Kinetic study of iron(III) – thiocyanate reaction by stopped flow method

Theoretical background: P.W. Atkins: *Physical Chemistry*, 26.1–3 (4th edition), or 25.1–3 (6th edution) chapters.
Type of practice: In pairs.
Purpose of the experiment: Kinetic study of fast chemical reactions by stopped flow method.

1. Introduction

Chemical reactions were previously classified into two groups based on their rate. One group comprised reactions whose rate could be determined, while the other consisted of reactions whose rate could not be measured (due to their slowness or rapidity). Reactions that took place in less than one second were termed fast reactions. The development of the stopped-flow method (in the 1960s) made it possible to investigate rapid reactions. A stopped-flow spectrophotometer is an instrument—typically operating in the UV-vis range—equipped with a special mixing chamber characterized by a very short mixing time; in state-of-the-art equipment, this is approximately 3 ms. This technique has become particularly significant in the study of enzyme reactions, as these reactions occur over a very short timeframe—though not instantaneously—making them impossible to study using classical methods. The stopped-flow method enabled the investigation of enzyme reactions under pseudo-first-order experimental conditions. During the practice, the following reaction will be studied via stopped flow method:

$$Fe^{3+} + SCN^{-} = FeSCN^{2+}$$

In aqueous solutions, Fe^{3+} does not exist; instead, $Fe(H_2O)_6{}^{3+}$ and its deprotonated form are present. For the sake of simplicity, despite of this, we use the Fe^{3+} term in the following. Similarly, $FeOH^{2+}$ will denote the deprotonated form. The iron(III) ion forms intensely red-brown complexes with the thiocyanate ion, with a maximum coordination number of six. In sufficiently dilute solutions and with a large excess of Fe(III), practically only the first coordination step occurs. This reaction takes place within a fraction of a second. The resulting complexes exhibit intense light absorption around 460 nm. The progress of the reaction can be monitored by measuring the solution's absorbance over time. Due to the simplicity and reproducibility of the mechanism, this reaction is used to calibrate stopped-flow photometers.

2. Literature overview

Numerous research groups have investigated the kinetics of the iron(III)–thiocyanate reaction, assuming the reaction to be first-order with respect to both iron(III) and thiocyanate. The following description is based on the paper from J.F. Bellow, Jr.R.E. Connick and C.P. Coppel (J. Am. Chem. Soc., 80, 2961–2967, 1958).

In an aqueous solution containing iron(III) and thiocyanate ions, the following equilibrium complex-formation processes take place ($c^{\ominus}$ denotes the standard 1 mol/dm^3 concentration):

$$Fe^{3+} + SCN^{-} \underset{k/K_1}{\overset{k}{\rightleftharpoons}} FeSCN^{2+} \qquad K_1 = \frac{[FeSCN^{2+}]\cdot c^{\ominus}}{[Fe^{3+}]\cdot[SCN^{-}]} = 146$$

$$FeSCN^{2+} + SCN^{-} \rightleftharpoons Fe(SCN)_2{}^{+} \qquad K_2 = \frac{[Fe(SCN)_2{}^{-}]\cdot c^{\ominus}}{[FeSCN^{2+}]\cdot[SCN^{-}]} = 15{,}5$$

$$Fe(SCN)_{i-1}{}^{(4-i)+} + SCN^{-} \rightleftharpoons Fe(SCN)_i{}^{(3-i)+} \qquad K_i = \frac{[Fe(SCN)_i{}^{(3-i)+}]\cdot c^{\ominus}}{[Fe(SCN)_{i-1}{}^{(4-i)+}]\cdot[SCN^{-}]},$$

where the value of i can range from 3 to 6. The values of K_1 and K_2 specified above were used in the cited article.

[1]

Since $K_1 > K_2$ and the values of K_3 through K_6 are even smaller than K_2, practically only the mono-thiocyanate complex is formed when iron(III) ions are present in a very large excess relative to thiocyanate ions. In this case, all equilibria other than the first one are negligible.

