# Spectrophotometric determination of equilibrium constant. Planning, carrying out an evaluation of measurement.

## 1. Introduction

*For more detailed theoretical introduction see Atkins' Physical Chemistry book, chapter "7.2 The description of equilibrium" page 202- 216.*

It is often necessary to know the precise concentration- distribution of a chemical system in equilibrium. The concentration- distribution can be simply calculated if the chemical composition and the equilibrium constants are known under given experimental conditions.

The complexing of aqueous iodine by iodide ion has long been of major interest, and studies have used solubility, distribution and potentiometric, conductimetric, and spectrophotometric technics. The measured values and the used analytical technics are presented in **Fig. 12.1** (J. Am. Chem. Soc., 87, 5001 (1965)). It can be seen from the figure that the measured points almost fit in a linear function. It is also expected according to the van't Hoff equation.

$$\frac{\partial \ln K_a}{\partial T} = \frac{\Delta H^\ominus}{RT^2}, \qquad (12.5)$$

where $\Delta H^\ominus$, T and R are the standard reaction enthalpy, temperature and molar gas constant, respectively.

The above equation is simply integrable if $\Delta H^\ominus$ is independent from the temperature:

$$\ln\frac{K_{a_2}}{K_{a_1}} = \frac{-\Delta H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \qquad (12.6)$$

By plotting the logarithmic value of equilibrium constants as a function of 1/T, a linear relationship is obtained, from where the equilibrium constants can be determined at any temperature.

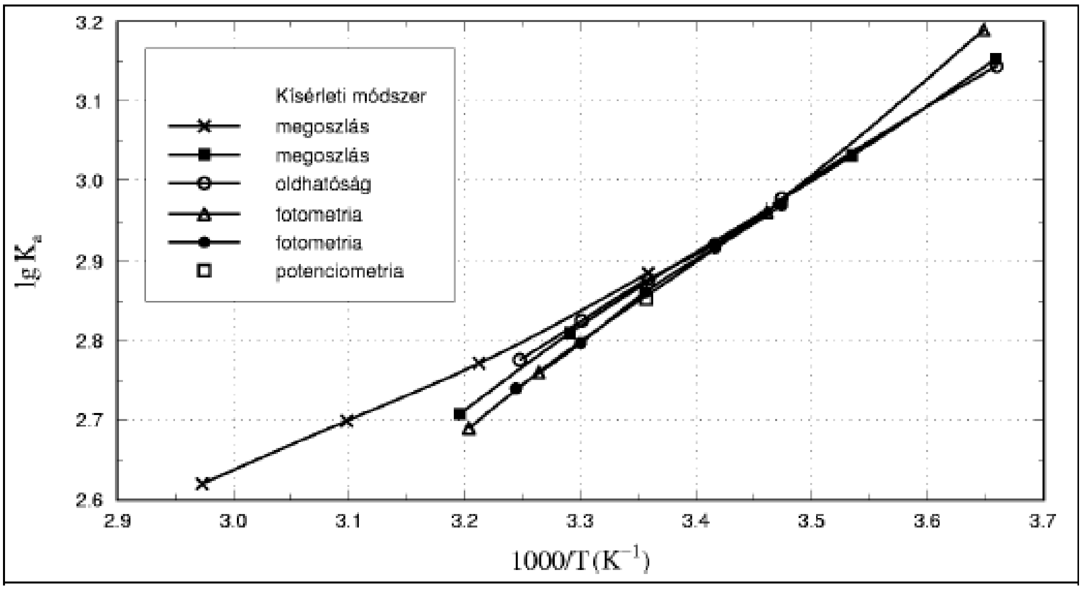

**Figure. 12.1.** Variation of iodine/ triiodide reaction's $K_a$ values with temperature represented in the literature (determined by solubility, spectrophotometric, distribution and potentiometric measurements)

However, there are some disturbing reaction according to the literature. Higher iodine concentration favours the formation of poly iodide:

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

While at higher pH values the measurement can be interfered by the disproportion of $I_2$:

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

In acidic media (pH<6) the equilibrium shifts to the left, so the measurement has to be carried out at lower pH. The ionic strength is also influenced to the equilibrium constant, therefor it has to be kept at constant value.

