

# Kinetics and Mechanism of Iodide Oxidation by Iron(III):

## A Clock Reaction Approach

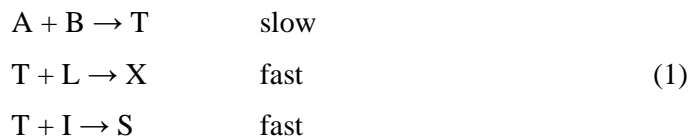
### Student handout

#### *Clock reactions*

Clock reactions are named after the analogy between chemical changes in such reactions and an alarm clock. You cannot tell whether the alarm clock is working or not until it goes off; it is only then that you know it has been working the whole time.

In a clock reaction, chemical change becomes visible (“the alarm clock goes off”) only after the reaction has reached a certain extent. There are three steps in each clock reaction. The first is a slow formation of a chemical intermediate. The second is a fast consumption of the intermediate by the limiting reagent. The third step is responsible for the colour change. However, that step takes place only after the limiting reagent has been consumed.

The three steps are easily presented by the equations:



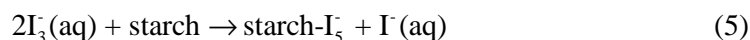
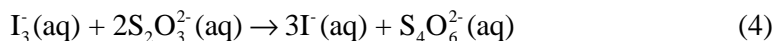
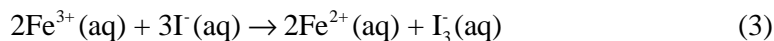
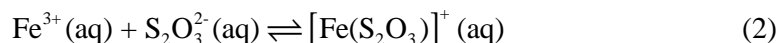
where the initial reaction mixture contains A, B, L and I. L is the limiting reagent, and I is the indicator. S is the chemical species that sends out a signal (colour change) (*I*).

#### Experiment 1:

- Prepare 250 mL of solution A ( $[\text{Fe}(\text{NO}_3)_3] = 0.025 \text{ mol L}^{-1}$ ,  $[\text{HNO}_3] = 0.3 \text{ mol L}^{-1}$ ) in a 400 mL beaker.
- Dissolve 1 g of starch in 100 mL of boiling distilled water with stirring.
- Prepare 250 mL of solution B ( $[\text{KI}] = 0.043 \text{ mol L}^{-1}$ ,  $[\text{Na}_2\text{S}_2\text{O}_3] = 3.2 \text{ mmol L}^{-1}$ ,  $w(\text{starch}) = 0.04 \%$ ) in a 600 mL beaker.
- Quickly pour solution A into solution B.

*Questions:*

1. What have you observed and how is this consistent with clock reaction behaviour?
2. Chemical changes in this clock reaction can be presented by the following set of equations (1):



The complex  $[\text{Fe}(\text{S}_2\text{O}_3)]^+$  is purple and the starch-pentaiodide complex is blue. Note that equation (2) presents a reversible reaction which occurs in the reaction mixture but is not included in the clock reaction scheme (1) given above.

Explain how the set of chemical changes (2–5) is responsible for the clock effect in this reaction. Which of steps (2–5) is the slow step, and why is this so? Identify the limiting reagent.

***Clock reaction kinetics***

The kinetics of a reaction transformed into a clock reaction (i.e. the kinetics of reaction  $\text{A} + \text{B} \rightarrow \text{T}$  in reaction scheme (1)) is easily investigated by the initial rates method. All one has to measure is the time elapsed from the mixing of the two solutions to the sudden colour change (sending out a signal) (2–4).

For the oxidation of iodide by ferric ions (3) the reaction rate can be defined as:

$$v = -\frac{d[\text{Fe}^{3+}]}{dt} \quad (6)$$

The initial reaction rate can then be approximated by:

$$v_0 \approx -\frac{\Delta[\text{Fe}^{3+}]}{\Delta t} \quad (7)$$

with  $\Delta[\text{Fe}^{3+}]$  being the change in the concentration of ferric ions in the initial period of the reaction. If  $\Delta t$  is the time measured, then  $\Delta[\text{Fe}^{3+}]$  is the decrease in ferric ion concentration from the moment of mixing to the moment of complete thiosulfate (the limiting reagent) consumption. Therefore, from the reactions' stoichiometry it follows:

$$-\Delta[\text{Fe}^{3+}] = [\text{S}_2\text{O}_3^{2-}]_0, \quad (8)$$

and consequently:

$$v_0 = \frac{[\text{S}_2\text{O}_3^{2-}]_0}{\Delta t}. \quad (9)$$

The initial thiosulfate concentration is constant and significantly lower than that of ferric and iodide ions. The above expression enables us to measure the initial reaction rate by measuring the time required for the sudden colour change to take place,  $\Delta t$ .

Suppose that the dependence of the initial reaction rate on ferric and iodide ion concentrations can be expressed as:

$$v_0 = k [\text{Fe}^{3+}]_0^x [\text{I}^-]_0^y; \quad (10)$$

$x$  is the reaction order with respect to  $\text{Fe}^{3+}$  and  $y$  is the reaction order with respect to  $\text{I}^-$ .

