Kinetic study of ionic reactions

Theoretical background: P.W. Atkins: *Physical Chemistry* (10th ed.), Chapters 5 (The activities of ions) and 20 (Chemical kinetics).
Type of practice: Individual.
Aim of practice: To demonstrate how the ionic strength affects on the rate of ionic reactions in solution.

1 Introduction

Experimental observations prove that the rate coefficient of ionic reactions taking place in a certain liquid at a given temperature depends on the concentration of salts (electrolytes) add to the solution even if those are not involved in the chemical reaction (i.e., inert). The qualitative picture is the following. The reaction of compounds requires a certain vicinity (collision). However, the motion of the reactant ions in the liquid phase is affected by any ion due to electrostatic interactions. Let us assume that the reaction takes place between ions of like charge which thus repel each other. If counter (i.e., oppositely charged) ions are added to the solution by dissolving an inert salt, the electrostatic repulsion of the reacting ions is reduced *via* charge shielding. As a consequence, the reaction rate increases. Following the same logic, the addition of an inert salt to the solution in which ions of unlike charge react decreases the reaction rate by partially diminishing the electrostatic attraction.

We now apply the transition state theory to quantitatively describe the above introduced kinetic salt effect. The reactants (A and B) of numerous second order (not only ionic) reactions transform into product (P) through a *quasi* pre-equilibrium state, the so called transition state (activated complex, $(AB)^{\ddagger}$):

$$\mathrm{A+B} \rightleftharpoons \mathrm{(AB)^{\ddagger}} \xrightarrow{\mathrm{k^{\ddagger}}} \mathrm{P}. \tag{1}$$

The rate of transformation from activated complex to product is

$$\mathrm{r} = \frac{\mathrm{d\,[P]}}{\mathrm{d\,t}} = \mathrm{k^{\ddagger}\,[(AB)^{\ddagger}]}, \tag{2}$$

which includes the concentration of the activated complex which cannot be measured experimentally. To transform the rate equation, we now state the *quasi* equilibrium constant for the pre-equilibrium by considering the activated complex as a *real* chemical compound:

$$\mathrm{K^{\ddagger}} = \frac{\mathrm{a_{(AB)^{\ddagger}}}}{\mathrm{a_A \times a_B}} = \frac{\gamma_{\mathrm{(AB)^{\ddagger}}}}{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}} \times \frac{\mathrm{[(AB)^{\ddagger}]\,c^0}}{\mathrm{[A]\,[B]}} = \Gamma \times \frac{\mathrm{[(AB)^{\ddagger}]\,c^0}}{\mathrm{[A]\,[B]}}, \tag{3}$$

where a is activity, γ is activity coefficient, c^0 is the standard concentration, and square brackets denote equilibrium concentrations. We then express the concentration of the activated complex

$$\mathrm{[(AB)^{\ddagger}]} = \frac{\mathrm{K^{\ddagger}}}{\Gamma} \times \frac{\mathrm{[A]\,[B]}}{\mathrm{c^0}}. \tag{4}$$

Substituting expression (4) into equation (2) results in the reaction rate only including the concentration of the reacting ions:

$$\mathrm{r} = \frac{\mathrm{d\,[P]}}{\mathrm{d\,t}} = \frac{\mathrm{k^{\ddagger}\,K^{\ddagger}}}{\Gamma \mathrm{c^0}} \times \mathrm{[A]\,[B]} = \mathrm{k\,[A][B]}. \tag{5}$$

$[A]$ and $[B]$ still denote the equilibrium concentrations of A and B. Assuming that the concentration of the activated complex is negligible, i.e., $K^{\ddagger}$ is small, those concentrations can be treated as analytical concentrations. Therefore, equation (5) is the rate equation of a second order elementary reaction, however, the rate coefficient also depends on the activity coefficients. If the activity coefficients are unity (infinitely dilute solution; ideal solution behavior where the ion–ion electrostatic interactions can be neglected) and thus $\Gamma = 1$ we obtain a limit for the rate coefficient: $k_0 = \dfrac{\mathrm{k}^{\ddagger}\,\mathrm{K}^{\ddagger}}{c^0}$. In every other case

$$\mathrm{k} = \frac{\mathrm{k}_0}{\Gamma}\,. \tag{6}$$

Although the activity coefficients cannot be determined during the practice, their dependence on the ionic strength can be expressed according to the Debye–Hückel limiting law. For the component A with a charge of z_A we write

