

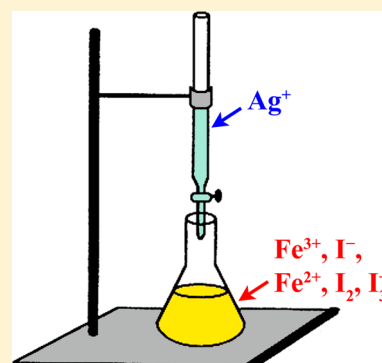
Studying Equilibrium in the Chemical Reaction between Ferric and Iodide Ions in Solution Using a Simple and Inexpensive Approach

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S Supporting Information

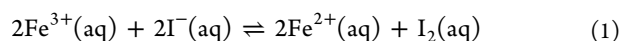
ABSTRACT: A laboratory experiment on the study of the chemical equilibrium based on the reaction between ferric and iodide ions in solution with the formation of ferrous ions, free iodine, and triiodide ions is developed. The total concentration of iodide and triiodide ions in the reaction mixture during the reaction is determined by the argentometric titration; the concentrations of the other reagents and products are calculated using the material balance equations. The dependence of the equilibrium constant on temperature is also considered. The average values of K_c are $2.5 \times 10^4 \text{ M}^{-1}$ ($35 \text{ }^\circ\text{C}$) and $4.5 \times 10^4 \text{ M}^{-1}$ ($45 \text{ }^\circ\text{C}$). The experiment uses common reagents and simple equipment and can be performed in any educational laboratory. The basic procedure of processing the experimental data is quite simple and can be easily performed even by first-year students; however, the experiment can be extended in several ways to be suitable for advanced laboratory courses for upper-year undergraduates. Possible extensions are discussed, including calculating the activity coefficients and activities of the aqueous species using the extended Debye–Hückel equation, and comparing the experimental equilibrium constant with the values calculated from the thermodynamic data on the standard electrode potentials or the standard enthalpies and Gibbs energies of formation.



KEYWORDS: First-Year Undergraduate/General, Second-Year Undergraduate, Upper-Division Undergraduate, Inorganic Chemistry, Physical Chemistry, Aqueous Solution Chemistry, Equilibrium, Thermodynamics, Titration/Volumetric Analysis, Hands-On Learning/Manipulatives

INTRODUCTION

The reaction between ferric and iodide ions in a solution



is well suited to demonstrate a concept of chemical equilibrium to the students. The reaction proceeds with a moderate rate,¹ which significantly depends on temperature: the equilibrium is established within 3–4 h at room temperatures, within 1.5–2 h at $35\text{--}40 \text{ }^\circ\text{C}$, and within 40–70 min at $45\text{--}50 \text{ }^\circ\text{C}$. The students clearly see how the concentrations of the reaction participants change, how the system approaches equilibrium, and how it depends on temperature. This experiment is present in classic and modern Russian textbooks on laboratory experiments in physical chemistry and is widely used in physical chemistry laboratory courses of Russian universities (see Supporting Information “The methods of a titrimetric determination of the reaction components”). Some attempts to transform the reaction 1 into a “clock reaction” and examine the kinetics of the oxidation of an iodide by ferric ions using the initial rates methods were performed,² but the description of an experiment concerning the study of the chemical equilibrium in this reaction is not present in textbooks written in English.

However, an original experimental technique contains a very serious methodological error. The goal of this study is to develop a new variation of this experiment.

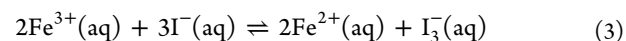
ORIGINAL EXPERIMENT AND ITS METHODOLOGICAL ERROR

The determination of the equilibrium concentrations of reagents and products is based on an assumption that the iodine, which is obtained while the reaction 1 proceeds, is titrated by the sodium thiosulfate. However, this assumption is wrong because sodium thiosulfate reacts not only with iodine but also with ferric ions² forming the complex ion $[\text{Fe}(\text{S}_2\text{O}_3)_2]^{-}$.

In addition, the authors of an original experiment took into account only the formation of free iodine and overlooked the possibility of the triiodide formation:



The sum of the reactions 1 and 2 gives the following equilibrium:



This study presents a new version of processing the experimental data, which considers the mutual formation of iodide and triiodide ions.