If the *p*H of the solution exceeds 1-–1.5, the iron(III) aqua complex undergoes notable deprotonation and may also form polynuclear complexes. At higher pH values, these processes cannot be described solely by the equations above; the following processes must also be taken into account:

$$\mathrm{Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+} \qquad K_\mathrm{H} = \frac{[\mathrm{FeOH^{2+}}]\cdot[\mathrm{H^+}]}{[\mathrm{Fe^{3+}}]\cdot c^\ominus} = 2{,}05 \times 10^{-3}$$

$$\mathrm{2\,FeOH^{2+} \rightleftharpoons Fe_2(OH)_2{}^{4+}} \qquad K_\mathrm{D} = \frac{[\mathrm{Fe_2(OH)_2{}^{4+}}]\cdot c^\ominus}{[\mathrm{FeOH^{2+}}]^2} = 390$$

The rate equation describing the change in the concentration of the monocomplex:

$$\frac{\mathrm{d}\,[\mathrm{FeSCN^{2+}}]}{\mathrm{d}t} = k\cdot[\mathrm{Fe^{3+}}]\cdot[\mathrm{SCN^-}] - \frac{k}{K_1/c^\ominus}\cdot[\mathrm{FeSCN^{2+}}]. \tag{1}$$

If the thiocyanate does not undergo protonation under the experimental conditions, then at any point during the reaction it can exist only in the free state or bound in a monocomplex; thus, its concentration at any given time t can be expressed by the

$$[\mathrm{SCN^-}]_t = [\mathrm{FeSCN^{2+}}]_\infty + [\mathrm{SCN^-}]_\infty - [\mathrm{FeSCN^{2+}}]_t \tag{2}$$

equation (t=∞ is the equilibrium concentration). By combining equation (2) and equation (1), calculating $[\mathrm{SCN^-}]_\infty$ from K_1 kifejezéséből, and assuming that $[\mathrm{Fe^{3+}}]$ is constant (it is in large excess!), we can rearrange the equations to (the t index is omitted here):

$$\frac{\mathrm{d}\,[\mathrm{FeSCN^{2+}}]}{\mathrm{d}t} = k\cdot\left([\mathrm{FeSCN^{2+}}]_\infty - [\mathrm{FeSCN^{2+}}]\right)\cdot\left([\mathrm{Fe^{3+}}] + \frac{1}{K_1/c^\ominus}\right) \tag{3}$$

Integrating a (3) considering the boundary conditions of known iron(III) monothiocyanate concentration at t=0 and t=∞ leads to the following equation:

$$k\cdot t = \frac{1}{[\mathrm{Fe^{3+}}] + \dfrac{1}{K_1/c^\ominus}}\cdot\ln\frac{[\mathrm{FeSCN^{2+}}]_\infty - [\mathrm{FeSCN^{2+}}]}{[\mathrm{FeSCN^{2+}}]_\infty - [\mathrm{FeSCN^{2+}}]_0} \tag{4}$$

With the exception of the rate constant k, the quantities appearing in Equation (4) can be measured experimentally. In the cited article, plotting the values of $\ln([\mathrm{FeSCN^{2+}}]_\infty - [\mathrm{FeSCN^{2+}}])$ against time yielded a straight line, demonstrating the first-order dependence on thiocyanate—that is, under the conditions employed, only the mono-thiocyanate complex was formed. To calculate the rate constant, the values of $\ln([\mathrm{FeSCN^{2+}}]_\infty - [\mathrm{FeSCN^{2+}}])$ were plotted against time, and a straight line was fitted to the resulting points. Its slope is:

$$\mathrm{m} = k\cdot\left([\mathrm{Fe^{3+}}] + \frac{1}{K_1/c^\ominus}\right),$$

from which the second-order rate constant can be calculated, given the iron(III) concentration and the equilibrium constant. Values in the range of 200˜250 $\mathrm{M^{-1}s^{-1}}$ were obtained for the rate constants determined in this way. Comparing these values with data measured by other researchers under more basic conditions (around 24 $\mathrm{M^{-1}s^{-1}}$), they found that the hydrogen ion concentration has a significant effect on the reaction rate. To demonstrate this, they performed measurements in solutions of varying pH. Based on the results, they concluded that the reaction rate increases with increasing pH and that a base-catalyzed process must