$$\ln\gamma_{\mathrm{A}} = -\frac{\mathrm{z}_{\mathrm{A}}^2\,\mathrm{e}^3\,(2\,\mathrm{N}_{\mathrm{A}})^{1/2}}{8\pi\,(\varepsilon_0\,\varepsilon_{\mathrm{r}}\,\mathrm{k}_{\mathrm{B}}\,\mathrm{T})^{3/2}} \times \left(\frac{1}{2}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{c}_{\mathrm{i}}\,\mathrm{z}_{\mathrm{i}}^2\right)^{1/2}\,, \tag{7}$$

where e is elementary charge (1.602×10^{-19} C), N_{A} is Avogadro number ($6.022 \times 10^{23}\,\mathrm{mol}^{-1}$), k_{B} is Boltzman constant ($1.381 \times 10^{-23}\,\mathrm{J\,K}^{-1}$), T is thermodynamic temperature, ε_0 is permittivity of vacuum ($8.854 \times 10^{-12}\,\mathrm{A\,s\,V}^{-1}\,\mathrm{m}^{-1}$) and ε_{r} is relative (static) permittivity of the solution. In equation (7)

$$\mathrm{I} = \frac{1}{2}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{c}_{\mathrm{i}}\,\mathrm{z}_{\mathrm{i}}^2 \tag{8}$$

is the so called molar ionic strength, which expresses the cumulative effect of ions, where c_i and z_i are the molar concentration and charge of compound i, respectively, and n is the number of different ions in the solution. The constants in equation (7) are often merged and log base 10 is used instead of ln which then leads to

$$\lg\gamma_{\mathrm{A}} = -\mathcal{A}\,\mathrm{z}_{\mathrm{A}}^2\,\sqrt{\mathrm{I}}\,, \tag{9}$$

where the coefficient $\mathcal{A}$ is treated as a function of the solvent ($\varepsilon_{\mathrm{r,\,solvent}}$) and temperature ($T$) only. However, in reality, ε_r depends on the solution composition as well thus it implicitly includes ionic strength-dependence. Therefore it only can be approached by $\varepsilon_{\mathrm{r,\,solvent}}$ in appropriately dilute solutions. *This is the reason for which it is called Debye–Hückel limiting law.* $\mathcal{A} = 0.51\,\mathrm{M}^{-1/2}$ in aqueous solutions at 25 °C. (Since the relative permittivity decreases upon raising the temperature, this value is appropriate for experiments performed within $20-30$°C temperature range.) Equation (9) holds for compound B with charge z_B and for activated complex $(AB)^{\ddagger}$ with charge $z_A + z_B$ as well, thus by rearranging eq. (6) we obtain the Brønsted–Bjerrum-equation[1]:

$$\lg\frac{\mathrm{k}}{\mathrm{k}_0} = -\lg\Gamma = 2\,\mathcal{A}\,\mathrm{z}_{\mathrm{A}}\,\mathrm{z}_{\mathrm{B}}\,\sqrt{\mathrm{I}} \quad \text{or} \quad \lg\mathrm{k} = \lg\mathrm{k}_0 + 2\,\mathcal{A}\,\mathrm{z}_{\mathrm{A}}\,\mathrm{z}_{\mathrm{B}}\,\sqrt{\mathrm{I}}\,. \tag{10}$$

According to eq. (10) the rate of an ionic reaction is not exclusively determined by the concentration of the reactants. Any ion present in the solution affects the rate through the ionic strength dependent rate coefficient, even if those ions are inert with respect to the reaction. This effect is called primary kinetic salt

---

[1] Since $\Gamma = \dfrac{\gamma_{(\mathrm{AB})^{\ddagger}}}{\gamma_{\mathrm{A}}\,\gamma_{\mathrm{B}}}$, by applying rule for the logarithm of fractions

$$\lg\Gamma = \lg\gamma_{(\mathrm{AB})^{\ddagger}} - \lg(\gamma_{\mathrm{A}}\,\gamma_{\mathrm{B}}) = \lg\gamma_{(\mathrm{AB})^{\ddagger}} - \lg\gamma_{\mathrm{A}} - \lg\gamma_{\mathrm{B}}\,.$$

