wavelength: the molar extinction coefficients of iodine and triiodide, and the equilibrium

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Figure 2: The ratio of the equilibrium concentration of triiodide and the total concentration of iodine, in function of the product of the equilibrium constant and the equilibrium iodide concentration.

constant. This implies that performing measurements at a fixed wavelength with 3 different solution compositions we get 3 equations with 3 unknowns - a nonlinear equation system that can be solved to determine K_c.

Any experimental error can however notably distort the results, and therefore it is necessary to measure more data than this required minimum. In our case it means that the measurements must be performed at multiple wavelengths, and with more solution compositions. As an example, measuring 10 solution compositions at 7 wavelengths leads to 70 equations with only 15 unknown parameters (2–2 molar extinction coefficients at the 7 wavelengths, and K_c). This amount of experimental result is typically enough for reliable nonlinear parameter fitting.

2 Students' experiment

The aim of this experiment is to determine the equilibrium constant of the iodine–triiodide system, based on the experimental plan **designed by the students**. As the starting point of the planning, the Instructor defines:

- the type of the used instrument,
- the total iodine concentration in the solutions in the range of $1 \cdot 10^{-4} - 8 \cdot 10^{-4}$ M,
- the ionic strength of the solutions between $0.2 - 1.0$ M,
- the measurement temperature between $25 - 40$ °C,
- the solution *p*H between $3 - 6$, set using acetic acid–sodium acetate buffer. The dissociation constant of the acetic acid can be calculated from the $pK_d = 3.586 + 275.6/T - 0.051 \cdot \sqrt{I}$ empirical formula, where T is the thermodynamic temperature and I is the ionic strength (in molar concentration).

All what needs to be considered during the planning of the experiments will be provided in the following paragraphs. Note, that only taking all these aspect into consideration will allow to gather precise results.

2.1 Planning the experiments

1. A series of solutions with $10 - 12$ different composition should be planned and prepared with the $[I_3^-]/T_{I_2}$ ratio varying equidistantly between 0.0 and 0.9, while the total iodine concentration is constant. The necessary information can be gathered from Figure **2**, showing the

$$\frac{[I_3^-]}{T_{I_2}} = \frac{K_c \cdot ([I^-]/c^0)}{1 + K_c \cdot ([I^-]/c^0)}$$

relation that can be derived from the equations above. This way enough experimental results will be gathered for the determination of all the parameters. The value of K_c can be determined most precisely from the measurements at $[I_3^-]/T_{I_2} \sim 0.5$. The molar absorbance coefficient of iodine can be most precisely determined from the data points where a $[I_2]/T_{I_2} \sim 1$. As for triiodide, the molar absorbance coefficient can be most precisely measured at compositions where $[I_3^-]/T_{I_2} \sim 1$. An approximate value for K_a can be read from figure 1. Because of the low iodine total concentrations, K_c and K_a are very close to each other in value. This K_c value and equation 2 should be used to calculate the equilibrium concentration of iodide. At any chosen $[I_3^-]/T_{I_2}$ ratio the equilibrium triiodide concentration can be calculated, that allows the calculation of the total iodide concentration (as detailed above).

2. The solutions can be made in separate volumetric flask, or the targeted compositions can be formed directly in the cuvette, mixing the appropriate stock solutions. The first method is more energy demanding, but it also offers more precise experiments. As for mixing in a cuvette, the final volume of ca. $3\,cm^3$ should be considered. To avoid volume contraction during the mixing of two different solutions, the same ionic strength and *p*H should be set in the solutions. One of these solutions should contain only iodine, while the other should contain mostly triiodide, while having the same total iodine concentration in both. Mixing these two solutions allow to form any composition that was planned in the 1st step. In case the iodide concentration should be varied in a very wide range (i.e., several orders of magnitude), it is sometimes beneficial to prepare two triiodide solutions, with significantly different total iodine concentrations, to avoid the measurement of very small volumes.
3. First, the salt for setting the ionic strength should be chosen, and its concentration should be calculated. Application of sodium perchlorate should be avoided, as it can lead to precipitate formation. The most straightforward (hence suggested) salt for setting the ionic strength is sodium acetate, as it is used for setting the solution *p*H anyway.
4. It should be also planned which volumetric equipment will be used (check the inventory for the available equipment!), and all the necessary ones should be carefully cleaned.
5. The experimental plan must be checked and approved by the Instructor before the students could start the experiments!