## Mathematical description of the equilibrium

Before the planning of the measurement an evaluation method must be chosen. For the choice of the method the mathematical description of the studied equilibrium has to be known which means the knowing of correlation between the experimentally variable parameters (here the adjusted total concentrations) and the measured data (here the spectrophotometric absorbance values).

The association equilibrium constant of the $I_2+I^- \leftrightarrow I_3^-$ equation is

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} \qquad (12.7)$$

expressed the equilibrium concentration of triiodide:

$$[I_3^-] = K_c[I_2][I^-] \qquad (12.8)$$

the total concentration of iodine and iodide ion:

$$T_{I_2} = [I_2]+[I_3^-] = [I_2](1+K_c[I^-]) \qquad (12.9a)$$

$$T_{I^-} = [I^-]+[I_3^-] = [I^-](1+K_c[I_2]) \qquad (12.9b)$$

According to the equations of (12.7) and (12.9) the equilibrium concentration of the particles can be expressed by the analytical concentrations:

$$[I_3^-] = \left(\frac{1}{K_c}+T_{I_2}+T_{I^-}-\sqrt{\left(\frac{1}{K_c}+T_{I_2}+T_{I^-}\right)^2-4T_{I_2}T_{I^-}}\right)\Big/2 \qquad (12.10a)$$

$$[I_2] = T_{I_2}-[I_3^-] \qquad (12.10b)$$

$$[I^-] = T_{I^-}-[I_3^-] \qquad (12.10c)$$

It can be seen from the equations (12.10) that the equilibrium concentration values simply calculated from the total concentration values knowing of $K_c$.

It follows the equations (12.10) that, by knowing the $K_c$ value, we can simply calculate the equilibrium concentrations from the total concentration values.

Both the iodine and triiodide has absorbance in the visible range of spectrum and according to the Beer- Lambert low the concentrations of species are proportional to the measured absorbance values.

$$A_{\lambda_i} = (\varepsilon_{\lambda_i}^{I_3^-}[I_3^-]+\varepsilon_{\lambda_i}^{I_2}[I_2])l, \qquad (12.11)$$

where A, ε and l are the absorbance, molar absorption coefficient and, path length of the beam of light through the sample, respectively.

Comparing the equations (12.10) and (12.11), it can be seen, that at a given wavelength three parameters make connection between the analytical concentration and the measured absorbance values: the molar absorbance values of iodine molecules and iodide ions, and the determined equilibrium constant value. So, if the absorbance measurements of the solutions with three different composition are carried out at the same wavelength, $K_c$ can be clearly determined with the solution of a nonlinear equation system with three variables.

The weakness of the described evaluation method that does not consider the experimental errors. Therefore, much more experimental date have to be collected than the needed number. It means in practical that the measurements have to be carries out at many different wavelength and the three different concentration solutions are not enough. The obtained measurement data can be evaluated by a nonlinear parameter estimation process.

## 2. Experimental

Your assignment is the spectrophotometric determination of the equilibrium constant between the iodide ion and iodine molecule to form the tri-iodide ion in aqueous solution according to your pre-made measurement plan. Before your planning activity the instructor should have to give the following parameters:

- total iodine concentration of the solutions (between $1*10^{-4}$ and $8*10^{-4}$ M)

- the applied ionic strength value between 0.2 and 1 M

- the measuring temperature between 25 and 40 °C

- and the applied pH value between 3 and 6. The desired pH value set by acetic acid/ sodium-acetate buffer system. The actual dissociation constant of the acetic acid can be calculated with the following empiric formula: $pK_d = 3.586+275.6/T-0.051\sqrt{I}$, where T and I are absolute temperature and molar ionic strength values, respectively.