From equations (9) and (10), it follows:

$$\frac{[\text{S}_2\text{O}_3^{2-}]_0}{\Delta t} = k [\text{Fe}^{3+}]_0^x [\text{I}^-]_0^y. \quad (11)$$

If the initial concentration of only one reactant is varied while the initial concentrations of the other participants are kept unchanged, it is possible to determine the order of reaction with respect to the reactant whose concentration is being varied.

*Questions:*

3. Why is it important to keep the initial thiosulfate concentration significantly lower than that of ferric and iodide ions?

***The measuring method***

The experiments are conducted in a thermostated cell placed on a magnetic stirrer (Fig. 1). A total of 55 mL of solution A (containing  $\text{Na}_2\text{S}_2\text{O}_3$ , KI,  $\text{KNO}_3$  and starch) is placed in the cell and 5 mL of solution B (containing  $\text{Fe}(\text{NO}_3)_3$  and  $\text{HNO}_3$ ) is placed in the syringe. Solution A is stirred by a magnet. Solution B is injected into solution A and a stop watch is started at that point. Time is recorded at the moment the solution suddenly turns dark blue. The experiment is conducted three times for each concentration.

The ionic strength is set to  $I_c = 1.0 \text{ mol L}^{-1}$  by  $\text{KNO}_3$  and  $\text{HNO}_3$  in order to keep it constant during the course of reaction.

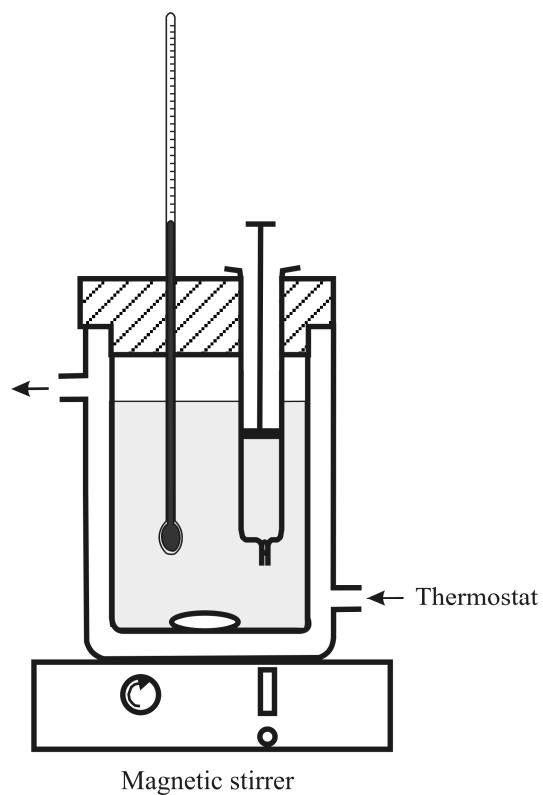


Figure 1. The apparatus used for the monitoring of reaction kinetics.

*Questions:*

4. Why are the experiments performed in a thermostated cell?
5. Why is it important to keep the ionic strength constant during the course of the reaction?
6. Why are  $\text{HNO}_3$  and  $\text{KNO}_3$  used to set the ionic strength?

### *The effect of thiosulfate concentration on reaction rate*

#### Experiment 2:

- Vary the initial thiosulfate concentration according to Table 1 and measure the time  $\Delta t$  for each concentration three times. Note the results in Table 1.
- The initial concentrations of other species (at the time of mixing of solutions A and B) should be as follows:  
 $[\text{Fe}(\text{NO}_3)_3]_0 = 6.5 \text{ mmol L}^{-1}$ ,  $[\text{KI}]_0 = 20.0 \text{ mmol L}^{-1}$ ,  $[\text{HNO}_3]_0 = 0.1 \text{ mol L}^{-1}$ ,  
 $[\text{KNO}_3]_0 = 0.9 \text{ mol L}^{-1}$ ,  $w(\text{starch}) = 0.02 \%$ .
- The measurements are conducted at 25 °C.

Table 1. The values of  $\Delta t$  for varying sodium thiosulfate initial concentration.

$[\text{Na}_2\text{S}_2\text{O}_3]_0/10^{-4} \text{ mol L}^{-1}$	$\Delta t_1/\text{s}$	$\Delta t_2/\text{s}$	$\Delta t_3/\text{s}$	$\overline{\Delta t}/\text{s}$
1.0				
2.0				
3.0				
4.0				
5.0				
6.0				
7.0				

#### *Questions:*

7. Analyze the results (average  $\Delta t$  values) according to equation (11) both graphically and by means of regression analysis.
8. Are the results consistent with equation (11)?
9. Explain the dependence of  $\Delta t$  on the initial thiosulfate concentration in terms of clock reaction behaviour.