2.2 Execution of the experiments

– Preparation of the stock solutions:

1. First, a V=1 l saturated iodine solution must be prepared. The dissolution of iodine is a slow process, therefore this solution must be prepared at least two days before performing the experiments, and during this time the solution must be vigorously stirred. A single droplet of concentrated acetic acid should be added to the ion exchanged water before adding the iodine to the solution. This will not notably affect the *p*H of the solutions, but helps to suppress the disproportion reaction iodine. The amount of iodine should be calculated from the it's solubility. At least double of the calculated amount should be measured in the solution bottle. After saturation, the solution should be filtered.
2. The following stock solutions should be prepared: one containing iodine, and one (or two, of necessary according to the plans) containing both iodine and iodide. The total concentration of iodine, the *p*H and the ionic strength of the solutions should be the same, and the amount of the dissolved iodide must be measured with the most precise available balance.
3. Although the solubility of iodine in pure water is known from the scientific literature (0.029 g iodine 100 g water at 25 °C), this is affected by both other compounds dissolved in the solution and the temperature. Hence the total iodine concentration must be determined in each **stock solutions**. This is most easily done by titration with $Na_2S_2O_3$ solution. The precise concentration of the $Na_2S_2O_3$ solution must be previously determined using a KIO_3 solution, that was prepared with analytical precision.
4. The concentration of the $Na_2S_2O_3$ and KIO_3 solutions must also be planned by the students. A general rule is that the titrant volume must allow the $\sim$0.3 % precision determination of the concentration. The volume of the burette should be checked before planning the experiments.

– Recording the UV-visible spectra:

1. The spectrophotometer and subsequently the lamps (both the UV and the visible lamps) should be turned on, and the instruments should be allowed to warm up for at least 30 minutes to ensure

constant and stable ligth intensity during the experiments. A background (blank) measurement should be performed before recording the spectra of the different solutions.

2. The wavelength range should be chosen after recording the absorbance spectrum of the solution with the lowest and the highest iodide concentration.
3. The same cuvette must be used for all measurements. The cuvette is either properly cleaned and dried between the measurements, or it should be rinsed 4–5 times with the next studied solution before recording its spectrum. This requires higher solution volumes, that should be considered when planning the experiments.
4. Record again the baseline after the measurements (i.e., record the spectrum of pure water again). This allows to check the stability of the instrument.
5. The spectrum of the solutions should be measured in the increasing or decreasing iodide concentration order to simplify the data evaluation and also decrease the experimental errors.

– Some practical advice:

Some important practical things will be listed here. These are not always based on strong theoretical background but more on experimental findings. These will allow the students to gather easily interpretable and precise experimental data.

1. The measurements will only provide good results if the experimental plan is followed precisely, the prepared solution compositions are closed the planned compositions.
2. The measurements should be performed with high precision! Always use the most precise tools available. Ass for mass measurements, $\sim$0.1 g, or higher masses are required for precise mass measurements, even if an analytical balance is used.
3. The used chemicals might contain crystalline water.
4. Paper based filters might contain starch, or similar compounds. The I_2 containing solutions should therefore be filtered on glass filters.
5. Iodine sublimates, that can distort the solution compositions. When handling iodine containing solutions, the experiments should be performed rapidly. As an example, when preparing the triiodide solution the iodine solution should be measured into the iodide solution, and not vice versa.
6. The iodometric titration was designed for 10-100 times higher concentrations than what is applied during the experiments. Because of this, there are some deviations here from the typical experimental descriptions, found in established textbooks. An example is that the reaction is slow under the experimental conditions, therefore acetic acid is used to decrease the *p*H of the solution instead of the typically applied inorganic acids, in order to avoid the acid catalysed decomposition of thiosulphate. Appendix 1. describes the applied conditions for the iodometric titration.