### 2.1. Planning of measurements (first week)

1. For the spectrophotometric measurement a series of solutions (consists of 10-12 members) should be prepare where the $[I_3^-]/ T_{I2}$ ratio varies uniformly in the range of 0.0-0.95 and the total iodine content is approximately equal in each solutions. **Figure 12.2.** helps to select the optimal concentration values of the solutions. The figure shows the correlation of

$$\frac{[I_3^-]}{T_{I_2}} = \frac{K_c[I^-]}{1+K_c[I^-]}, \qquad (12.12)$$

deduced from the equations of (12.7) and (12.10).

For the determination of $K_c$ value the most suitable points are in the range where the $[I_3^-]/ T_{I2}$ is approximately 0.5. The molar absorbance of iodine can be exactly determine from the set of the points, where $[I_2]/ T_{I2} \sim 1$. The molar absorbance values of triiodide are the most important in the range where the $[I_3^-]/ T_{I2} \sim 1$. The $K_a$ value reading from the figure 12.1 is not deviate significantly from the $K_c$ value due to the low concentration. So the $K_a$ value is an acceptable estimation of the $K_c$ value. The iodide ion concentration can be calculate by the using of the estimated $K_c$ value according to the **Figure 12.2**. Knowing the $K_c$ value and the $[I_3^-]/ T_{I2}$ ratio of the solutions the total iodide concentration can also be calculated.

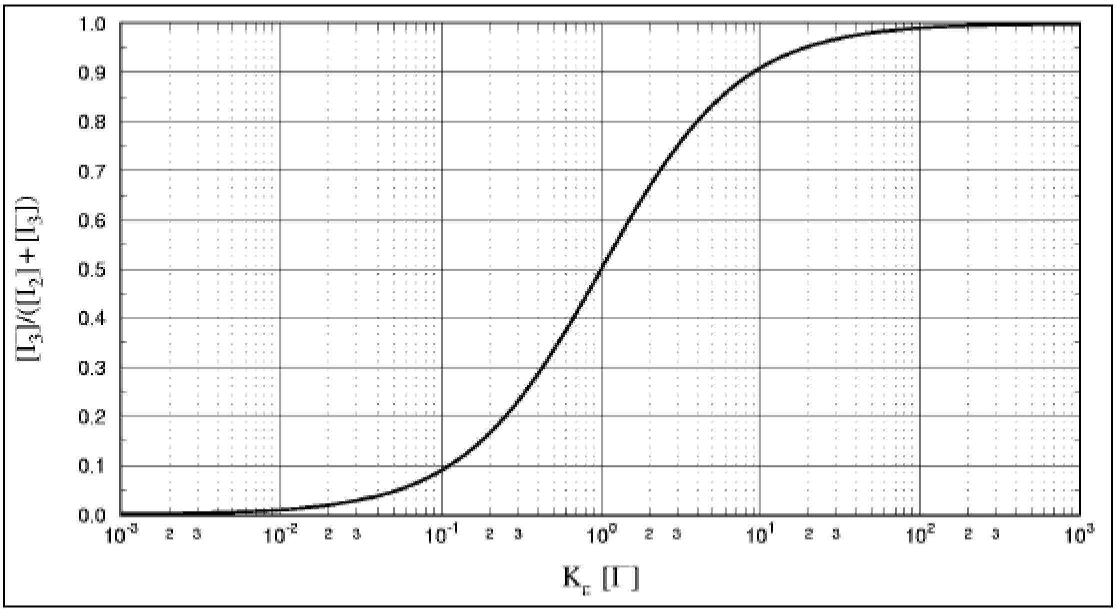

**Figure 12.2.** The ratio of formed tri-iodide complex and total iodine concentration as a function of $K_c \bullet [I^-]$

2. The series of solutions can be prepared in separate volumetric flasks. In order to avoid the volumetric contraction two stock solution must be prepared where the ionic strength and the pH equivalent but the first solutions contains only the pure iodine form, while the second solution contains only the tri-iodide complex form (However, the total iodine concentration of the solutions must be approximately equal in each member of series). The previously calculated concentration ratio values of solutions can be produced by the mixing of the stock solutions in

various proportions. In some cases dilution of the iodine stock solution may be necessary depending on the calculated weight volume of the iodine solution.