[1] In the practical experiment, K_2 is not used, and the value of K_1 can be calculated using the empirical formula $\ln K_1 = 454/T + 0.429\cdot I + 2.98$ for a given thermodynamic temperature T and ionic strength I. This formula was derived from stability constants provided by IUPAC and yields the value of K_1 with an accuracy of at least 5 % within the applicable temperature and ionic strength ranges.

also be involved. Consequently, they supplemented their mechanism with steps whose rates depend on the hydrogen ion concentration. In addition to the deprotonation of the aqua complex, they considered the following reactions:

$$\mathrm{FeOH^{2+} + SCN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Fe(OH)(SCN)^+}$$
$$\mathrm{Fe(OH)(SCN)^+ + H^+ \rightleftharpoons FeSCN^{2+} + H_2O.}$$

A value in the order of $10^4\,\mathrm{M^{-1}s^{-1}}$ was determined for the rate coefficient k_3.

By plotting the rate coefficient k calculated from the measured data against the reciprocal of the hydrogen ion concentration, a straight line was obtained. Based on this, the following rate equation was formulated:

$$\frac{\mathrm{d}\,[\mathrm{FeSCN^{2+}}]}{\mathrm{d}t} = k_1 \cdot [\mathrm{Fe^{3+}}] \cdot [\mathrm{SCN^-}] + \frac{k_2 \cdot [\mathrm{Fe^{3+}}] \cdot [\mathrm{SCN^-}]}{[\mathrm{H^+}]} - \frac{k_1}{K_1/c^\ominus} \cdot [\mathrm{FeSCN^{2+}}] - \frac{k_2 \cdot [\mathrm{FeSCN^{2+}}]}{K_1/c^\ominus \cdot [\mathrm{H^+}]}.$$

Combining this with equation (1):

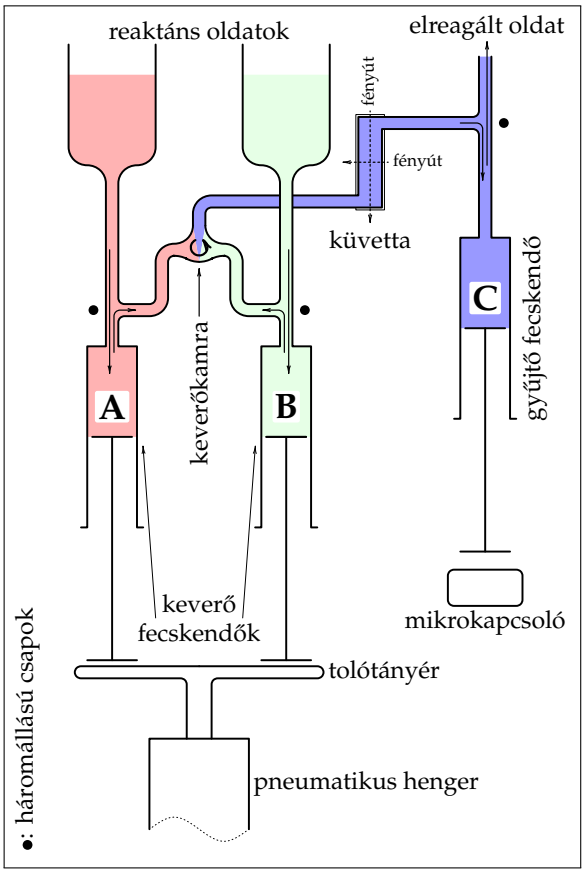
$$k = k_1 + \frac{k_2}{[\mathrm{H^+}]} \tag{5}$$

Here k is the formal second order rate constant at the pH of the investigation, k_1 is the pH independent rate constant,while k_2 is the hydroxide concentration dependent second order rate constant. The catalytic effect was explained by the fact that the hydroxide ion in the coordination sphere weakens the dative bond between the iron(III) ions and the water molecules, thereby facilitating the exchange of thiocyanate ions and water molecules. According to another hypothesis, the hydroxide ion interacts with the electron system of the iron(III), resulting in a more stable activated complex.

3. The stopped-flow technique

Only a few companies worldwide manufacture commercially available instruments of this type. These are typically single-beam photometers in which the sample's absorbance is measured relative to the previously measured absorbance of a reference solution. Monochromatic light is generated using an optical grating connected via an optical glass fiber to a temperature controlled quartz reactor.