2.3 Data acquisition and processing

2.3.1 Calculation of the concentrations

As the first step of data evaluation, the total concentration of iodine and iodide must be calculated in each measured solution, based on the results of the titration of the stock solutions.

2.3.2 Choosing the data for evaluation

After finishing the experiments, the spectrophotometry data should be copied from the PC to a flash drive and transferred to another computer to analyze the data. The spectra should be plotted (after data conversion, if necessary). Subsequently, the spectra should be plotted on the same graph. Based on this graph, $7-9$ wavelengths should be chosen where the analysis will be performed. This should be done considering the followings:

Table 1: The absorbance matrix, containing the experimental results.

Solution Number	Total concentration		Absorbance					
			λ_1	λ_2	$\cdots$	λ_i	$\cdots$	λ_n
1	$T^1_{I_2}$	$T^1_{I^-}$	$A_{1,1}$	$A_{1,2}$	$\cdots$	$A_{1,i}$	$\cdots$	$A_{1,n}$
2	$T^2_{I_2}$	$T^2_{I^-}$	$A_{2,1}$	$A_{2,2}$	$\cdots$	$A_{2,i}$	$\cdots$	$A_{2,n}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$		$\vdots$
j	$T^j_{I_2}$	$T^j_{I^-}$	$A_{j,1}$	$A_{j,2}$	$\cdots$	$A_{j,i}$	$\cdots$	$A_{j,n}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$		$\vdots$	$\ddots$	$\vdots$
m	$T^m_{I_2}$	$T^m_{I^-}$	$A_{m,1}$	$A_{m,2}$	$\cdots$	$A_{m,i}$	$\cdots$	$A_{m,n}$

– One wavelength should be chosen at the isosbestic point (where the molar extinction coefficient of the two absorbing species are identical).

– Half of the remaining wavelengths should be chosen below, while the other half above the isosbestic point. It is worth choosing wavelengths at which the measured absorbances differ notably from each other.

– Choose wavelengths at which all the absorbance values fall in the $0.1-1.3$ range, where the spectrophotometric measurements are most reliable.

The chosen wavelengths, the total concentration and the measured absorbances should be collected in a data file, according to Table 1. If the light path length was not 1.0 cm, the measured absorbance values should be calculated to this cuvette size (based on the Beer–Lambert law). In this absorbance matrix (**AM**) n is the number of the chosen wavelengths, while m is the number of the investigated, different solution compositions. This **AM** will be further processed. The solution number is not part of the **AM**.

2.3.3 Identifying inaccurate data points

Any bad data point can affect the nonlinear parameter fitting process, and therefore these data points should be identified and deleted before analyzing the data. These data points are typically easy to spot on the plotted spectra. Furthermore, erroneous data points can also be identified during data fitting, investigating the deviation between the fitted and the experimental results.

2.3.4 Calculation of the equilibrium constant

The data evaluation is based on equations (1)–(4). Including the equilibrium concentration of iodine and triiodide in (4), combined with equations (1) and (2), the following equation is derived:

$$\frac{A_{j,\lambda_i}}{\ell} = \varepsilon^{I_2}_{\lambda_i} \cdot T_{I_2} + (\varepsilon^{I_3^-}_{\lambda_i} - \varepsilon^{I_2}_{\lambda_i}) \cdot \frac{\frac{c^0}{K_c} + T_{I_2} + T_{I^-} - \sqrt{\left(\frac{c^0}{K_c} + T_{I_2} + T_{I^-}\right)^2 - 4 \cdot T_{I_2} \cdot T_{I^-}}}{2} \tag{5}$$