According to eq. (9):

$$\lg\gamma_{\mathrm{A}} = -\mathcal{A}\,\mathrm{z}_{\mathrm{A}}^2\,\sqrt{\mathrm{I}}\,, \qquad \lg\gamma_{\mathrm{B}} = -\mathcal{A}\,\mathrm{z}_{\mathrm{B}}^2\,\sqrt{\mathrm{I}}\,, \qquad \lg\gamma_{(\mathrm{AB})^{\ddagger}} = -\mathcal{A}\,(\mathrm{z}_{\mathrm{A}} + \mathrm{z}_{\mathrm{B}})^2\,\sqrt{\mathrm{I}}\,.$$

Substituting the expressions obtained for the activity coefficients into the equation above and after rearranging

$$\lg\Gamma = -2\,\mathcal{A}\,\mathrm{z}_{\mathrm{A}}\,\mathrm{z}_{\mathrm{B}}\,\sqrt{\mathrm{I}}\,.$$

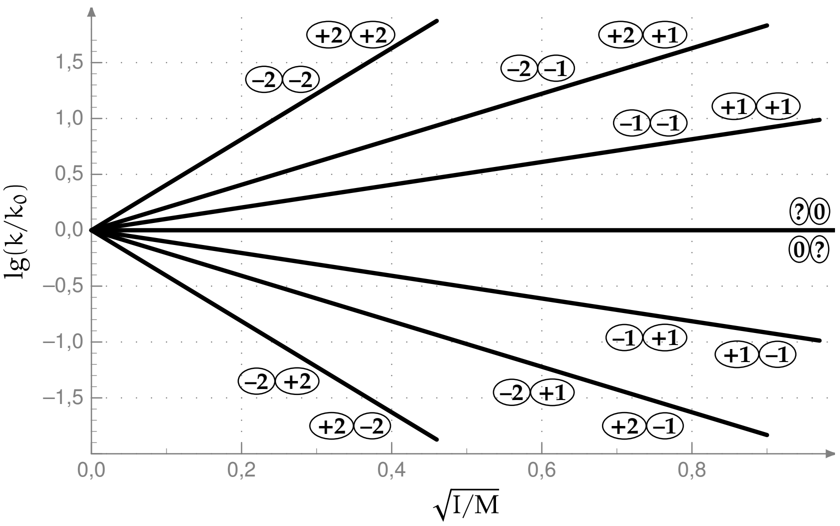

Figure 1: The ionic strength-dependence of the rate coefficient of a second order reaction according to the transition state theory and the Debye–Hückel law for the reactions of various ions. The numbers in the circles stand for the ion charges (interrogation mark can be any charge).

effect (Fig. 1). Based on the figure, in the scenario of increasing ionic strength the reaction between ions of like charge becomes faster (positive kinetic salt effect), whereas the rate of reaction between ions of unlike charge decreases (negative kinetic salt effect). An other important consequence of eq. (10) is that in the reaction of ions of multiple charge the change of ionic strength may affect more on the rate than changing the concentration of one of the reactants.

According to the above paragraphs and eq. (10), if the rate of an ionic reaction is investigated at various ionic strength while the reactant concentrations are kept constant, the ionic strength dependent variation of the rate coefficient can be explored. Keep in mind that this strongly depends on the charge of the reacting ions (sign and absolute value) and on the order of the reaction as well but the variation of these parameters will not be focused during the practice. The next section will introduce the reaction to be investigated. Furthermore, it is described how to apply the initial rate method during kinetic investigations to determine the empirical rate law of the reaction (i.e., order of the reaction and rate coefficient).

1.1 The reaction

The reaction between peroxodisulfate and iodide ions will be performed in order to investigate how its rate depends on the ionic strength. The reaction is described by the

$$\mathrm{S_2O_8^{2-}} + 2\,\mathrm{I^-} = 2\,\mathrm{SO_4^{2-}} + \mathrm{I_2} \tag{11}$$

stoichiometric equation. Kinetic investigations proved that the reaction takes place in two consecutive steps. An intermediate is produced in the first slow, rate-determining step:[2]

$$\mathrm{S_2O_8^{2-}} + \mathrm{I^-} \left(\rightleftharpoons (\mathrm{X})^{\ddagger}\right) \xrightarrow{\text{slow}} (\mathrm{S_2O_8I})^{3-}\,. \tag{12}$$

This is then followed by a second fast step

$$(\mathrm{S_2O_8I})^{3-} + \mathrm{I^-} \xrightarrow{\text{fast}} 2\,\mathrm{SO_4^{2-}} + \mathrm{I_2}\,. \tag{13}$$

The mechanism is similar to that of eq. (1) thus eq. (10) can be applied to study the ionic strength-dependence of the rate coefficient.

