Experiment 8

IODINE CLOCK — THE INITIAL RATE METHOD

Objective

The purpose of this experiment is to use the reduction-oxidation reaction between a known amount of thiosulfate ($S_2O_3^{2-}$) and iodine (I_2) as a measuring tool to determine the rate of the reaction between persulfate ($S_2O_8^{2-}$) and iodide (I^-) ions; to determine the rate law of reaction by the initial rate method.

Lab techniques

- Operating graduated pipet and laboratory dispenser

Introduction

I. The reaction rate and the rate law

Iron nails will slowly rust when left in the air. If acid is present, the corrosion rate will be accelerated. Such studies on reaction rates and factors that affecting them (such as concentration, temperature, catalysts, *etc.*) are called chemical kinetics.

Reaction rate is defined as the change in concentration of a reactant or a product per unit time. For the reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow c\,\mathrm{C}$$

The rate is shown as equation 8-1:

$$\text{rate} = \frac{-\mathrm{d[A]}}{a \cdot \mathrm{d}t} = \frac{-\mathrm{d[B]}}{b \cdot \mathrm{d}t} = \frac{\mathrm{d[C]}}{c \cdot \mathrm{d}t} \qquad (8\text{-}1)$$

The relationship between the rate and the concentrations of reactants is called the rate law and is expressed in a general form (8-2):

$$\text{rate} = k\,[\mathrm{A}]^m\,[\mathrm{B}]^n \qquad (8\text{-}2)$$

where k is the rate constant; m and n are the orders of reactants A and B, respectively. The overall reaction order is the sum of m and n. It should be emphasized that m and n are experimentally determined and are not deduced from the stoichiometry of the reaction. The reaction order may be positive or negative, integral or fractional, and even zero. Principally, there are two methods to determine the reaction order: the initial rate method and the graphical method of integrated rate law.

II. Determining the reaction rate of persulfate and iodide ions

In this experiment, we are going to study the reaction of $S_2O_8^{2-}$ with I^- (8-3) and its rate law (8-4) by using the initial rate method:

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \rightarrow 2\,SO_4^{2-}(aq) + I_2(aq) \tag{8-3}$$

$$\text{rate} = k\,[S_2O_8^{2-}]^m\,[I^-]^n \tag{8-4}$$

To determine the rate of the reaction, we will add a known and small amount of $S_2O_3^{2-}$ to the reaction mixture to act as a timer, which can react with I_2 rapidly (8-5). Hence, the I_2 produced in the previous reaction is reacted immediately with $S_2O_3^{2-}$ to reproduce I^-. As $S_2O_3^{2-}$ is present in the solution, I_2 cannot exist concurrently. Once the limited amount of $S_2O_3^{2-}$ is consumed completely, I_2 reacts with I^- to form I_3^-, which will form a blue-black complex with the starch indicator pre-added to the reaction mixture. By recording the time for the blue-black color to appear (Δt) and using the stoichiometric relationship between $S_2O_3^{2-}$ and $S_2O_8^{2-}$ (8-6), the initial rate of reaction can be calculated according to equation 8-7:

$$2\,S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2\,I^-(aq) + S_4O_6^{2-}(aq) \tag{8-5}$$

$$\Delta[S_2O_3^{2-}] = 2\,\Delta[S_2O_8^{2-}] \tag{8-6}$$

$$\text{rate} = \frac{-\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{-\frac{1}{2}\Delta[S_2O_3^{2-}]}{\Delta t} \tag{8-7}$$

III. The initial rate method

To investigate the effect of reactant concentration on reaction rate, each trial we change the initial concentration of one reactant while keeping others constant as shown in Table 8-1. In each reaction, 2% starch is used as the indicator; 1.0 mL of 0.0050 *M* $Na_2S_2O_3$ is the limiting reagent; NaCl(aq) and K_2SO_4(aq) are used to keep the total volume and ionic strength(2) constant. After adding the last reactant $K_2S_2O_8$, start timing and recording the time Δt for the reaction mixture changing color, and determine the initial rate of each trial.

Table 8-1 Volumes of reagents for the initial rate method

Trial No.	**0.20 *M* NaI (mL)**	0.20 *M* NaCl (mL)	0.0050 *M* $Na_2S_2O_3$ (mL)	2% starch (mL)	0.10 *M* K_2SO_4 (mL)	**0.10 *M* $K_2S_2O_8$ (mL)**
1	**2.0**	**2.0**	1.0	1.0	**2.0**	**2.0**
2	2.0	2.0	1.0	1.0	**0**	**4.0**
3	**4.0**	**0**	1.0	1.0	2.0	2.0

In trial No. 2, the initial concentration of the reactant $S_2O_8^{2-}$ is doubled as compared to that of trial No. 1. In trial No. 3, the initial concentration of I^- is doubled to that of trial No. 1. By comparing the initial rates, r_1, r_2, and r_3, we can determine the reaction orders m and n (8-8 and 8-9).

$$\frac{r_2}{r_1} = \frac{k\left(2.0\left[\mathrm{S_2O_8^{2-}}\right]_1\right)^m\left([\mathrm{I^-}]_1\right)^n}{k\left(\left[\mathrm{S_2O_8^{2-}}\right]_1\right)^m\left([\mathrm{I^-}]_1\right)^n} = 2.0^m \tag{8-8}$$

$$\frac{r_3}{r_1} = \frac{k\left(\left[\mathrm{S_2O_8^{2-}}\right]_1\right)^m\left(2.0\,[\mathrm{I^-}]_1\right)^n}{k\left(\left[\mathrm{S_2O_8^{2-}}\right]_1\right)^m\left([\mathrm{I^-}]_1\right)^n} = 2.0^n \tag{8-9}$$

By using one of the initial rates, we can calculate the rate constant *k*, and obtain the rate law. According to the rate law, we can change the initial concentration of one reactant in the solution by changing volume, such as 0.10 *M* $K_2S_2O_8$, to alter the initial rate and let the reaction mixture change color at an assigned time.