This equation relates the absorbance measured in the j^{th} solution at a given wavelength (λ_i) and the total concentrations in the solution. As the measurements are performed with $\ell = 1.0$ cm cuvette path length, the left side of this equation can be simplified to A. Three unknown parameters are seen in equation (5): two molar extinction coefficients and the equilibrium constant. Also, two independent and a dependent variable is seen in the equation: the total concentrations and the measured absorbance, accordingly. With every further wavelength, the number of independent variables increases by one, while the number of unknowns increases

by two. Hence equation (5) cannot be linearized, the data must be handled with nonlinear parameter fitting. For this, the followings should be considered:

- First, consider to evaluate the data measured at a single wavelength. Assuming values for the molar extinction coefficients and the equilibrium constant, we can calculate an absorbance value based on equation (5).
- The difference between the fitted and the measured absorbance values differ less if the initial "guessed" parameters are closer to the real values. This idea is formulated in the following equation:

$$S_i(K_c,\varepsilon_{\lambda_i}^{I_2},\varepsilon_{\lambda_i}^{I_3^-}) = \sum_{j=1}^{m}\left(A_{j,\lambda_i}^{\text{experimental}} - A_{j,\lambda_i}^{\text{calculated}}\right)^2 \tag{6}$$

  This equation shows the sum of squared residuals (S), that should be minimized as function of the variables that we want to determine. Note, that the experimental data are known here, and we are looking for the variables in this case!
- If data measured at all wavelengths is to be analyzed together, we get the following expression:

$$S(K_c,\text{all }\varepsilon) = \sum_{i=1}^{n} S_i(K_c,\varepsilon_{\lambda_i}^{I_2},\varepsilon_{\lambda_i}^{I_3^-}) = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(A_{j,\lambda_i}^{\text{experimental}} - A_{j,\lambda_i}^{\text{calculated}}\right)^2. \tag{7}$$

  This function has many variables - as an example, measuring at 7 wavelengths results in 15 variables. The sum of squared residuals is minimized as function of these 15 variables in this case.

This method is called nonlinear parameter estimation which is one of the most important methods to determine the value of different chemical parameters from experimental data. Different mathematical methods are known from the scientific literature for the minimization of S [1,2].

Appendix 2 describes a method and a possible software for data analysis, but the students can choose other solutions as well. Note, that in case of using other software, the data might not be collected in Table 1, but in other formats.

2.3.5 Analyzing the results of data fitting

The most important task of the students after performing the calculations is the analysis of the results, and the reliability of the fitting. Any parameter estimating software calculates certain statistical parameters that give information on this, hence this should be extracted from the results.

Visualizing the reliability of the fitting is often a very complex task. In this case, however, it is relatively simple to create a figure showing the merit of the fitting. For this, we have to transform the experimental results and plot these according to Figure 2, also showing the theoretical curve. The more precise is a certain data point, the closer it is located to the theoretical curve. This way an easily understandable figure is provided. The data transformation is done according to the following considerations:

- Using the calculated molar extinction coefficients, an equilibrium triiodide concentration can be calculated ($\ell = 1\,\text{cm}$) from all of the measured absorbances:

$$A = \varepsilon^{I_2}\cdot[I_2] + \varepsilon^{I_3^-}\cdot[I_3^-] = \varepsilon^{I_2}\cdot(T_{I_2} - [I_3^-]) + \varepsilon^{I_3^-}\cdot[I_3^-] \quad\longrightarrow\quad [I_3^-] = \frac{A - \varepsilon^{I_2}\cdot T_{I_2}}{\varepsilon^{I_3^-} - \varepsilon^{I_2}}. \tag{8}$$

- For Figure 2, the x values can be calculated according to the following equation:

$$x = K_c^{\text{fitted}}\cdot(T_{I^-} - [I_3^-]) \tag{9}$$

  The y values can be calculated from the following equation:

$$y = \frac{[I_3^-]}{T_{I_2}} \tag{10}$$

Table 2: Table containing the result of the nonlinear parameter estimation.