---

[2] Note that the intermediate (inhere $(\mathrm{S_2O_8I})^{3-}$) linking together various reaction steps is not identical with the activated complex $(\mathrm{X})^{\ddagger}$, which is both produced and consumed fast and is only present in a negligible concentration, thus we depict it in parenthesis.

The rate equation for the rate-determining step of eq. (12) can be written as

$$r = -\frac{d[S_2O_8^{2-}]}{dt} = k\,[S_2O_8^{2-}]^{\beta_{S_2O_8^{2-}}}\,[I^-]^{\beta_{I^-}}\,, \tag{14}$$

where β is the reaction order with respect to each reactant. Therefore, the initial rate of the reaction is

$$r_0 = k\,[S_2O_8^{2-}]_0^{\beta_{S_2O_8^{2-}}}\,[I^-]_0^{\beta_{I^-}} = -\left(\frac{d[S_2O_8^{2-}]}{dt}\right)_{t=0}\,. \tag{15}$$

Do not confuse the $_0$ subscript referring to values which belong to the beginning of the reaction with that used in the previous equations to indicate $I = 0\,M$ ionic strength. Assuming that the initial concentrations and the reaction order are known, only the change of the peroxodisulfate concentration is required to calculate the rate coefficient *k*. This concentration change can be determined by adding thiosulfate ion to the reaction mixtures as discussed in the following paragraph.

The reaction rate is obtained by visually detecting the color of iodine (I_2) produced in reaction (11). Intense blue color is observed when a solution contains iodine, iodide, and starch because they form a complex. However, iodine is consumed in a fast reaction if the solution contains thiosulfate ion as well:

$$2\,S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2\,I^-\,. \tag{16}$$

Since reaction (16) is significantly faster than reaction (13), thus the blue color cannot be detected until $S_2O_3^{2-}$ is fully consumed. Then a suddenly appearing blue color indicates the increasing concentration of iodine. The time elapsed between mixing the solutions and detecting the color is the reaction time Δt.

Now we only need to possess the reaction order for being able to calculate the rate coefficient by applying eq. (15). The rate of ionic reactions depends both on the ionic strength maintained by the addition of an inert salt and on the concentration of the reactants. Therefore, separate sets of experiments must be performed to independently address the reaction order and the ionic strength-dependence. The reaction order according to eq. (15) is going to be determined via the initial rate method. It is assumed that the empirical rate law is valid during the entire reaction, including the initial phase as well. The logarithmic form of eq. (15) reads as

$$\lg\frac{r_0}{M\,s^{-1}} = \lg\frac{k}{M^{\beta_{S_2O_8^{2-}}+\beta_{I^-}-1}\,s^{-1}} + \beta_{S_2O_8^{2-}}\lg\frac{[S_2O_8^{2-}]_0}{M} + \beta_{I^-}\lg\frac{[I^-]_0}{M}\,. \tag{17}$$

Expression (17) shows that the logarithm of the initial rate is a linear function of both the logarithm of I^- and $S_2O_8^{2-}$ initial concentrations. Therefore, if the reaction rate is determined for various initial I^- concentrations while that of $S_2O_8^{2-}$ is kept constant over the separate experiments, and the logarithm of the initial rate is fitted as a function of logarithm of $[I^-]_0$, the slope of the linear is β_{I^-}. The intercept contains information about the rate coefficient. In the same way, the reaction order with respect to $S_2O_8^{2-}$ ions can be obtained if $[I^-]_0$ is kept constant and $[S_2O_8^{2-}]_0$ is systematically varied.

There are two practical questions related to the initial rate method:

1. *How can we satisfy such condition that the reactant concentrations do not change during the reaction thus eq.* (15) *is applicable?*

   Mathematically speaking, there is no solution to fulfill this criterion. However, appropriately chosen experimental conditions can ensure reliable results within experimental error. The following solutions are often applied:

   (a) The reaction is followed only until a small conversion (1–2 %), therefore the change of the initial concentrations is negligible. This method is applicable for each reactant at the same time.

   (b) Some reactant is present in large stoichiometric excess thus its concentration change is small even for large conversion. This method is not applicable for each reactant at the same time, since at least one reactant must possess small concentration compared to the others.