Apparatus

Graduated pipet (5 mL, 2), pipet filler (2), Erlenmeyer flask (50 mL, 10), cork stopper (6), beaker (100 mL, 2), timer, and scientific calculator (self-prepared).

Chemicals

0.20 *M* Sodium iodide, NaI
0.20 *M* Sodium chloride, NaCl
0.10 *M* Potassium persulfate, $K_2S_2O_8$
0.10 *M* Potassium sulfate, K_2SO_4
0.0050 *M* Sodium thiosulfate pentahydrate, $Na_2S_2O_3{\cdot}5H_2O$
2% Starch indicator

Procedure

Procedure		Illustration
1.	Wash and oven-dry ten 50 mL Erlenmeyer flasks, and allow them to cool to room temperature. Label the flasks for the three trials listed in Table 8-1.	
2.	Use dispensers to add accurately 0.20 *M* NaI, 0.20 *M* NaCl, 0.0050 *M* $Na_2S_2O_3$, and 2% starch to the Erlenmeyer flask according to trial No. 1.	
3.	(1) Use a 5 mL graduated pipet to measure and add 0.10 *M* K_2SO_4 to the flask accordingly. Use another 5 mL graduated pipet to measure accurately the last reagent, 0.10 *M* $K_2S_2O_8$, then add to the flask and start timing simultaneously.	

(2) Immediately stopper the flasks with the cork, swirl the solution in the flask for 20 s, and then leave it on the benchtop.

Note: The operations shall remain consistent to raise the precision. Be careful not to splash the solution when swirling.

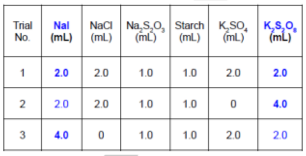
4. Once the solution changes color, stop timing and record the reaction time. (At this moment, the timing reagent $Na_2S_2O_3$ has been consumed completely; I_3^- and starch indicator form a blue-black complex.)

Note: The whole solution should change color abruptly at the same time. If it does not, the solution has not been mixed thoroughly.

5. Repeat trial No. 1 to check the consistency. If two tests show a time difference exceeding 3 s, the test should be repeated a third time.

Note: Wash and oven-dry the Erlenmeyer flasks for later use.

6. According to the volumes of reagents in trials No. 2 and No. 3 in Table 8-1, conduct two repeated tests with different initial concentrations.



Trial No.	NaI (mL)	NaCl (mL)	$Na_2S_2O_3$ (mL)	Starch (mL)	K_2SO_4 (mL)	$K_2S_2O_8$ (mL)
1	2.0	2.0	1.0	1.0	2.0	2.0
2	2.0	2.0	1.0	1.0	0	4.0
3	4.0	0	1.0	1.0	2.0	2.0

7. Calculate m, n, and k values of the rate law.

$$\text{rate} = k[S_2O_8^{2-}]^m[I^-]^n$$

8. Substitute a specific Δt value assigned by the instructor into the obtained rate law and design a set of reagents that will change color at the given time. Carry out the test based on the designed set of reagents and measure the actual time taken for color change.

Note: In order to simplify calculations, fix the volume of I^- (*i.e.* 2.0 or 4.0 mL) and then calculate the volume needed for $S_2O_8^{2-}$ and K_2SO_4.

$$\frac{r_x}{r_1}=\frac{\Delta t_1}{\Delta t_x}=\frac{(x\times 0.10/10.0)^m}{(2.0\times0.10/10.0)^m}=(\frac{x}{2.0})^m$$

$$\frac{r_y}{r_3}=\frac{\Delta t_3}{\Delta t_y}=\frac{(y\times 0.10/10.0)^m}{(2.0\times0.10/10.0)^m}=(\frac{y}{2.0})^m$$

9.	Play "iodine-clock symphony": Prepare a set of measured reagents and bring it to the front along with other students. At a signal from the lab instructor, all students begin the reaction simultaneously while music is being played. Observe whether the prepared reaction mixtures change color on the correct beats of the music.	
10.	(1) Dispose of the chemical wastes that contain iodine in appropriate waste containers. (2) Brush and wash clean the glassware; remove the sticky labels.	

References

1. Dept. of Chemistry, U. of Illinois at Urbana-Champaign *General Chemistry Experiments, Chemistry 102*; Stipes Publishing Co,1991.
2. Skoog, D. A.; West, D. M.; Holler, F. J. *Fundamentals of Analytical Chemistry*; 5th ed., Saunders College Publishing: Chicago, 1988; pp 124-130.