Kinetic study of ionic reactions

Theory: P.W. Atkins: *Physical Chemistry*, Chapters 10 and 28.
Type: Individual.
Aim: To determine the order of a reaction and show the effect of ionic strength on the rate of an ionic reaction.

1 Introduction

The rate coefficient of an ionic reaction in a given solvent and at a given temperature is significantly affected by the concentration of a chemically inert salt. This dependence is described quantitatively by the Debye–Hückel limiting law derived by Brønsted and Bjerrum as

$$\mathrm{lg}\,\frac{\mathrm{k}}{\mathrm{k_0}} = 2\cdot \mathrm{A}\cdot(\mathrm{z_1}\cdot \mathrm{z_2})\cdot\sqrt{\mathrm{I}} \tag{1}$$

where k is the rate coefficient, A is a constant dependent on solvent and temperature, z_1, z_2 the charges of the ions that comprise the activated complex, I is the ionic strength and k_0 is the rate coefficient at $\mathrm{I} = 0\,\mathrm{M}$. Coefficient A in dilute aqueous solutions can be approximated by

$$\mathrm{A} = \frac{2621}{\mathrm{T}^{3/2}}\left(\frac{\mathrm{mol}}{\mathrm{K^3dm^3}}\right)^{-1/2}\,.$$

The definition of the ionic strength is

$$\mathrm{I} = \frac{1}{2}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{c_i}\cdot \mathrm{z_i^2}\,,$$

where c_i is the concentration of the i-th ion, z_i is its charge and n is the number of components.

If the reacting ions have charges of the same sign, the rate coefficient increases on increasing the ionic strength (cf. Eqn. (1)), while for ions with opposite charges, it decreases. The former is the positive, the latter is the negative kinetic salt effect.

1.1 The reaction between peroxydisulfate and iodide ions

For the reaction between the peroxydisulfate and iodide ions

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

the following reaction mechanism has been proposed to describe the net reaction:

$$\mathrm{S_2O_8^{2-} + I^- = (S_2O_8I)^{3-}} \quad \text{and} \tag{3}$$

$$\mathrm{(S_2O_8I)^{3-} + I^- = SO_4^{2-} + I_2}\,. \tag{4}$$

where reaction (3) is the rate determining step. The rate law of reaction (2) is

$$\mathrm{r} = -\frac{\mathrm{d[S_2O_8^{2-}]}}{\mathrm{dt}} = \mathrm{k[S_2O_8^{2-}]^{\beta_{S_2O_8^{2-}}}[I^-]^{\beta_{I^-}}}\,, \tag{5}$$

where $\beta_{S_2O_8^{2-}}$ and β_{I^-} are the order of the reaction with respect to ${S_2O_8}^{2-}$ and I^-, respectively. In the presence of a known amount of $Na_2S_2O_3$ in the reactant mixture, the product iodine is consumed in the fast reaction of

$$\mathrm{I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}}\ . \tag{6}$$

Iodine is not present in the system as long as there is any thiosulfate in the solution. Furthermore $[I]^-$ is constant because of reaction (6). If the reactant mixture contains starch, the blue color of the starch-triiodide complex becomes visible once all the thiosulfate is consumed. (In solutions with higher concentrations the reaction between thiosulfate and peroxydisulfate takes place as well

$$2S_2O_3^{2-} + S_2O_8^{2-} = 2SO_4^{2-} + S_4O_6^{2-} \ . \tag{7}$$

Reaction (7) is negligible in the applied experimental conditions.)

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 %-os starch
- 100 cm^3 0.01 M $Na_2S_2O_3$

The measurements should be performed in the following systems:

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

All the reactants except $K_2S_2O_8$ have to be pipetted into a dry beaker of 50 mL (or smaller), the corresponding potassium peroxydisulfate solution into a dry Erlenmeyer flask of 50 mL (or smaller). The stop watch should be started when the solution mixture in the beaker is added to the $K_2S_2O_8$ solution. The solution should be mixed. Measure the time until the blue color of starch appears.

Special care should be taken for the following:

- Pipets should not be placed into the solution container. The solutions should be poured into clean and dry beaker 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.
- 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.