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Improving the Original Experiment

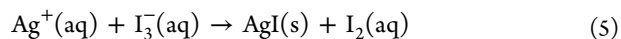
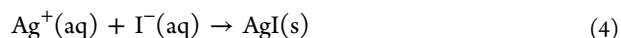
The advantage of the original experiment is that it does not require any complicated laboratory equipment and can be easily performed and reproduced even by the first or second-year undergraduate students. A new version of the experiment should also pass these requirements. The simplest solution was to find another titrimetric method with the indicator-based end point detection, which allows the determination of the equilibrium concentration of one of the reaction participants. A titration reaction should not have an influence on the main equilibrium, and the addition of extrinsic compounds into the reaction mixture should be avoided; therefore, only direct and substitution titration methods were considered but not back-titration ones. An argentometric titration of iodides with eosin was selected to develop the improved experiment.

The detailed description of the methodological error as well as the procedure of choosing the new suitable titration method is described in the [Supporting Information](#) "The methods of a titrimetric determination of the reaction components".

■ MODIFIED EXPERIMENT

The experiment starts with a preparation of 0.015 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.03 M KI solutions. The $\text{Fe}_2(\text{SO}_4)_3$ solution is used as the initial reagent instead of the FeCl_3 solution as in the original experiment because the presence of Cl^- in the reaction mixture prevents the correct argentometric determination of iodides. Two reaction mixtures with slightly different initial compositions (50 mL $\text{Fe}_2(\text{SO}_4)_3$ + 50 mL KI and 55 mL $\text{Fe}_2(\text{SO}_4)_3$ + 45 mL KI, respectively) are prepared and placed into a thermostat at the desired temperature (e.g., 35 °C), so that the total volume of the reaction mixture is 100 mL. While the reaction proceeds, aliquots of 10 mL are taken from the mixture every 15 min, 50 mL of distilled water cooled to 0 °C is added to them, and the resulting solutions are titrated with 0.02 M AgNO_3 solution using eosin as an indicator until a very noticeable precipitate appears. The titration does not affect the main reaction, because the [reaction 1](#) is quite slow at the low temperature, whereas the AgI formation reaction is very fast. After a while, the titration volumes from the consecutive samples become equal to each other within the experimental uncertainty. It is assumed that at this point the reaction reaches equilibrium. Then, the whole experiment is performed at the higher temperature (e.g., 45 °C).

The titration determines the total concentration of iodide and triiodide ions in the mixture:



The students make up and solve a system of equations, consisting of equivalence law and material and charge balance equations, to determine the equilibrium concentrations of all species in the solution. The data on the equilibrium constant of the [reaction 2](#) is required for calculations. The dependency of this constant (K_f) on temperature³ is the following:

$$\log K_f = \frac{555}{T} + 7.355 - 2.575 \cdot \log T \quad (6)$$

The students calculate the equilibrium constants of the [reaction 1](#) and, if needed, of the [reaction 3](#) for each of four experiments and the average values for each temperature. Then, they use the integral form of van't Hoff equation to estimate the

average enthalpy and entropy change of the reaction in the temperature interval under study.

A detailed description of the experiment is provided in the [Supporting Information](#) "The laboratory practice description".

Performing the Experiment with Students

The experiment can be incorporated into a standard laboratory practice lesson. Usually, 8–10 consecutive titrations (up to 150 min) at 35 °C and 4–6 titrations (up to 90 min) at 45 °C are needed. Therefore, the full experiment usually lasts for 4–5 h if all the necessary reagents and equipment were prepared beforehand. The instructor can assign higher reaction temperatures to reduce the experiment duration. To shorten it even further, the experiment can be run partially at single temperature without calculation of the enthalpy and entropy of reaction.

For the best performance, students are encouraged to work in pairs. One student takes care on the clock, pays attention on preparing a cooled distilled water, and takes the aliquots from the reaction mixture, while the other one performs all the titrations. An individual work is also possible, although it would increase the time needed for the experiment completion. The work in groups of three or more persons is discouraged.

Students must be warned that the titrations should be performed very carefully. The dropwise titration in the vicinity of the end point is very crucial. Since the samples contain the reaction mixture, there is no possibility to make several parallel titrations of one sample. Therefore, the careless titration may lead to an incorrect determination of the equilibrium point.

The instructor can assign an identical set of temperatures to all student groups and then ask them to pool their results and make a statistical analysis of K_c values. Alternatively, the instructor can give each group its own set of temperatures and then ask them to combine the results, plot a $\ln K_c = f\left(\frac{1}{T}\right)$ dependency, and calculate the average enthalpy and entropy of reaction using the least squares method.