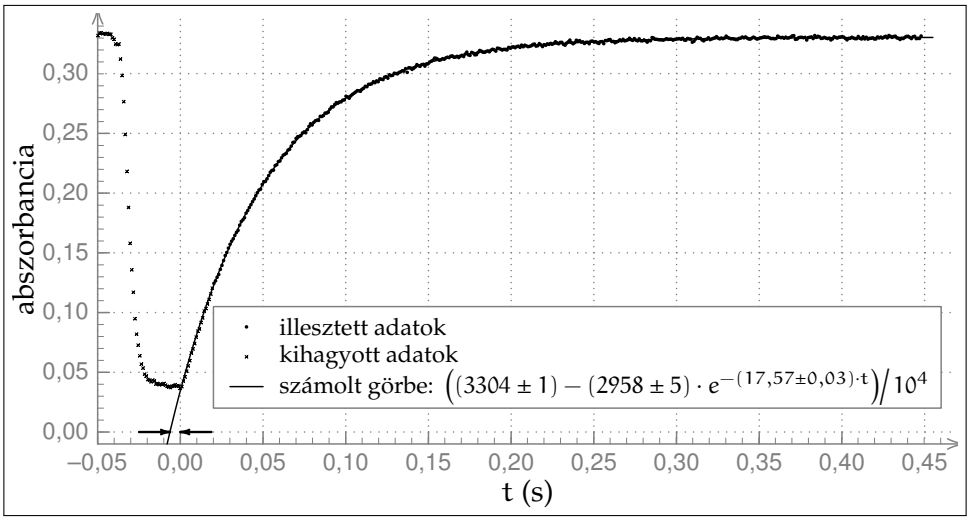
In the stopped-flow technique, reagents are delivered into a mixing chamber using two pneumatic syringes (A and B) (see Figure 1). Downstream of the mixing chamber, there is a cuvette followed by another syringe (C). When solution is driven from syringes (A) and (B) through the cuvette, the fresh solution displaces the solution remaining from the previous measurement. Additionally, the flowing solution pushes syringe (C) until it activates a microswitch; upon actuation, the flow stops and the recording of the absorbance-versus-time curve begins. This technique enables the monitoring of reactions with half-lives significantly shorter than one second.



1. ábra. Schematic diagram of stopped-flow instruments.

3.1. Dead-time

When the plunger of syringe (C) depresses the microswitch, the flow stops and the spectrophotometric measurement begins. The reaction commences within the mixing chamber; consequently, a portion of the reactants has already been converted by the time detection starts. A few milliseconds



2. ábra. Illustration of dead time. The distance between the two arrows indicates this time interval on an increasing absorbance-vs.-time curve measured using a stopped-flow apparatus. (The sharp drop in absorbance at the beginning of the curve is observed due to the washing out of the solution that has already reacted.)

elapse as the reaction mixture travels from the mixing chamber to the cuvette, meaning the start time of detection does not coincide with the onset of the reaction. This interval is known as the dead time. This can significantly affect measurement accuracy (see Figure 2), particularly during the initial phase of the reaction, as the true absorbance-versus-time data points differ most markedly from the values read from the graph in this region.