(c) If one reactant is a catalyst, it is reproduced over the reaction. The concentration of the catalyst can be taken constant if the reproduction step is fast.

(d) If one of the reactants is the hydrogen ion, its constant concentration can be maintained by applying an appropriate *p*H-buffer solution.

2. *How to determine the reaction rate?*

   The initial rate of a reaction can be determined from the slope of the tangent drawn to the initial part of the concentration – time plot and from the stoichiometric numbers. This differential quotient is satisfactorily approached by the difference quotient provided that the conversion is small:

$$\frac{\mathrm{d}\,[\mathrm{X}]}{\mathrm{d}\mathrm{t}} = \lim_{\Delta\mathrm{t}\to 0} \frac{\Delta[\mathrm{X}]}{\Delta\mathrm{t}} \approx \frac{\Delta[\mathrm{X}]}{\Delta\mathrm{t}}, \tag{18}$$

   where X denotes the chemical compound whose concentration change is technically the less challenging to follow. Expression (18) facilitates the approximation of reaction rate via analytical measurements. If the concentration of X is known at two instances – the initial concentration is a practical choice as one – then the concentration difference and the reaction time result in the difference quotient.

2 Experimental

2.1 Determination of the reaction order

Prepare the following stock solutions *if they are not available*:

- 25 cm^3 0.10 M KI
- 25 cm^3 0.10 M KNO_3
- 25 cm^3 0.125 M $K_2S_2O_8$
- 25 cm^3 0.125 M K_2SO_4
- 25 cm^3 0.2 % starch (see Appendix for preparation)
- 100 cm^3 0.01 M $Na_2S_2O_3$

The measurements should be performed according to the solution compositions presented in Table 1. All the reactants except $K_2S_2O_8$ have to be pipetted into a dry beaker of 50 cm^3 (or smaller), and the corresponding potassium peroxodisulfate solution into a dry Erlenmeyer flask of 50 cm^3 (or smaller). The stop watch should be started when the solution mixture in the beaker is added to the $K_2S_2O_8$ solution. Measure the time until the blue color of starch appears. Special care should be taken for the followings:

- Pipettes should not be placed into the solution container. The solutions should be poured into clean and dry beakers from which pipetting is allowed.
- All the experiments can be carried out by one stopwatch. Using the split time mode of the watch you can store, read, and write down the mixing time and the time of the color change.
- The reactant solutions should be well-mixed.
- Try to read the time at the same blue color. The color change is easier to observe if a white sheet of paper is placed below the flasks.

Table 1: Solution compositions to experimentally determine reaction order.

Sample number	KI	$Na_2S_2O_3$	KNO_3	K_2SO_4	starch	$K_2S_2O_8$
	Volume / cm^3					
1.	4	1	-	-	1	4
2.	4	1	-	2	1	2
3.	4	1	-	3	1	1
4.	4	1	-	3.5	1	0.5
5.	2	1	2	-	1	4
6.	1	1	3	-	1	4
7.	0.5	1	3.5	-	1	4

2.2 Kinetic salt effect: The ionic strength-dependence of the reaction rate

Prepare the following stock solutions *if they are not available*:

- 25 cm^3 0.03 M $K_2S_2O_8$
- 25 cm^3 0.15 M KI
- 50 cm^3 0.12 M KNO_3
- 100 cm^3 0.001 M $Na_2S_2O_3$ (can be prepared by dilution)
- 25 cm^3 0.2 % starch (see Appendix for preparation)

The measurements should be performed according to the solution compositions presented in Table 2. The experimental protocol is identical with the previous one.

Table 2: Solution compositions to experimentally investigate the ionic strength-dependence of the rate coefficient.