3. The desired ionic strength value adjusts with sodium acetate salt. The amount of weighed acetate salt also has to be given.

4. The prepared measurement plan has to be presented to the instructor.

### 2.2 Carrying out of experiments (second week)

Preparation of stock solutions:

1.) At first a saturated iodine solution has to be prepared on the first week of the laboratory practice. One drop of concentrated acid has to be added to the solution before the adding of the iodine in order to prevent the above mentioned disproportion reaction of iodine. After the dissolution process, the undissolved portion of added iodine should be separated by filtration using a frit.

2.) In the next step it has to be prepared a pure iodine stock solution and an iodine- iodide stock solution. Depending on the calculated measured volumes of iodine- iodide stock solution, dilution may be necessary. Use an analytical balance for the accurate measurement of iodide ion (KI). Because the sublimation of iodine, fast and precise work is necessary. For example during the preparation of triiodide solutions the iodine stock solution has to be poured into the previously pipetted iodide.

3.) Although the solubility of iodine in pure water is well known from the literature (0.029 g iodine in 100 g water at 25 ° C), it is strongly influenced by its environmental parameters (e.g., temperature changes and other dissolved substances). Therefore, the accurate iodine concentration of each stock solutions has to be measured by suitable analytical methods. The preferred method is the iodometric titration, where the unknown concentration of iodine solution is determined by volumetric titration with $Na_2S_2O_3$ solution. The exact concentration of $Na_2S_2O_3$ solution is measured with known concentration $KIO_3$ solution.

4.) $Na_2S_2O_3$ and $KIO_3$ solutions with appropriate volume and concentration have to be also prepared in order to measure the accurate iodine concentration. During the planning of the solution the available equipment and the concentration of initial iodine solution have to be also considered. The confident knowledge of iodometric analytical method is also very important.

Recording procedure of absorbance spectra:

1.) In order to ensure the constant light intensity during the measurement, the spectrophotometer allows at least half hour to warm up to achieve the steady state temperature.

2.) First, the spectra of the most diluted and the most concentrated solutions of iodide have to be recorded in order to determination of the applied wavelength and the absorbance range.

3.) All the solutions have to be measured with the same cuvette and always wash the cuvette with distilled water and then with acetone. The cuvette has to be rinse very thoroughly with the measurable solution before reading a new sample.

4.) The subsequent evaluations of data will be facilitated if the samples are recorded in increasing or decreasing concentration.

Evaluation method of the obtained measurement data

At first, the accurate concentration values of the series of solutions have to be calculated from the titration results of the stock solutions.

Next the measured absorbance spectra have to be plotted in one common figure in order to be able to choose 7-9 wavelength values, where the absorbance values need to be read according to the following consideration:

- one of the selected wavelength will be closed the isobestic point (where the absorbance of two different species is almost the same)
- In case of half of the other selected wavelengths the absorbance of iodine will be higher, even in the other case, the absorbance of triiodide.
- It is worth to select such wavelengths values where the minimum and maximum value of the read absorbance falls between 0.1 and 1.3.

After the selection of the wavelength, the total concentration and measured absorbance values have to be collected and stored according to the formula of the table (12.1.) (The serial number of the solution is not part of the data file!). In this data matrix “n” means the numbers of used wavelength, while “m” means the number of solutions with different total concentration values. This matrix will be used for further calculation.