### *The effect of iodide concentration on reaction rate*

#### Experiment 3:

- Vary the initial iodide concentration according to Table 2 and measure the time  $\Delta t$  for each concentration three times. Note the results in Table 2.
- The initial concentrations of other species (at the time of mixing of solutions A and B) should be as follows:  
 $[\text{Fe}(\text{NO}_3)_3]_0 = 8.5 \text{ mmol L}^{-1}$ ,  $[\text{Na}_2\text{S}_2\text{O}_3]_0 = 0.2 \text{ mmol L}^{-1}$ ,  $[\text{HNO}_3]_0 = 0.1 \text{ mol L}^{-1}$ ,  
 $[\text{KNO}_3]_0 = 0.9 \text{ mol L}^{-1}$ ,  $w(\text{starch}) = 0.02 \%$ .
- The measurements are conducted at 25 °C.

Table 2. The values of  $\Delta t$  for varying potassium iodide initial concentration.

$[\text{KI}]_0 / (10^{-3} \text{ mol L}^{-1})$	$\Delta t_1 / \text{s}$	$\Delta t_2 / \text{s}$	$\Delta t_3 / \text{s}$	$\overline{\Delta t} / \text{s}$
7.50				
8.75				
10.00				
11.25				
12.50				
13.75				
15.00				

#### *Questions:*

10. Analyze the results (average  $\Delta t$  values) according to equation (11) both graphically and by means of either linear ( $\ln \Delta t$  vs.  $\ln [\text{I}]_0$ ) or nonlinear ( $\Delta t$  vs.  $[\text{I}]_0$ ) regression analysis.
11. What is the reaction order with respect to iodide?

### *The effect of ferric ion concentration on reaction rate*

#### Experiment 4:

- Vary the initial ferric ion concentration according to Table 3 and measure the time  $\Delta t$  for each concentration three times. Note the results in Table 3.
- The initial concentrations of other species (at the time of mixing of solutions A and B) should be as follows:  
 $[\text{KI}]_0 = 0.013 \text{ mol L}^{-1}$ ,  $[\text{Na}_2\text{S}_2\text{O}_3]_0 = 0.25 \text{ mmol L}^{-1}$ ,  $[\text{HNO}_3]_0 = 0.1 \text{ mol L}^{-1}$ ,  
 $[\text{KNO}_3]_0 = 0.9 \text{ mol L}^{-1}$ ,  $w(\text{starch}) = 0.02 \%$ .
- The measurements are conducted at 25 °C.

Table 4. The values of  $\Delta t$  for varying ferric nitrate initial concentration.

$[\text{Fe}(\text{NO}_3)_3]_0/10^{-3} \text{ mol L}^{-1}$	$\Delta t_1/\text{s}$	$\Delta t_2/\text{s}$	$\Delta t_3/\text{s}$	$\overline{\Delta t} / \text{s}$
5.0				
6.0				
7.0				
8.0				
9.0				
10.0				
11.0				
12.0				

#### *Questions:*

12. Analyze the results (average  $\Delta t$  values) according to equation (11) both graphically and by means of either linear ( $\ln \Delta t$  vs.  $\ln [\text{Fe}^{3+}]_0$ ) or nonlinear ( $\Delta t$  vs.  $[\text{Fe}^{3+}]_0$ ) regression analysis.
13. What is the reaction order with respect to ferric ions?

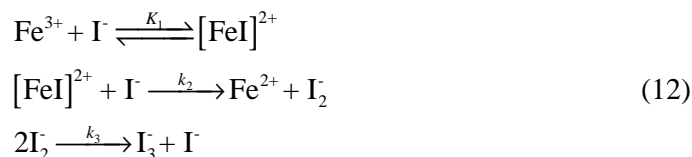


### *Combining the results*

Chemical kinetics investigates reactions rates and reaction mechanisms. To study the reaction rate means to determine reaction orders which give us the rate law. From the rate law, one can easily calculate the reaction rate coefficient. Based on the rate law and possibly other kinetic measurements, one can suggest a reaction mechanism.

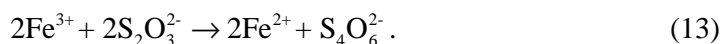
### *Questions:*

14. Write the rate law (equation (10)) for the reaction studied.
15. Calculate the values of the reaction rate coefficient,  $k$ , from the results of experiments 2–4.
16. A possible mechanism of the oxidation of iodide by ferric ions is (5–8):



By applying the steady state approximation for the intermediate  $\text{I}_2^-$ , show that this mechanism is in accordance with the rate law obtained experimentally.

17. There is another redox reaction taking place in the system investigated, namely the oxidation of thiosulfate to tetrathionate by ferric ions (9,10):



Are you able to say if this reaction has interfered with the monitoring of the kinetics of reaction (3)?