Wavelength / nm	K_c	ε^{I_2} / $M^{-1}cm^{-1}$	$\varepsilon^{I_3^-}$ / $M^{-1}cm^{-1}$	Avereage absorbance difference (fitting parameter)

2.4 Evaluation of the experimental results

1. The students should record in the labnote the details of the planning and the experimental results as well (including the measured volumes, weights, etc.). The figure containing the spectra should be printed and attached to the document.
2. The labnote should contain the primary measurement data according to Table 1 (written or printed).
3. After performing the nonlinear parameter estimation for each separate wavelength (according to equation (5)), and the results (and their uncertainty) should be collected in a table (Table 2). In this equation the absorbance (A) is the dependent, while T_{I_2} and T_{I^-} are the two independent variables and the three parameters to be derived from the fitting are K_c, $\varepsilon_{\lambda_i}^{I_3^-}$ and $\varepsilon_{\lambda_i}^{I_2}$. The analysis should be performed in two different ways:

   – First - according to the experimental plans - assume, that T_{I_2} is constant (use the average value from the titrations). This way equation (5) contains only one independent variable (T_{I^-}) and the three fitted parameters. Using a suitable software (e.g., QtiPlot or Excel Solver) fit the three parameters at the lowest and highest chosen wavelengths. Plot the results according to equation (5).

   – Depending on how quickly and precisely were the solutions prepared for the experiments, T_{I_2} might vary in the different studied solution. Perform the nonlinear parameter estimation by handling both T_{I^-} and T_{I_2} as independent variable. These total concentrations are calculated from the composition of the stock solutions (as calculated from the titrations and from the weighed iodide) that were mixed to form the different solutions. For this, use the Octave software as described in **Appendix 2**, and perform the fitting for all the chosen wavelengths separately.

   Compare the results of the two different approaches and comment on the differences based on the T_{I_2} in the different stock solutions, determined by titration.
4. A similar nonlinear parameter estimation should be performed for the whole data set (all wavelengths) combined, and these results should be included in table 2.
5. Shortly analyze the statistical parameters of the fittings! Pay special attention to the correlation between the deviation of the molar absorption coefficient, and that of the equilibrium constant!
6. Prepare the figure that illustrates the precision of the measurements! Include the theoretical curve (as seen in figure 2) and the transformed (according to equations (8)–(10)) experimental results.

   Note: The x-axis of Figure 2 is in logarithmic scale. In case of linear scaling, the theoretical curve follows the $y=10^x/(1+10^x)$ formula (and not the $y=x/(1+x)$ form)!
7. The labnote must contain all the deviations from the description of the experiments, and from the plan of the students. Any experimental errors should also be indicated.
8. Comment shortly on the experiences of the experiment, on the results, and on the learned methods!

Control questions

Week I.: experimental planning, preparation of the saturated iodine solution

1. Why is it important to (re-)determine the equilibrium constant of a previously studied system?
2. Give the definition of activity and the activity coefficient in dilute electrolyte solutions!
3. Describe in 4–5 sentences what is considered in the Debye-Hückel theory during the calculation of the activity coefficient!
4. Give the diffential and integrated form of the van't Hoff equation!
5. Describe shortly what is the total-, the equilibrium-, the analytical-, and the measured in concentration of a given compound!
6. Why is it beneficial to measure more data than the necessary minimum?
7. What is a distribution curve of an equilibrium system? Give an example (with figure)!
8. How is the ratio of the triiodide and total iodine concentration used for planning the experiments?
9. Give the chemical equations on that the iodometric titration are based (thiosulphate–iodine and iodide–iodate reactions)!
10. What is the ionic strength in a 10^{-4} M acetic acid solution ($K_d = 1{,}8 \cdot 10^{-5}$)?
11. Define the ionic strength! What is the ionic strength in the solution that is formed by mixing the following solutions (consider the full dissociation of all species): 100.0 cm^3 0.1 M Na_2SO_4, 300.0 cm^3 0.2 M $FeCl_3$ and 100.0 cm^3 1.0 M HCl?
12. Calculate $[I_3^-]$ in a solution that is formed by mixing 100.0 – 100.0 cm^3 $5 \cdot 10^{-4}$ M I_2- and I^--solutions ($K_a = 500$)?