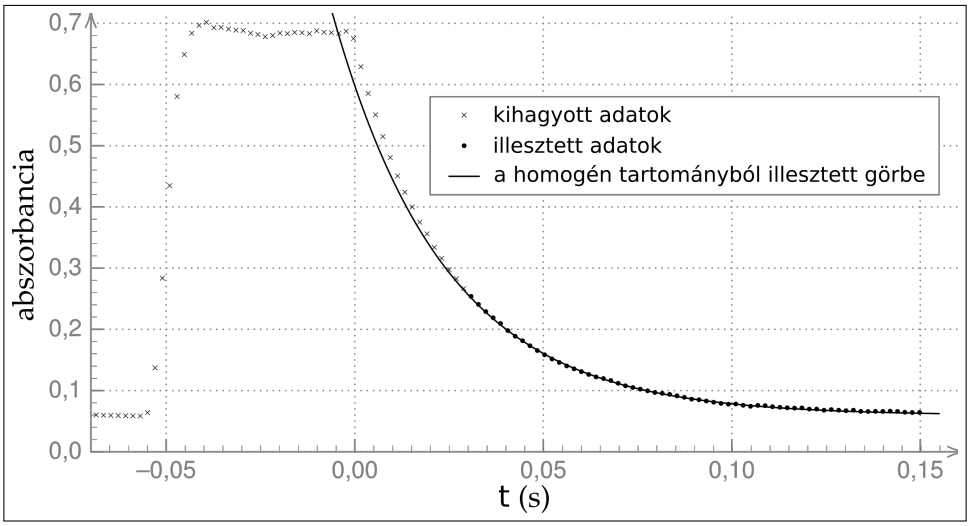
The dead time can be easily determined by examining a pseudo-first-order reaction in which colored species are converted into a colorless product. Let A_1 be the absorbance at the moment the flow stops ($t = 0$). Let A_0 denote the true initial absorbance—that is, the absorbance measured in a mixture completely devoid of the colorless product. The dead time (t_d) is equal to the time required for the absorbance to change from A_0 to A_1. For a first-order reaction, this is given by $t_d = \ln(A_0/A_1)/k$, where k is the reaction rate constant. If the process is merely pseudo-first-order, then k represents an apparent rate constant.

3.2. Mixing-time

Based on the principles of fluid dynamics, mixing in a stopped-flow apparatus proceeds in two or three stages. In the first stage, the mixer "segments" the solutions by alternately injecting small aliquots—on the order of a few tenths of a microliter—from syringes (A) and (B) into the mixing chamber. In the second stage, turbulent flow and diffusion equalize the concentration differences between the alternating segments of solutions (A) and (B). This concentration equilibration occurs within the dead volume and continues into the cuvette if it was not fully completed within the dead volume.

The third stage occurs when mixing is not yet complete at the moment the flow stops. From that point on, only diffusion is at work, yet this is sufficient, as diffusion fully homogenizes such small volume elements within a few milliseconds.

For a few milliseconds after the solutions are "shot together" (the mixing time), the reaction proceeds more slowly because the reactant concentration has not yet reached the level corresponding to complete mixing. Consequently, if the reactant is "colored" (light-absorbing) and the product is "colourless" the measured absorbance is higher than the true value—appearing as though the reaction were slower (Figure 3). Mixing efficiency increases as the mixer divides the solutions into smaller volume elements, as the flow becomes more turbulent, and as the rate of diffusion increases. Diffusion, in turn, is faster when the viscosity of the solutions and the mass of the reacting particles are lower. Figure 2 illustrates how the solution's absorbance changes within the stopped-flow cuvette for the reaction under study, in which the product is the light-absorbing species.



3. ábra. Illustration of the effect of mixing time on a decreasing absorbance vs. time curve measured with a stopped-flow apparatus.

4. Execution of the exercise

4.1. A végrehajtandó feladat

Determine the rate coefficients (k_1 and k_2; see equation (5) and the preceding equations) for the iron(III)–thiocyanate reaction at room temperature using a stopped-flow spectrophotometer, based on a pre-prepared measurement plan!

4.2. Measurement Design

290 Following the instructor's guidelines, design a series of 13 solutions for measurement in which the initial concentrations of iron(III) and thiocyanate ions vary in direct proportion, while the reciprocal of the initial hydrogen ion concentration varies uniformly within the following ranges:

$$[Fe^{3+}]_0 = 0{,}01 - 0{,}001\,\mathrm{M}; [SCN^-]_0 = 0{,}001 - 0{,}0001\,\mathrm{M}; [H^+]_0 = c_H - 0{,}01\,\mathrm{M},$$

where the value of c_H is specified by the lab instructor within the range of 0.2—0.4 M.