## Literature

1. Shakhshiri, B. Z. *Chemical Demonstrations*; The University of Wisconsin Press; Wisconsin, 1992; Vol. 4, pp 51–55.
2. Creary, X.; Morris, K. M. *J. Chem. Educ.* **1999**, *76*, 530–531.
3. Vitz, E. *J. Chem. Educ.* **2007**, *84*, 1156–1157.
4. Copper, C. L.; Koubek, E. *J. Chem. Educ.* **1998**, *75*, 87–89.
5. Nord, G.; Pedersen, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233–2242.
6. Langmuir, M. E.; Hayon, E. *J. Phys. Chem.* **1967**, *71*, 3808–3814.
7. Hubbard, C. D.; Jones, J. G.; McKnight, J. J. *Chem. Soc., Dalton Trans.* **2000**, 3143–3148.
8. Fudge, A. J.; Sykes, K. W. *J. Chem. Soc.* **1952**, 119–124.
9. Schmid, H. Z. *Phys. Chem. A* **1930**, *148*, 321–336.
10. Holluta, J.; Martini, A. Z. *Anorg. Allg. Chem.* **1924**, *140*, 206–226.

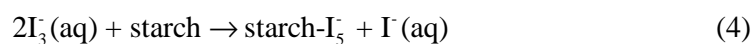
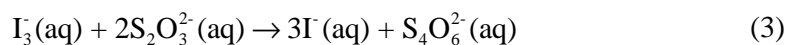
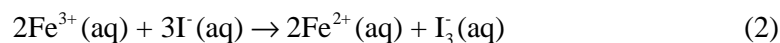
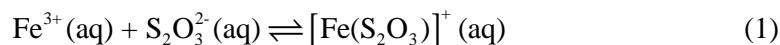
# Kinetics and Mechanism of Iodide Oxidation by Iron(III):

## A Clock Reaction Approach

### Instructors' notes

The subject of investigation is the oxidation of iodide by ferric ions. The limiting reagent is sodium thiosulfate (present in significantly lower concentration than the ferric and iodide ions), and starch is the indicator. Medium acidity is set by nitric acid.

Chemical changes in the clock reaction investigated can be presented by the following equations (1–3):



The complex  $[\text{Fe}(\text{S}_2\text{O}_3)]^+$  is purple and the starch-pentaiodide complex is blue.

The reaction is started by mixing a colourless acidic solution of ferric nitrate with a colourless solution containing sodium thiosulfate, potassium iodide and starch (Fig. 1a). The solution immediately turns purple (Fig. 1b). The colour gradually fades (Fig. 1c and 1d) until the solution becomes colourless (Fig. 1e). At that very moment, the solution suddenly turns dark blue (Fig. 1f).



a)



b)



c)



d)



e)



f)

Figure 1. Colour changes during the reaction (Experiment 1).

Immediately after mixing the two solutions, ferric ions form the thiosulfate complex and make the solution turn purple. The excess ferric ions oxidize iodide forming triiodide ions that immediately react with thiosulfate. The purple complex starts breaking down releasing thiosulfate ions (needed for the reaction with triiodide)

which in turn fades the solution colour. This reaction sequence goes on until all the thiosulfate ions (present in a small quantity) have been consumed. Only then does the reaction between triiodide and starch take place forming the dark blue complex.

The aim is to study the kinetics of reaction (2), i.e. to establish the dependence of the reaction rate on reactant concentrations, and possibly to get insight into the reaction mechanism.

The kinetics of a reaction transformed into a clock reaction is easily investigated by the initial rates method. All one has to measure is  $\Delta t$  i.e. the time elapsed from the mixing of the two solutions to a sudden colour change (sending out a signal) (4–6).

From the stoichiometry of the reactions (1–4), one can deduce the following expression for the initial rate of reaction (2):

$$v_0 \approx -\frac{\Delta[\text{Fe}^{3+}]}{\Delta t} = \frac{[\text{S}_2\text{O}_3^{2-}]_0}{\Delta t}, \quad (5)$$

where  $\Delta[\text{Fe}^{3+}]$  is the change in the concentration of ferric ions in the initial period of the reaction. If  $\Delta t$  is the time measured, then  $\Delta[\text{Fe}^{3+}]$  is the decrease in ferric ion concentration from the moment of mixing to the moment of complete thiosulfate (the limiting reagent) consumption. Relation (5) holds if the initial concentration of thiosulfate is sufficiently low compared to that of ferric and iodide ions. In this case the extent of reaction (2) at the time  $\Delta t$  is rather small, and consequently the quotient  $\Delta[\text{Fe}^{3+}]/\Delta t$  can be taken as a satisfactory approximation of the initial reaction rate. However, if the initial thiosulfate concentration is too low the time period  $\Delta t$  is short and cannot be measured accurately. Therefore, both of these considerations must be taken into account in the experimental design.

The dependence of the initial reaction rate on ferric and iodide ion concentrations can be expressed as:

$$v_0 = k [\text{Fe}^{3+}]_0^x [\text{I}^-]_0^y = \frac{[\text{S}_2\text{O}_3^{2-}]_0}{\Delta t}. \quad (6)$$

$x$  is the reaction order with respect to  $\text{Fe}^{3+}$  and  $y$  is the reaction order with respect to  $\text{I}^-$ . If the initial concentration of only one reactant is varied while the initial concentrations of the other participants are kept unchanged, it is possible to determine the order of reaction with respect to the reactant whose concentration is being varied.