Week II: measurements and evaluation

1. What parasitic reactions have to be considered in parallel with the formation of triiodide?
2. How are the equilibrium calculations affected by the parasitic reactions?
3. Derive the formulas to calculate the equilibrium concentrations of triiodide, iodine and iodide, as function of the total concentrations and the equilibrium constant.
4. What is the Beer-Lambert law? Provide the formula for calculating the absorbance in the $I_2 - I^- - I_3^-$ equilibrium system!
5. How do you prepare the saturated iodine solution?
6. How do you determine the total iodine concentration?
7. What considerations should be taken into account when choosing the appropriate wavelengths for data analysis?
8. What is the absorbance matrix?
9. What is the sum of squared residuals and what is this used for during nonlinear parameter estimation?
10. How can you represent the errors of the measured data graphically?

Appendix 1.: Iodometric titrations

Iodometric titration is used to determine the total iodine concentration in the stock solutions. First we have to determine the exact concentration of the prepared sodium-thiosulphate solution using a KIO_3 solution (that is prepared by weighing of high purity chemical). Subsequently, the iodine concentration in the stock solutions is determined using the sodium-thiosulphate solution. Because of the low iodine concentration in the samples, the followings must be considered for precise measurements:

- Iodine sublimates, that can change the solution composition notably. *Solution*: The iodine containing samples are always measured in solutions containing iodide in excess amount (compared to what is necessary for triiodide formation). The formed triiodide reacts with thiosulphate identically to the iodine, but it will not sublimate.
- At the used concentration the reaction is not immediate. *Solution*: The titration must be performed slowly around its endpoint, it is worth waiting 10–15 seconds before adding the next titrant portion.
- The iodate–iodide reaction is also not immediate: *Solution*: A few minutes should be waited after mixing the solutions (before the titration).
- The dissolved oxygen can react with the iodide ions to form iodine. *Solution*: Oxygen should be removed from the samples before adding the iodide (for forming triiodide). This can be achieved by adding bicarbonate to the acidic solution to form CO_2. This removes the oxygen from the solution and – being heavier than air – forms a gas pillow above the solution. Avoid moving the samples too much during titration to protect this gas pillow (that prevents the dissolution of oxygen)! $KHCO_3$ should be added before the iodine containing solution, as the forming CO_2 can also remove iodine from the solution.
- Thiosulphate decomposes in and acid catalyzed reaction. *Solution*: Use acetic acid during the titration instead of strong acids.
- It is difficult to observe the endpoint of the titration because of the low concentrations. *Solution*: Use the clear part of a fresh starch solution (not older than a month)! Only add the starch solution (a few-droplets) to the sample close to the endpoint. The solution temperature should be equal or lower than the room temperature. If necessary, cool it using ice.

These difficulties can be avoided following the practical hints below:

- Titration of the KIO_3 solution with $Na_2S_2O_3$ solution: Measure the necessary KIO_3-ot solution in a iodine flask (or an Erlenmeyer flask with ground in glass stopper), add ca. $5\,cm^3$ concentrated acid and $\sim 20-50\,cm^3$ ion exchanged water. Add $\sim$1 g $KHCO_3$ to the solution and wait until the intense bubble formation stops. Subsequently add ca. 0.3 g KI to the solution and dissolve it. Close the flask (with a moistened flask stopper) and put the solution in a dark place (e.g., cupboard) for 5 minutes. Titrate the solution.
- Titration of the I_2 containing samples with $Na_2S_2O_3$ solution: Put $\sim 30-40\,cm^3$ ion exchanged water and ca. $5\,cm^3$ concentrated acetic acid in the iodine flask. Add $\sim$1 g $KHCO_3$ to the solution, and after the intense bubble formation stopped, dissolved ca. 0.3 g KI in it. Subsequently, the iodine containing sample should be added, and this sample should be titrated immediately.

Appendix 2: using the Octave software for data evaluation

The program written in Octave for evaluating the results (`trijodid.m`) can be downloaded from the website of the Department. To use this, the followings should be ensured:

1. Octave 4.0.3 or newer should be installed on the computed. This can be downloaded from *https://www.gnu.org/software/octave* .