505 Ionic strength also affects the rate coefficient; therefore, it must be maintained at a constant value during the measurement using a highly soluble, inert salt. The specific salt and the magnitude of the ionic strength (between 0.6 and 1.0 M) are determined by the laboratory instructor, taking into account the ionic strength that can be kept constant within the concentration ranges specified above. [2]

618 To ensure the measurement plan is clear, it is advisable to create a table listing the measurement sequence number, the initial concentrations of iron(III), thiocyanate, and hydrogen ions in the cuvette, the ionic strength, and the salt concentration required to adjust it. It is practical to prepare three series of reaction mixtures, each consisting of five samples, in which the concentrations of two reagents remain constant while that of the third component varies within the specified ranges. This would entail 15 mixtures; however, with careful planning, the middle sample of each series can be the same solution. If the planned initial concentrations in the cuvette are as follows:

$[Fe^{3+}]_0$:	f1,	f2,	f3,	f4,	f5 M
$[H^+]_0$:	h1,	h2,	h3,	h4,	h5 M
$[SCN^-]_0$:	s1,	s2,	s3,	s4,	s5 M

[2] For example, if the maximum acid concentration is 0.4 M, the ionic strength cannot be lower than 0.812 M due to the dilution detailed later in the description.

1. táblázat. An example of designing the composition of reaction mixtures.

Varied parameter	$[Fe^{3+}]_0$				$[SCN^-]_0$				$[H^+]_0$				
Solution number	1	2	3	4	5	6	7	8	9	10	11	12	13
$[Fe^{3+}]_0$	f1	f2	f4	f5	f3				f3	f3	f3	f3	f3
$[H^+]_0$	h3	h3	h3	h3	h3				h1	h2	h4	h5	h3
$[SCN^-]_0$	s3				s1	s2	s4	s5	s3				s3

Then table 1 shows the composition of the reaction mixtures to be prepared. The reaction mixture corresponding to the last column is common to all three previous solution series, thereby reducing the number of solution pairs to be prepared to 13. The table also indicates that only those solutions containing the reagent whose concentration is being systematically varied need to be prepared individually. For instance, if the value of $[Fe^{3+}]_0$ in the reaction mixture varies while $[SCN^-]_0$ remains constant, it is advisable to prepare the solution with concentration $s3$ in a volume sufficient for all measurements requiring that specific concentration; this significantly reduces the time required for solution preparation.

4.3. Preparing stock solutions

Based on the measurement plan, prepare four stock solutions and prepare the solutions at the calculated concentrations by mixing them in various proportions or by diluting them. Each series of measurements requires 50 cm³ of iron(III) solution and 50 cm³ of thiocyanate solution; the solutions—which are to be used for multiple measurements and thus require a larger total volume—must be prepared with this in mind. The stock solutions are

1. $Fe(NO_3)_3$ (+acid)
2. $HClO_4$ or HNO_3
3. NaSCN or KSCN
4. $NaClO_4$ or $NaNO_3$,

The iron(III) stock solution must also contain at least 0.005 M strong acid to suppress metal ion hydrolysis and reliably prevent precipitation. In the design, this amount of acid also contributes to the target $[H^+]_0$.

When preparing the solutions, account for the fact that, due to the dilution occurring when the iron(III)- and thiocyanate-containing solutions are mixed, the concentration of the solution entering the stopped-flow cuvette will be half that of the original.

Prepare the solution pairs for the measurement by combining all components—except for the thiocyanate—into a single solution. Mixing time can be reduced by rapidly combining solutions of equal ionic strength, as mixing efficiency depends on the difference in ionic strength (due to variations in density and viscosity). Therefore, add a sufficient amount of ionic strength-adjusting solution to the thiocyanate solutions to ensure that the ionic strengths of the two solutions are identical.

Weigh the materials required for preparing the stock solutions on an analytical balance!

Due to the variable water-of-crystallization content of iron(III) nitrate, a stock solution of precise concentration cannot be prepared simply by weighing; therefore, the exact iron(III) concentration must be determined using a classical analytical method.

The measurement plan must be presented to the laboratory instructor before the experiments begin!

4.4. Determination of iron(III) concentration by complexometry

Iron(III) ions form a stable complex with EDTA, allowing for direct titration at pH 2–3 (an acidic solution is required to prevent the precipitation of iron(III) hydroxide). Sulfosalicylic acid (forming a violet complex) or Tiron (forming a blue complex) can be used as an indicator to signal the endpoint. In both cases, the solution

2. táblázat. Details of the evaluation of a representative series of measurements.