## *The effect of thiosulfate concentration on reaction rate*

### **Experiment 2 – typical results**

Table 1. The values of  $\Delta t$  for varying sodium thiosulfate initial concentrations.

$[\text{Na}_2\text{S}_2\text{O}_3]_0/10^{-4} \text{ mol L}^{-1}$	$\Delta t_1/\text{s}$	$\Delta t_2/\text{s}$	$\Delta t_3/\text{s}$	$\overline{\Delta t}/\text{s}$
1.0	2.3	2.5	2.3	2.4
2.0	4.5	4.2	4.4	4.4
3.0	6.6	6.7	6.6	6.6
4.0	9.0	9.0	9.1	9.0
5.0	11.2	11.0	11.3	11.2
6.0	13.9	13.7	13.6	13.7
7.0	16.3	16.2		16.3

The data from Table 1 are analyzed and the results are shown in Fig. 2 and Table 2.

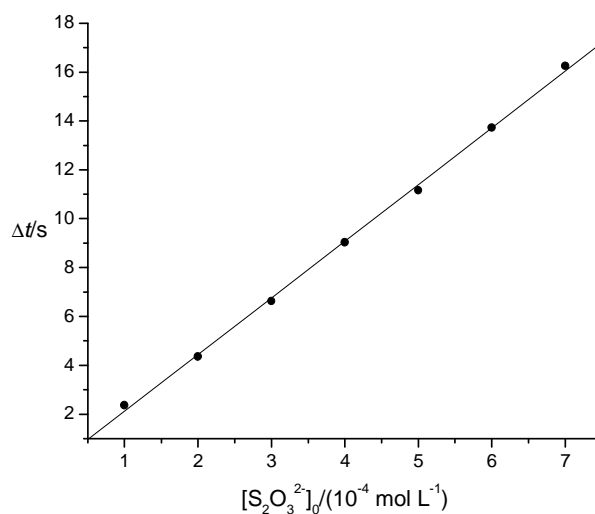


Figure 2. Graphical presentation of the data from Table 1; • experimental, — calculated according to equation (6).

Table 2. Results of regression analysis of the data from Table 1 and Fig. 2 according to the model:  $\Delta t/s = a + b [\text{S}_2\text{O}_3^{2-}]_0/(\text{mol L}^{-1})$ .

Variable	
$\hat{a}$	-0.20
$\text{SE}(\hat{a})$	0.17
$10^{-4}\hat{b}$	2.32
$10^{-2}\text{SE}(\hat{b})$	3.62
$R^2$	0.9988

$\hat{a}, \hat{b}$  – estimations of the straight-line intercept and slope, respectively;

SE- standard error;  $R^2$ - coefficient of determination.

$\Delta t$  is found to be approximately proportional to the initial thiosulfate concentration. This result must be interpreted carefully. It confirms equation (6) but it also states that the reaction rate does not in fact depend on thiosulfate concentration; thiosulfate is merely the limiting reagent in the clock reaction. The initial thiosulfate concentration determines  $\Delta t$  but it does not determine the reaction rate.

### *The effect of iodide concentration on reaction rate*

#### **Experiment 3 – typical results**

Table 3. The values of  $\Delta t$  for varying potassium iodide initial concentration.

$[\text{KI}]_0/(10^{-3} \text{ mol L}^{-1})$	$\Delta t_1/s$	$\Delta t_2/s$	$\Delta t_3/s$	$\overline{\Delta t} / s$
7.50	25.0	24.9	24.9	24.9
8.75	18.7	18.6	18.4	18.6
10.00	14.5	14.3	14.0	14.3
11.64	10.6	10.5	10.6	10.6
12.50	9.0	8.9	9.0	9.0
13.75	7.4	7.5	7.4	7.4
15.00	6.3	6.2	6.4	6.3

The data from Table 3 are analyzed by nonlinear (Fig. 3, Table 4) and/or linear regression (Fig. 4, Table 5).

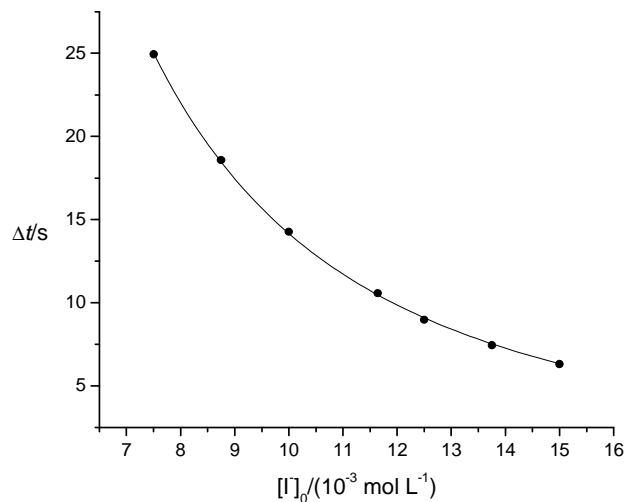


Figure 3. Graphical presentation of the data from Table 3; • experimental, — calculated according to equation (6).