2. The `optim` package of Octave should be installed. In Windows based versions this is typically included in the originally installed version. For other operating systems, see the help menu at the above mentioned website.

Preparations for data evaluation

1. Collect the data files containing the recorded spectra in a folder. The name of the folder should only contain characters from the English alphabet (and no spaces). Use the (maximum 5) characters given during the measurements. The folder name will be referenced in the followings as *basename*. Always replace this with the folder name when performing the analysis.(e.g., if the $JJTJ$ file name is used during the measurements, *basename* should always be replaced by $JJTJ$).

   A suggestion for the folder path is C : \Users \ Public \ Documents. On the shared computers, use the C : \OctaveWork folder.

2. Copy the `trijodid.m` file in the same folder. Always check if the newest file version is used.

3. Create a *basename.cnc* text file in this folder.[1] Each raw of this data file is attributed to a measured spectrum and containing three data: the total concentration of iodine and iodide (the 2nd and 3rd columns in table 1), and the number in the file name of the respective spectrum. *Dot should be used as decimal separator in the numbers instead of comma!* **The first row must contain the reference spectrum**! The file should look like the lines 124 – 137 in the `trijodid.m` file without the percentage signs and the semicolons.

Evaluation

1. Start Octave.
2. Go to the folder containing the file in the *File Browser*, on the top left side of the screen.
3. Load the `trijodid.m` file by double-clicking on it. This will be shown on the right side of the software window. This program can be initiated in the *Editor* window either by pressing the *F5* button, or by clicking on the *Save File and Run* icon.
4. Choose the appropriate language in the pop-up window, and click on *OK*.
5. In the next pop-up window the *basename* should be provided, considering that capital and small letters are not equivalent in Octave! Some time might pass after pressing the *OK* button (caused by data reading and the initialization of the graphics). If this time is longer than two minutes, check the *Command Window* for errors. Solve the error (if there is any) and re-start the process.
6. A figure is shown with all the spectra (corrected for the reference spectrum). A new pop-up window also appears, where the 7 wavelengths for data analysis should be defined. When choosing wavelenght, also consider the resolution of the measurement (the wavelength difference of the data points). Choosing incorrect wavelengths will result in an an error message in the *Command Window*.
7. The software shows the wavelengths on the figure, generates Table 1, and saves the figure in PDF format (*basename_curves.pdf*).
8. 9 options are shown in the next pop-up window, allowing to perform all necessary calculations. The initial values are set automatically in the software.
9. The results of the fittings at a single wavelength will be shown on separate figures (one with linear, and another one with logarithmic x-scale) for each wavelength. Clicking on *OK* the figures will be saved as *basename_???nm.pdf*, where ??? will be replaced by the studied wavelength. If the fitting was not successful, no figure, but a message will be shown. Press *OK* to proceed.

[1] If the file is generated in Windows Notepad, change the file type to "all files" when saving.

10. If a systematic error with any of the spectra is revealed during the fitting, check the input file containing the total concentrations and the name of the spectra. If a spectrum is not correct, it can be omitted from the evaluation (delete the respective row in the *basename.cnc* file) and restart the evaluation.
11. Evaluation of the data at all wavelengths together is performed similarly, resulting the *basename_all.pdf* output.
12. After performing all 8 fittings will bring two further options in the *Calculations* window. The first generates a table with all the results (*basename_results.txt*), the second generates a figure showing the precision of the measurements (*basename_distribution.pdf*).
13. Close Octave after finishing the evaluation.
14. All the necessary figure are created in Octave. The lab-note should be finished with a detailed discussion on the results.

References

[1] P. Valkó, S. Vajda, *Műszaki–tudományos feladatok megoldása személyi számítógéppel*, Műszaki Könyvkiadó, Budapest, 1987.

[2] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes in FORTRAN/Pascal/C. The art of Scientific Computing*. Cambridge, University Press, 1989–1992.