**Table 12.1:** The formula of experimental data in electronic file

| Numbers of solutions | Total concent-ration valus | | Absorbance | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $\lambda_1$ | $\lambda_2$ | $\cdots$ | $\lambda_i$ | $\cdots$ | $\lambda_n$ |
| 1 | $T_{I_2}^1$ | $T_{I^-}^1$ | $A_{1,1}$ | $A_{1,2}$ | $\cdots$ | $A_{1,i}$ | $\cdots$ | $A_{1,n}$ |
| 2 | $T_{I_2}^2$ | $T_{I^-}^2$ | $A_{2,1}$ | $A_{2,2}$ | $\cdots$ | $A_{2,i}$ | $\cdots$ | $A_{2,n}$ |
| $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\ddots$ | $\vdots$ | | $\vdots$ |
| j | $T_{I_2}^j$ | $T_{I^-}^j$ | $A_{j,1}$ | $A_{j,2}$ | $\cdots$ | $A_{j,i}$ | $\cdots$ | $A_{j,n}$ |
| $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | | $\vdots$ | $\ddots$ | $\vdots$ |
| m | $T_{I_2}^m$ | $T_{I^-}^m$ | $A_{m,1}$ | $A_{m,2}$ | $\cdots$ | $A_{m,i}$ | $\cdots$ | $A_{m,n}$ |

Elimination of incorrect data

The incorrect data have to be eliminated or corrected before the calculation process. Perception of data with large errors is easy do the “sticking out of line” behaviour. Smaller errors can be noticed during the calculation.

Calculation of the equilibrium constant

The evaluation based on the equations of (12.10) and (12.11). If the equilibrium concentration values of iodine (12.10a) and iodide (12.10b) are substituting into equation (12.11), we find

$$\frac{A_{j,\lambda_i}}{l} = \varepsilon_{\lambda_i}^{I_2} T_{I_2} + (\varepsilon_{\lambda_i}^{I_3^-} - \varepsilon_{\lambda_i}^{I_2}) \frac{\frac{1}{K_c} + T_{I_2} + T_{I^-} - \sqrt{\left(\frac{1}{K_c} + T_{I_2} + T_{I^-}\right)^2 - 4 T_{I_2} T_{I^-}}}{2} \qquad (12.13)$$

The above equation shows the correlation between the total concentration and absorbance values of solutions measured at given wavelength. Three parameters are in the equation 12.13, what we will have to determine: two molar absorbance and the equilibrium constant values, moreover, two independent and a dependent variables (the two total concentration and the absorbance values, respectively). Furthermore, the increasing number of used wavelength is further increasing the number parameters. Therefore, the simply linearization method of equation (12.13) is excluded, *nonlinear parameter estimation process* is necessary for the evaluation.

During this calculation process the sum of squares (the difference between the experimentally measured and calculated values) is minimized. For one given wavelength:

$$S_i(K_v, \varepsilon_{\lambda_i}^{I_2}, \varepsilon_{\lambda_i}^{I_3^-}) = \sum_{j=1}^{m} \left(A_{j,\lambda_i}^{\text{measured}} - A_{j,\lambda_i}^{\text{calculat.}}\right)^2 \qquad (12.14)$$

For all of the measured wavelength values:

$$S(K_v, \text{summa } \varepsilon) = \sum_{i=1}^{n} S_i(K_v, \varepsilon_{\lambda_i}^{I_2}, \varepsilon_{\lambda_i}^{I_3^-}) = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(A_{j,\lambda_i}^{\text{measured}} - A_{j,\lambda_i}^{\text{calculat.}}\right)^2 \qquad (12.15)$$

This *nonlinear parameter estimation process* is one of the most important method for the calculation of different chemical parameters from experimental data. For more detailed description of this method see: *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.*

The above presented evaluation method will be carrying out by the using of “*NLREG - Nonlinear Regression Analysis Program*”

## Annex 1: Carrying out of iodometric titrations

During the measurements the accurate concentration of the stock solutions will be determined by iodometric titration method.

At first, the concentration of used sodium- thiosulfate will be determined by the titration of known concentration potassium iodate solution. Next the concentrations of stock solutions will be determined.