Table 4. Results of regression analysis of the data from Table 3 and Fig. 3 according to the model:  $\Delta t/s = C_1 \{[I]_0/(\text{mol L}^{-1})\}^{-\gamma}$ .

Variable	
$10^3 \hat{C}_1$	1.54
$10^3 \text{SE}(\hat{C}_1)$	0.11
$\hat{\gamma}$	1.98
$\text{SE}(\hat{\gamma})$	0.02
$R^2$	0.9997

$\hat{C}_1$ ,  $\hat{\gamma}$  – estimations of parameters  $C_1$  and  $\gamma$ ; SE- standard error;

$R^2$ - coefficient of determination.



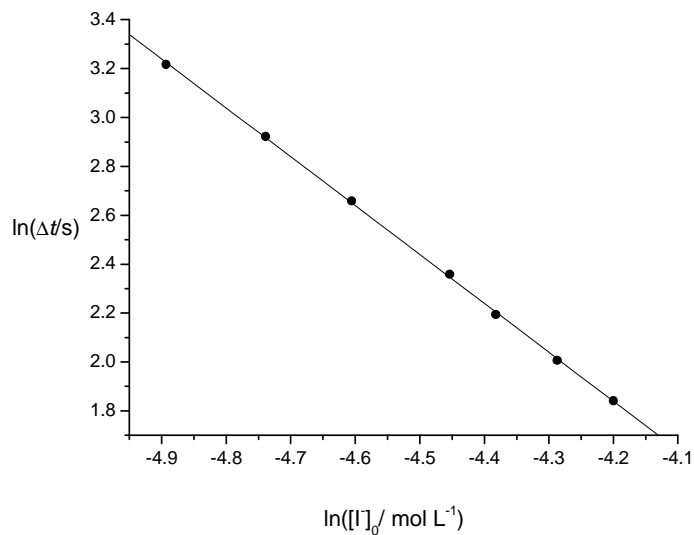


Figure 4. Graphical presentation of the data from Table 3; • experimental, — calculated according to the model  $\ln(\Delta t/s) = c - y \ln\{[I]_0/(\text{mol L}^{-1})\}$ .

Table 5. Results of regression analysis of the data from Table 3 and Fig. 4 according to the model:  $\ln(\Delta t/s) = c - y \ln\{[I]_0/(\text{mol L}^{-1})\}$ .

Variable	
$\hat{c}$	-6.56
$\text{SE}(\hat{c})$	0.07
$\hat{y}$	2.00
$\text{SE}(\hat{y})$	0.02
$R^2$	0.9997

$\hat{c}$ ,  $-\hat{y}$  – estimations of the straight-line intercept and slope, respectively;

SE- standard error;  $R^2$ - coefficient of determination.

The value of  $y$  (Tables 4, 5) shows that the reaction is second order with respect to iodide.

## The effect of ferric ion concentration on reaction rate

### Experiment 4 – typical results

Table 6. The values of  $\Delta t$  for varying ferric nitrate initial concentration.

$[\text{Fe}(\text{NO}_3)_3]_0/10^{-3} \text{ mol L}^{-1}$	$\Delta t_1/\text{s}$	$\Delta t_2/\text{s}$	$\Delta t_3/\text{s}$	$\overline{\Delta t}/\text{s}$
5.0	17.4	17.3	17.4	17.4
6.0	14.2	14.2	14.1	14.2
7.0	11.8	11.9	11.8	11.8
8.0	10.3	10.3	10.5	10.4
9.0	9.1	9.1		9.1
10.0	8.0	7.8	7.9	7.9
11.0	7.4	7.4	7.3	7.4
12.0	6.6	6.7		6.7

The data from Table 6 are analyzed by nonlinear (Fig. 5, Table 7) and/or linear regression (Fig. 6, Table 8).

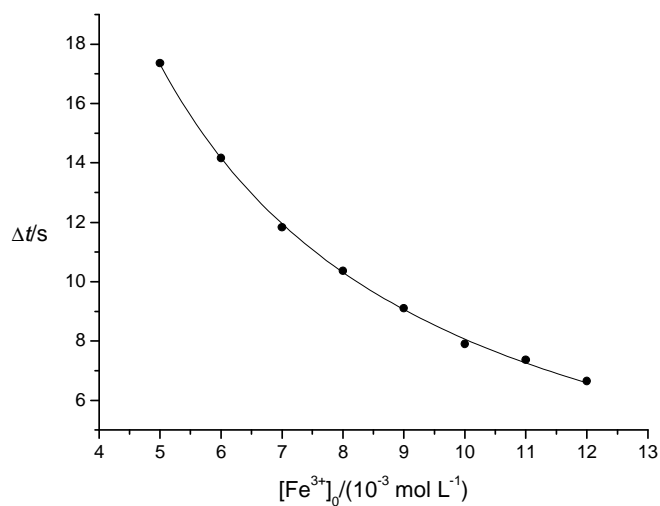


Figure 5. Graphical presentation of the data from Table 6; • experimental, — calculated according to equation (6).