Sample number	KI	$Na_2S_2O_3$	KNO_3	starch	H_2O	$K_2S_2O_8$
	Volume / cm^3					
1.	1	1.5	-	1.5	10	1
2.	1	1.5	1	1.5	9	1
3.	1	1.5	2.5	1.5	7.5	1
4.	1	1.5	5	1.5	5	1
5.	1	1.5	7.5	1.5	2.5	1
6.	1	1.5	10	1.5	-	1

2.3 Evaluation

According to the reactions (12), (13), and (16) the concentration of iodide ion is constant until the blue color appears. The experimental parameters are such that the reactions are followed only for small conversion in each case, hence the concentration of the peroxodisulfate ion changes only slightly. Therefore, the initial reaction rate can be approached by eq. (19) obtained with the combination of eqs. (14) and (18):

$$r_0 \approx -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} \approx k\,[S_2O_8^{2-}]_0^{\beta_{S_2O_8^{2-}}}\;[I^-]_0^{\beta_{I^-}}\,, \tag{19}$$

where $\Delta[S_2O_8^{2-}]$ is the concentration change during the reaction. This can be calculated from the initial concentration of $S_2O_3{}^{2-}$ (which is fully consumed during the reaction) by taking the stoichiometry into account: $\Delta[S_2O_8^{2-}] = -[S_2O_3^{2-}]_0/2$. Δt is reaction time. The rate coefficient can be calculated from the rate if the reaction order is known. The determination of reaction order is described in the following section.

2.4 Determination of reaction order

1. Calculate the initial reactant concentrations and reaction rates. Summarize the data according to Table 3.
2. Prepare two plots according to eq. (17) by applying the initial rates calculated for 4–4 data pairs with different $[I^-]_0$ and $[S_2O_8^{2-}]_0$. When selecting the data pairs pay attention to that the concentration of one reactant must be constant while determining the reaction order with respect to the other one. Determine the slope and intercept of the fitted lines together with their error (see Appendix).
3. Define the reaction order with respect to iodide and peroxodisulfate ions as well together with the standard deviations. If the reaction orders are integers within experimental error then treat and use them as such for further calculations.

Table 3: Summary of the experimental results (Determination of reaction order).

Sample number	t /s	$[I]_0^-$ /M	$\lg\left([I]_0^- / M\right)$	$[S_2O_8^{2-}]_0$ /M	$\lg\left([S_2O_8^{2-}]_0 / M\right)$	r $/(M\,s^{-1})$	$\lg\left(r/\left(M\,s^{-1}\right)\right)$

2.5 Kinetic salt effect: The ionic strength-dependence of the reaction rate

1. Calculate the ionic strengths and the rate coefficients by applying the initial reactant concentrations, reaction rates, and reaction orders. *Consider all ionic species which have non-negligible concentration to calculate the ionic strength.* Summarize the results as shown in Table 4.
2. Prepare a plot according to eq. (10) by applying the data of Table 4. Fit a line across the points and determine its slope and intercept together with their error (see Appendix).
3. Determine k_0 and its standard deviation (see Appendix).

Table 4: Summary of the experimental results (Ionic strength-dependence). The ? mark denotes a unit which should be determined according to the reaction order.

Sample number	t/s	$r_0/M\,s^{-1}$	I/M	$\sqrt{I/M}$	$k/?$	$\lg(k/?)$

4. Esteem the precision of the work by discussing the value of the regression coefficient of the fitted line. Compare the theoretically given and experimentally obtained value (together with its standard deviation) for parameter $\mathscr{A}$. Discuss the findings. Is the Debye–Hückel limiting law valid under the applied experimental conditions (ionic strength)?

Questions

1. Define the ionic strength-dependence for the rate coefficient of ionic reactions.
2. Define the ionic strength.
3. Sketch the graph of $\lg(k/k_0) - \sqrt{I}$ if the charge of the reactant ions are *(a)* +2 and –2; and *(b)* +2 and +1.
4. Give the two reaction steps between peroxodisulfate and iodide ions. Which step is the rate determining?
5. How is the reaction rate approximated? Why? Support your statement with reaction equation(s).
6. Briefly describe the aim and logic of the initial rate method (4–6 sentences).
7. What experimental solutions you know for keeping the reactant concentration *quasi* constant during the reaction so that the conditions are appropriate for determining the initial rate?
8. What kind of plots have to be prepared and what can be determined from them?
9. Why is sodium thiosulfate solution added to the reaction mixture? Support your statement with reaction equation(s).
10. The following reactant mixture is prepared: 10 cm^3 0.1 M KI solution, 10 cm^3 0.001 M $Na_2S_2O_3$ solution, 1 cm^3 0.4 M KNO_3 solution, 5 cm^3 starch solution, 20 cm^3 0.01 M $K_2S_2O_8$ solution and 54 cm^3 distilled water. The solution is turned blue after 630 s. Calculate the reaction rate.
11. Calculate the ionic strength of the reaction mixture given in question 10.