Due to the low iodine concentration of our solutions, the well- known general description of the analytical iodometric method is modified according to the follows:

- During the preparation of triiodide solutions the iodine stock solution has to be poured into the previously pipetted iodide in order to avoid the sublimation of iodine.

- Due to the relative slow reaction between the thiosulfate and iodine molecules, the titration should be carried out slowly near to the end point. You have to wait 10-15 seconds between adding drops.

- You have to wait a few minutes after the mixing of iodate and iodide ions containing solutions, because this reaction is not instantaneous.

- The dissolved oxygen must be removed from the sample (solution) before the addition of the necessary quantity of iodide. In order to achieve this purpose hydrogen carbonate has to be added to the acidic solution.

- The formed $CO_2$ displaces the oxygen from the solution and a $CO_2$ layer is formed above the titrated solution, which prevents oxygen to absorb into the solution during the titration process. Therefore, the solutions have to be agitated carefully during titration and the iodine will only be poured into the solution after the effervescency of solution!

- Acetic acid and freshly prepared starch solution should be used using the titration. Few drops of starch has to be added to the titrated solution just before the reaching of the end point.

**Titration of the $KIO_3$ solution with $Na_2S_2O_3$ solution:**

The calculated volume of $KIO_3$ solution, 5 $cm^3$ of concentrated acetic acid and ~20–50 $cm^3$ distilled water have to be pipetted into the iodine flask (Erlenmeyer-flask with polished plug). Next, ~1 g $KHCO_3$ should be cautiously added to the solution and after the effervescence, 0.3 g KI also has to be dissolved. The iodine flask has to be closed with the pre- moistened plug and put it in the dark place for 5 minutes. Finally, the titration processes should be carry out.

**Titration of the $I_2$ containing solution with $Na_2S_2O_3$ solution:**

~30-40 $cm^3$ distilled water and approx. 5 $cm^3$ of concentrated acetic acid have to be pipetted into the iodine flask. Next, ~1 g $KHCO_3$ should be cautiously added to the solution and after the effervescence, 0.3 g KI also has to be dissolved. After the KI dissolution, the iodine-containing sample has to be poured into the flask and the titration should be started immediately.

**The report should be containing the followings:**

- Theoretical background and formulas used in the evaluation of data

- the detailed planning of the experiment with all of the calculation steps

- Each primary experimental data (weighed amount of components, the results of titrations etc.)

- The measured spectra of solution also have to be attached to the report
- the result of the nonlinear parameter estimation process
- the figure illustrating the accuracy of the measurement (see fig. 12.2.)
- a short and straightforward discussion

**Possible test questions**

### I. part: Experimental planning

1. Describe the van't Hoff equation!

2. Define the followings: total concentration, equilibrium concentration, analytical concentration

3. How can you avoid the disproportion of $I_2$ during the reaction?

4. How do you use the ratio of triiodide and total iodine concentration when you planning the measurements?

5. Write down the basic equations of iodometry?! (thiosulfate-iodine and iodide-iodate reactions)

6. Define the ionic strength! What is the ionic strength of a $10^{-4}$ M concentration acetic acid solution ($K_d=1.8\times10^{-5}$)?

7. Define the ionic strength! What will be the ionic strength – assuming complete dissociation - after mixing the next solutions: 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?

8. What will be the concentration of $[I_3^-]$, if we mix together 100,0–100,0 $cm^3$ $5\times10^{-4}$ M of $I_2^-$ and $I^-$ solutions ($K_a=500$)?

### II. part: Measuring and evaluation

1. What kind of disturbing reactions may occur during the formation of triiodide?

2. What is the Beer-Lambert law? How can be expressed the absorbance in the $I_2$/ $I^-$/ $I_3^-$ equilibrium system?

3. Describe how to prepare the required $I_2$ solution?

4. How the total iodine concentration is determined?

5. What is the absorbance matrix?

6. How do you select the wavelength values for the evaluation process?