■ HAZARDS

Silver salts are toxic! A brief exposure will not produce any immediate side effects other than the purple, brown, or black stains on the skin, but upon a constant exposure, the side effects including burns and eye damage will be noticeable. Silver nitrate is known to be a skin and eye irritant.⁴ In case of contact with silver nitrate solution or the silver iodide precipitate with skin or eyes, students should wash the affected area with water immediately. The waste silver salts should not be drained into the sink; they must be collected into the special vessels and then properly utilized.

■ DISCUSSION

The presented version of the experiment is very simple and may be implemented even into the general chemistry laboratory course for the first year students. In this case, the students simply calculate the equilibrium constants and thermodynamic properties of reaction. However, if the experiment is used in the physical chemistry or chemical thermodynamics courses for the upper-division undergraduates, the experimental results may be processed even further:

- The thermodynamic values of the equilibrium constants of [reactions 1](#) and [3](#) at the temperatures of the experiment may be calculated using the data on the standard enthalpies and the standard Gibbs energies of

formation of the reactants and the products⁵ or on the standard electrode potentials of the $\text{Fe}^{3+}/\text{Fe}^{2+}$, I_2/I^- , and I_2/I_3^- redox couples and their temperature coefficients⁶ and compared with the experimental results. This will however reveal an order-of-magnitude difference between the measured and the calculated constants. For example, the experimentally obtained values of K_c of the reaction 1 are $2.5 \times 10^4 \text{ M}^{-1}$ at 35 °C and $4.5 \times 10^4 \text{ M}^{-1}$ at 45 °C, and of the reaction 3 are $1.4 \times 10^7 \text{ M}^{-2}$ at 35 °C and $2.0 \times 10^7 \text{ M}^{-2}$ at 45 °C, whereas the calculated values of K of the reaction 1 are $2.3 \times 10^5 \text{ M}^{-1}$ at 35 °C and $4.3 \times 10^5 \text{ M}^{-1}$ at 45 °C, and of the reaction 3 are $1.4 \times 10^8 \text{ M}^{-2}$ at 35 °C and $2.1 \times 10^8 \text{ M}^{-2}$ at 45 °C. It is not a problem, however, since even the first year students are familiar with the concept of activities as well as with the fact that reactions involving charged species are affected by the ionic strength of the solution, and can at least qualitatively explain this difference.

- (b) Instead of calculating the concentration equilibrium constant, the students can calculate the ionic strength of the solution, the activity coefficients, and the activities of the ions using the extended Debye–Hückel equation and estimate the activity equilibrium constants K_a . The parameters in the Debye–Hückel equation at the temperatures of the experiment can be calculated using the electrostatic radii of the individual ions⁷ and the dependence of the dielectric constant of water on temperature:⁸

$$\begin{aligned} \epsilon(T) = & 87.74 - 0.4008(T - 273.15) \\ & + 9.398 \times 10^{-4}(T - 273.15)^2 \\ & + 1.41 \times 10^{-6}(T - 273.15)^3 \end{aligned} \quad (7)$$

The activity equilibrium constants are in a good agreement with the values calculated from the thermodynamic data.

The Supporting Information “The example of processing and analyzing the experimental data” gives a very detailed step-by-step example of the processing of experimental data.

The modified experiment was successfully implemented into the laboratory practice course on physical chemistry in Department of Analytical and Physical Chemistry of Chelyabinsk State University. The experiment is however still open for improvements, see the Supporting Information “The methods of a titrimetric determination of the reaction components” for further details. Some titration methods listed there were not tested due to the lack of appropriate reagents. Perhaps some of the readers could test them and find more applicable or offer another simple method to determine the equilibrium concentrations of the components in the reactions 1 and 3.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00958.

The methods of a titrimetric determination of the reaction components: the detailed description of the original experiment and the procedure of choosing the appropriate method for the modified one (PDF, DOC) The spreadsheet (“chem_equilib_calc.xls”) is designed for the instructor and helps him to quickly check the correctness of the students’ results (XLS)

Manual to the spreadsheet “chemical equilibrium calculation” (PDF, DOC)

The example of processing and analyzing the experimental data: a very detailed step-by-step explanation of the processing of experimental data, which describes the calculation of the activity corrected equilibrium constants and compares them with the theoretical values (PDF, DOC)

The laboratory practice description is designed for the students and contains the detailed description of the modified experiment (PDF, DOC)

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Notes

The authors declare no competing financial interest.

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