Table 7. Results of regression analysis of the data from Table 6 and Fig. 5 according to the model:  $\Delta t/s = C_2 \{[\text{Fe}^{3+}]_0/(\text{mol L}^{-1})\}^{-x}$ .

Variable	
$10^2 \hat{C}_2$	5.01
$10^2 \text{SE}(\hat{C}_2)$	0.29
$\hat{x}$	1.10
$\text{SE}(\hat{x})$	0.01
$R^2$	0.9994

$\hat{C}_2, \hat{x}$  – estimations of parameters  $C_2$  and  $x$ ; SE- standard error;

$R^2$ - coefficient of determination.

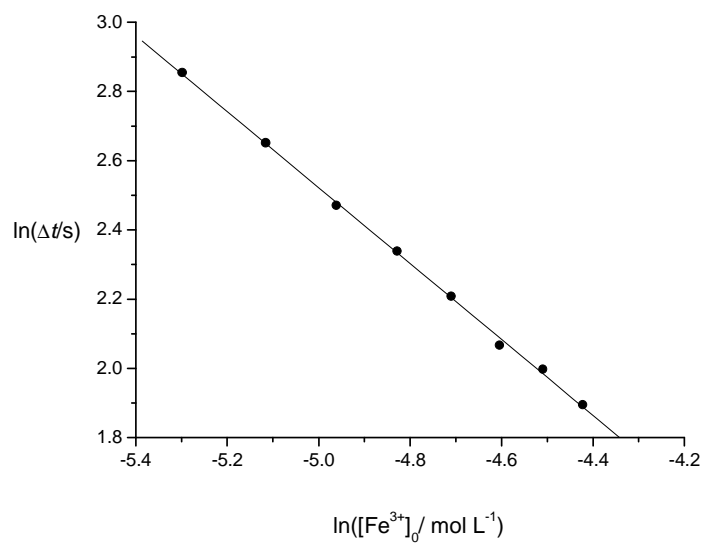


Figure 6. Graphical presentation of the data from Table 6; • experimental, — calculated according to the model  $\ln(\Delta t/s) = d - x \ln\{[\text{Fe}^{3+}]_0/(\text{mol L}^{-1})\}$ .

Table 8. Results of regression analysis of the data from Table 6 and Fig. 6 according to the model:  $\ln(\Delta t/s) = d - x \ln\{[\text{Fe}^{3+}]_0/(\text{mol L}^{-1})\}$ .

Variable	
$\hat{d}$	-2.96
$\text{SE}(\hat{d})$	0.07
$\hat{x}$	1.10
$\text{SE}(\hat{x})$	0.01
$R^2$	0.9989

$\hat{d}$ ,  $-\hat{x}$  – estimations of the straight-line intercept and slope, respectively;  
SE- standard error;  $R^2$ - coefficient of determination.

The value of  $x$  (Tables 7, 8) shows that the reaction is first order with respect to ferric ions.

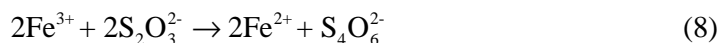
### ***Combining the results***

On the basis of the above results, the rate law (eq. 6) can be written as:

$$v = k [\text{Fe}^{3+}] [\text{I}^-]^2. \quad (7)$$

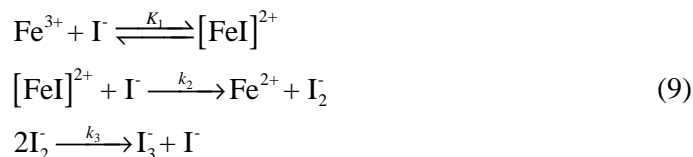
By comparing the results from Tables 2, 4 and 6 with equation (6), the rate coefficient values can easily be obtained from each set of experiments (described in detail in student handout):  $k = 16.6 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ;  $15.3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$  ( $16.6 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ );  $29.5 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$  ( $28.5 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ), respectively. (The values given in parentheses are obtained by the linear regression analysis of the data measured in the last two sets of experiments).

The oxidation of thiosulfate to tetrathionate by ferric ions (8) is another redox reaction taking place in the system investigated (7,8):



This reaction however has no significant influence on the experiments conducted. The reaction followed is zeroth order with respect to thiosulfate and second order with respect to iodide, clearly indicating that reaction (8) does not interfere significantly with the kinetics of the reaction studied.

From the data collected the following possible mechanism of reaction (2) can be deduced:



The mechanism is supported by confirmations of the existence of the species  $\text{I}_2^-$  (9–11) as well as by the fact that the disproportionation of  $\text{I}_2^-$  has already been proposed (12,13). An analogous reaction of  $\text{Br}_2^-$  has also been proposed in the mechanism of bromide oxidation by an iron(III) complex (14).