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 $Na_2S_2O_3$ (it can be prepared by dilution)
- 25 cm^3 0.2 m/V% starch (see Appendix for preparation)

The measurements should be performed in the following systems:

Sample No.	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 procedure

Use Eqn. (5) to calculate the rate coefficient. The concentration of iodide ion is constant until the appearence of the starch indicator as supported by Eqns (3), (4), and (6). The reaction rate can be approximated by Eqn. (8) as the conversion is small under the applied experimental conditions:

$$r \approx -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} \approx k[S_2O_8^{2-}]_0^{\beta_{S_2O_8^{2-}}}[I^-]_0^{\beta_{I^-}}, \tag{8}$$

where $\Delta[S_2O_8^{2-}]$ is the concentration change during the reaction which can be calculated from the initial concentration of $S_2O_3{}^{2-}$: $\Delta[S_2O_8^{2-}] = -[S_2O_3^{2-}]_0/2$, and Δt is the reaction time. The rate constant can be determined from the reaction rate using the reaction order from equation (5). The reaction order and the order of the reactants can be determined from the section below.

2.4 Determination of the reaction order

1. Calculate the reaction rates and reactant concentration using the experimental data based on equation (8). Summarize the data according to Table 1.
2. Plot the logarithm of the reaction rates with respect to the logarithm of $[I^-]_0$, and the logarithm of $[S_2O_8{}^{2-}]_0$. In the first case the concentration of peroxydisulfate, while in the second case the iodide concentration is constant. Determine the slope and the intercept of the straight lines with its errors by fitting (see Appendix).
3. Determine the order of the iodide and peroxydisulfate ions (β_{I^-} és $\beta_{S_2O_8^{2-}}$) from the appropriate slopes.

Table 1: Summary of the experimental results.

Sample No.	t /s	$[\mathrm{I^-}]_0$ /M	$\lg([\mathrm{I^-}]_0/\mathrm{M})$	$[\mathrm{S_2O_8^{2-}}]_0$ /M	$\lg([\mathrm{S_2O_8^{2-}}]_0/\mathrm{M})$	r /$(\mathrm{M\,s^{-1}})$	$\lg(\mathrm{r}/(\mathrm{M\,s^{-1}}))$

Sample No.	t/s	I/M	$\sqrt{\mathrm{I/M}}$	$\mathrm{k}/(\mathrm{M^{-1}\,s^{-1}})$	$\lg(\mathrm{k}/(\mathrm{M^{-1}\,s^{-1}}))$

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

1. Calculate the rate coefficients and the ionic strengths from the initial reactant concentrations, reaction rates and reaction orders according to the table below:

   Consider all ionic species which have non-negligible concentration to calculate the ionic strength
2. Plot lg k as a function of $I^{1/2}$. Determine graphically and by straight line fitting the slope and the intercept with the corresponding errors (see Appendix).
3. Determine $\lg[\mathrm{k_0}/(\mathrm{M^{-1}\,s^{-1}})]$ and $\mathrm{k_0}/(\mathrm{M^{-1}\,s^{-1}})$.
4. Compare the theoretically given and experimentally obtained value for parameter A. Discuss the findings.

Control questions

1. Give the ionic strength dependence for rate coefficients of ionic reactions.
2. Define the ionic strength.
3. Give the two reaction steps between peroxydisulfate and iodide ions. Which step is the rate determining?
4. How is the reaction rate approximated? Why?
5. Give the equation required to determine the rate coefficient when ionic strength is investigated.
6. What kind of graphs have to be prepared and what can be determined from them?
7. Why is sodium thiosulfate solution added to the reaction mixture?
8. The following reactant mixture is prepared: $10\,\mathrm{cm^3}$ 0.1 M KI solution, $10\,\mathrm{cm^3}$ 0.001 M $Na_2S_2O_3$ solution, $1\,\mathrm{cm^3}$ 0.4 M KNO_3 solution, $5\,\mathrm{cm^3}$ starch solution, $20\,\mathrm{cm^3}$ 0.01 M $K_2S_2O_8$ solution and $54\,\mathrm{cm^3}$ distilled water. The solution is turned blue after 630 s. Calculate the reaction rate.
9. Calculate the ionic strength of the reaction mixture given in question 8.