$[Fe(III)]_0$/M	$[SCN^-]_0$/M	$[H^+]$/M	I/M	k_{pseudo}/s^{-1}	$k/(M^{-1}s^{-1})$
0,0050	0,00025	0,025	0,249	17,71±0,16	1494
0,0050	0,00050	0,025	0,250	17,81±0,14	1503
0,0050	0,00100	0,025	0,250	18,30±0,04	1544
0,0025	0,00025	0,025	0,249	14,28±0,21	1527
0,0025	0,00050	0,025	0,250	14,27±0,13	1526
0,0025	0,00100	0,025	0,250	14,47±0,09	1547
0,0100	0,00025	0,100	0,249	10,98±0,03	652
⋮	⋮	⋮	⋮	⋮	⋮

is titrated until it becomes colorless or the characteristic color of iron(III) appears (at lower *p*H values, the iron(III) solution is colorless, whereas above *p*H 2, it turns increasingly yellow).

If necessary, adjust the *p*H of the solutions with 1.5 M HCl or 1.5 M NaOH (checking the *p*H with indicator paper); then, after adding 3 drops of indicator, heat the solution to 40–50°C and titrate with EDTA standard solution until the yellow color of the Fe(III)-EDTA complex persists.

4.5. Recording the spectra

Switch on the spectrophotometer approximately 15 minutes before starting the measurement. The instrument is switched on and set up in consultation with the laboratory instructor; only the general operating procedure is described here.

From the measurement plan, select the series of measurements with the highest concentrations of iron(III) and thiocyanate ions. Record the spectra in the 350–500 nm range for iron(III) monothiocyanate solutions prepared by mixing approximately 5–5 cm^3 of each solution in a 1:1 ratio. Based on the spectrum, select the wavelength to be used for the stopped-flow measurements. When selecting the wavelength, ensure that the absorbance of the iron(III) monothiocyanate complex falls within the 0.1–3.5 range, where it follows a linear trend in accordance with the Beer-Lambert law; consult the laboratory instructor if values outside this range are obtained.

When filling the syringes, ensure there are no air bubbles inside, as light scatters off air bubbles entering the cuvette, which can cause significant measurement errors. Rinse the syringes before measuring each solution.

Record the room temperature in the log during the measurement. The measurement of each solution must be repeated to ensure that a potentially faulty injection does not cause issues. At least three valid measurements are required for each pair of solutions.

4.6. Evaluation of experimental data

Copy the recorded spectra onto a (virus-free) USB storage device. Perform non-linear parameter estimation on the appropriate section of the spectra to determine the pseudo-first-order rate coefficients k_{pseudo} based on the following equation:

$$A_t = A_\infty - (A_\infty - A_0) \cdot e^{-k_{pseudo} \cdot t} \tag{6}$$

Here, A_∞ is the absorbance of the solution after equilibrium is reached, $(A_\infty - A_0)$ is the experimentally measured change in absorbance, and A_t is the absorbance at time t. In the equation, both A_∞ and A_0 are values to be determined via curve fitting. A plot illustrating the parameter estimation should be prepared for one arbitrarily selected case; for the other cases, it suffices to record the parameters in the report. Non-linear

parameter estimation may be performed using any software approved by the instructor (e.g., Origin, Excel Solver, QtiPlot, etc.).

The rate constant of the actual second-order process can be calculated from the determined apparent rate constant using the formula $k_{\text{pseudo}} = k \cdot \left([\text{Fe}^{3+}] + 1/K_1\right)$ based on equation (4), where K_1 is calculated at a given temperature and ionic strength using the formula provided in footnote 1 of the practical description.

Table 2 lists some representative compositions as well as the calculated rate constants k_{pseudo} and k. Data should be summarized in the report in a similar manner, including the experimental conditions. Taking these into account, the evaluation is performed as follows:

1. Calculate the value of k for each solution, separately for the repeated measurements.
2. Plot all the fitted second-order rate constants (k) as a function of the reciprocal of the hydrogen ion concentration. Interpret the distribution of the values determined for identical $[\text{H}^+]$ but varying $[\text{SCN}^-]$ and [Fe(III)] concentrations.
3. Construct a combined plot to illustrate the functional relationships k vs. $[\text{H}^+]^{-1}$, k vs. $[\text{SCN}^-]$, and k vs. [Fe(III)]. It is advisable to plot the latter two datasets using a shared abscissa axis—distinct from the one used for $[\text{H}^+]$—by plotting the $[\text{SCN}^-]$ values multiplied by ten. Fit a straight line to the k vs. $[\text{H}^+]^{-1}$ dataset, and determine the values of the rate constants k_1 and k_2 (see Eq. 5)—along with their statistical parameters—from the intercept and slope. Similarly, fit straight lines to the k vs. $[\text{SCN}^-]$ and k vs. [Fe(III)] datasets, and report their equations along with the standard deviations of the fitted parameters. Interpret the results of all three fits.