#### *Proposed mechanism analysis*

The rate of reaction (2) can be expressed as the change of triiodide concentration against time which in turn can be expressed from the proposed mechanism:

$$v = \frac{d[\text{I}_3^-]}{dt} = k_3 [\text{I}_2^-]^2. \tag{10}$$

As  $\text{I}_2^-$  is an intermediate, the steady state approximation can be applied:

$$\frac{d[\text{I}_2^-]}{dt} = k_2 [\text{FeI}^{2+}] [\text{I}^-] - 2k_3 [\text{I}_2^-]^2 \approx 0. \tag{11}$$

From equation (11) the following relations can be written:

$$k_2 [\text{FeI}^{2+}] [\text{I}^-] = 2k_3 [\text{I}_2^-]^2 \tag{12}$$

$$[\text{I}_2^-]^2 = \frac{k_2}{2k_3} [\text{FeI}^{2+}] [\text{I}^-]. \tag{13}$$

The equilibrium constant of the first step of the proposed mechanism is:

$$K_1 = \frac{[\text{FeI}^{2+}]}{[\text{Fe}^{3+}] [\text{I}^-]}. \tag{14}$$

From equations (10) and (13), it follows:

$$v = \frac{1}{2} k_2 [\text{FeI}^{2+}] [\text{I}^-], \tag{15}$$

and by introducing equation (14) one obtains:

$$v = \frac{1}{2} k_2 K_1 [\text{Fe}^{3+}] [\text{I}^-]^2. \tag{16}$$

The rate law (16) matches the one obtained experimentally. However, the obtained value of the reaction order with respect to ferric ions ( $x = 1.1$ ), as well as the (higher) value of the reaction rate coefficient ( $k = 29.5 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ) determined in the corresponding experiment, may indicate a slightly more complicated mechanism than the one proposed for which  $x = 1.0$ . These considerations, however, are beyond the scope of the exercise presented here.

### *Deducing the mechanism*

Having established the rate law experimentally, the students can be led to propose a possible reaction mechanism. Reaction (2) is second order with respect to iodide. Therefore, two iodide ions should appear as reactants in the mechanism. It is well known, however, that a trimolecular collision in solution is not likely to happen. A reaction between  $\text{Fe}^{3+}$  and  $\text{I}^-$  forming an intermediate may therefore be assumed. Being aware of the existence of iron(III) complexes with halides, it is also assumed that the intermediate is likely to be  $\text{FeI}^{2+}$ . In order for the obtained rate law to be adequate,  $\text{FeI}^{2+}$  is supposed to react with a second  $\text{I}^-$  ion. Knowing that  $\text{Fe}^{2+}$  is the reaction product, the chemical species  $\text{I}_2^-$  is “made up” as the product in order to make this reaction step appear plausible. If  $\text{I}_3^-$  exists, there is no apparent reason why  $\text{I}_2^-$  should not exist as well. The ion  $\text{I}_3^-$  can be taken as being “composed” of  $\text{I}_2$  and  $\text{I}^-$ , and  $\text{I}_2^-$  as being “composed” of  $\text{I}^-$  and  $\text{I}^-$ . The reaction product is  $\text{I}_2$ , i.e.  $\text{I}_3^-$ , so two  $\text{I}^-$  should combine, that is two  $\text{I}_2^-$  should react.

A similar mechanism had already been proposed for the reaction investigated (15). However, the method of studying a clock reaction described herein is experimentally simpler than the titrimetric analysis used in ref. (15).

## Literature

1. Shakhshiri, B. Z. *Chemical Demonstrations*; The University of Wisconsin Press; Wisconsin, 1992; Vol. 4, pp 51–55.
2. Page, F. M. *Trans. Faraday Soc.* **1953**, *49*, 635–643.
3. Page, F. M. *Trans. Faraday Soc.* **1954**, *50*, 120–126.
4. Creary, X.; Morris, K. M. *J. Chem. Educ.* **1999**, *76*, 530–531.
5. Vitz, E. *J. Chem. Educ.* **2007**, *84*, 1156–1157.
6. Copper, C. L.; Koubek, E. *J. Chem. Educ.* **1998**, *75*, 87–89.
7. Schmid, H. *Z. Phys. Chem. A* **1930**, *148*, 321–336.
8. Holluta, J.; Martini, A. *Z. Anorg. Allg. Chem.* **1924**, *140*, 206–226.
9. Gershgoren, E.; Banin, U.; Ruhman, S. *J. Phys. Chem. A* **1998**, *102*, 9–16.
10. Benjamin, I.; Barbara, P. F.; Gertner, B. J.; Hynes, J. T. *J. Phys. Chem.* **1995**, *99*, 7557–7567.
11. Walhout, P. K.; Alfano, J. C.; Thakur, K. A. M.; Barbara, P. F. *J. Phys. Chem.* **1995**, *99*, 7568–7580.
12. Nord, G.; Pedersen, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233–2242.
13. Langmuir, M. E.; Hayon, E. *J. Phys. Chem.* **1967**, *71*, 3808–3814.
14. Hubbard, C. D.; Jones, J. G.; McKnight, J. *J. Chem. Soc., Dalton Trans.* **2000**, 3143–3148.
15. Fudge, A. J.; Sykes, K. W. *J. Chem. Soc.* **1952**, 119–124.