Review questions

Week 1: planning the measurement, preparing stock solutions

1. What complex formation processes occur in a strongly acidic system containing iron(III) and thiocyanate?
2. How can it be ensured that only a 1:1 complex forms in the system under investigation?
3. Which equilibrium processes are significant around pH $\sim$ 2 in an Fe(III) solution?
4. What additional equilibrium processes become significant if the pH is increased in a solution containing both Fe(III) and thiocyanate?
5. What is ionic strength, and what is its significance in the study of ionic reactions?
6. How can constant ionic strength be ensured in the reaction mixture?
7. Why is it advisable to maintain the same ionic strength in the solutions to be mixed?
8. Why cannot the concentrations in the solutions to be mixed be identical to the intended concentrations of the reaction mixtures?
9. What considerations must be taken into account when preparing stock solutions?
10. If multiple series of solutions are measured simultaneously, how can the number of solutions to be prepared be reduced?
11. What is the maximum thiocyanate concentration in a solution that, when mixed in a 1:1 volume ratio with 0.0070 M $Fe(NO_3)_3$ solution, results in a 12-fold stoichiometric excess of Fe(III)?
12. A five-member series of solutions must be prepared in which $[H^+]$ varies between 0.015 and 0.35 M, such that the $1/[H^+]$ values change uniformly. What are the numerical values of the five concentrations?
13. What must the $NaClO_4$ concentration be in a solution with an ionic strength of 0.50 M, if the solution also contains 0.010 M $Fe(NO_3)_3$ and 0.10 M $HClO_4$?
14. What volume (in cm^3) of 0.0500 M $Fe(NO_3)_3$ solution (which also contains 0.0100 M perchloric acid) and what volume (in cm^3) of 0.800 M $HClO_4$ solution must be measured into a 50.0 cm^3 flask so that, after diluting to the mark, the resulting solution is 0.0100 M in Fe(III) and 0.020 M in H^+?

Week 2: Measurement and evaluation

1. How do you determine the iron(III) content of a solution using complexometry?
2. Describe the essence of the stopped-flow method in 3–5 sentences.
3. Draw a schematic diagram of a stopped-flow apparatus.
4. What is dead time? Explain in two or three sentences why dead time exists.
5. What is mixing time, and what effect does it have on the measured absorbance vs. time curves?
6. Write down the rate equation for the formation of $FeSCN^{2+}$ and explain it in 2–3 sentences.
7. How do you determine the wavelength to be used for the kinetic measurements?
8. What must be considered during the measurements to ensure the recorded kinetic curves are accurate?
9. Under what simplifying conditions can a second-order rate constant (k) be calculated for the system under investigation?
10. Based on what relationship do you evaluate your measurement data?
11. What does the term "pseudo-first-order kinetics" mean?
12. Based on the initial concentrations, a solution contains 0.6 M $NaNO_3$, 0.01 M HNO_3, 0.002 M $Fe(NO_3)_3$, and 0.0001 M KSCN. What is the ionic strength of the solution if *(a)* no reaction occurs in the solution or *(b)* the iron(III) monocomplex forms to 50% of the stoichiometrically possible extent? By what percentage does the reaction change the ionic strength calculated in point (a)?
13. How many grams of $Fe(NO_3)_3 \cdot 9H_2O$ must be accurately weighed on an analytical balance to prepare 250.0 cm^3 of a 0.04 M Fe(III) stock solution?
    A_r(Fe, O, N, H)=55.85; 16.00; 14.01 and 1.01
14. With initial concentrations of $[Fe(III)]_0$=0.005 M, $[SCN^-]_0$=0.0005 M, and $[H^+]_0$=0.02 M, the measured pseudo-first-order rate constant was found to be 18.5 s^{-1}. What is the value of the true second-order rate constant at the pH of the measurement?