

## Experiment 8

### IODINE CLOCK - THE INITIAL RATE METHOD

#### Objective

The purpose of this experiment is to use the reduction-oxidation reaction between known amount of thiosulfate ion ( $\text{S}_2\text{O}_3^{2-}$ ) and iodine ( $\text{I}_2$ ) as a measuring tool to determine the rate of reaction between persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) and iodide ( $\text{I}^-$ ) ions; to determine the rate law of reaction by initial rate method.

#### Lab techniques

- Operating graduated pipet and dispenser.

#### Introduction

##### I. The reaction rate and the rate law

Chemical kinetics is the study of reaction rate and factors that affecting it, such as concentration, temperature, and catalyst. Reaction rate is defined as the change in concentration of a reactant or product per unit time. For the reaction:

$a\text{A} + b\text{B} \rightarrow c\text{C}$ , the rate is shown as equation 8-1.

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

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

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

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 graphical method (the integrated rate law).

##### II. Determining the reaction rate of persulfate and iodide ions

In this experiment, we are going to study the reaction of  $\text{S}_2\text{O}_8^{2-}$  with  $\text{I}^-$  (8-3) and its rate law (8-4).



$$\text{Rate} = k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}^-]^n \quad (8-4)$$

To determine the rate of the reaction, we will add a known and small amount

of  $\text{S}_2\text{O}_3^{2-}$  to the reaction mixture to act as a timer, which can react with  $\text{I}_2$  rapidly (8-5). Hence, the  $\text{I}_2$  produced in previous reaction is reacted immediately with  $\text{S}_2\text{O}_3^{2-}$  to produce  $\text{I}^-$ . As  $\text{S}_2\text{O}_3^{2-}$  is present in the solution,  $\text{I}_2$  cannot exist concurrently. Once limited amount of  $\text{S}_2\text{O}_3^{2-}$  is consumed completely,  $\text{I}_2$  reacts with  $\text{I}^-$  to form  $\text{I}_3^-$ , which will form a blue-black complex with the starch indicator added to the reaction mixture. By recording the time taken for the blue-black color to appear ( $\Delta t$ ) and using the stoichiometric relationship between  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}_2\text{O}_8^{2-}$  (8-6), the average initial rate of reaction can be calculated as equation 8-7 shown.



$$\Delta[\text{S}_2\text{O}_3^{2-}] = 2\Delta[\text{S}_2\text{O}_8^{2-}] \quad (8-6)$$

$$\text{rate} = \frac{-\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = \frac{-\frac{1}{2}\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} \quad (8-7)$$

### III. The initial rate method

To investigate the effect of reactant concentration on reaction rate, we change the initial concentration of one reactant and keep others constant as Table 8-1 shown. In the reaction, 2% starch is used as the indicator; 1.0 mL of 0.0050 M  $\text{Na}_2\text{S}_2\text{O}_3$  is the limiting reagent;  $\text{NaCl}(\text{aq})$  and  $\text{K}_2\text{SO}_4(\text{aq})$  is used to keep the total volume and ionic strength constant. After addition of last reactant  $\text{K}_2\text{S}_2\text{O}_8$ , start record the time  $\Delta t$  for reaction mixture changes color, and determine the initial rate of each experiment.

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

Experiment	<b>0.20 M NaI (mL)</b>	0.20 M NaCl (mL)	0.0050 M $\text{Na}_2\text{S}_2\text{O}_3$ (mL)	2% starch (mL)	0.10 M $\text{K}_2\text{SO}_4$ (mL)	<b>0.10 M <math>\text{K}_2\text{S}_2\text{O}_8</math> (mL)</b>
1	<b>2.0</b>	2.0	1.0	1.0	2.0	<b>2.0</b>
2	2.0	2.0	1.0	1.0	0	<b>4.0</b>
3	<b>4.0</b>	0	1.0	1.0	2.0	2.0

Note:  $\text{NaCl}$  and  $\text{K}_2\text{SO}_4$  are added to maintain ionic strength in the solutions<sup>(2)</sup>.

In experiment 2, the initial concentration of the reactant  $\text{S}_2\text{O}_8^{2-}$  is doubled as compared to that of experiment 1. In experiment 3, the initial concentration of  $\text{I}^-$  is doubled to that of experiment 1. By comparing the initial rates (8-8 and 8-9), we can determine the reaction order m and n. Use one of the initial rates to calculate the rate constant k.

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{k(2.0 [\text{S}_2\text{O}_8^{2-}]_1)^m([\text{I}^-]_1)^n}{k([\text{S}_2\text{O}_8^{2-}]_1)^m([\text{I}^-]_1)^n} = (2.0)^m \quad (8-8)$$

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{k([\text{S}_2\text{O}_8^{2-}]_1)^m(2.0[\text{I}^-]_1)^n}{k([\text{S}_2\text{O}_8^{2-}]_1)^m([\text{I}^-]_1)^n} = (2.0)^n \quad (8-9)$$

### Apparatus

Graduated pipet (5 mL, 2), pipet filler, 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
- 0.10 M Potassium persulfate,  $\text{K}_2\text{S}_2\text{O}_8$
- 0.0050 M Sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$
- 0.20 M Sodium chloride, NaCl
- 0.10 M Potassium sulfate,  $\text{K}_2\text{SO}_4$
- 2% Starch solution

### Procedure

Procedure	Illustration
Wash and oven dry ten 50 mL Erlenmeyer flasks, and 1. allow them to cool to room temperature. Label the flasks for the three experiments listed in Table 8-1.	
Use dispensers add accurately 0.20 M NaI, 0.20 M NaCl, 0.0050 M $\text{Na}_2\text{S}_2\text{O}_3$ , and 2% starch solution to the Erlenmeyer flasks according to Table 8-1.	
Use 5 mL graduated pipet, measure and add 0.10 M $\text{K}_2\text{SO}_4$ to the flasks accordingly. With another 5 mL graduated pipet measure accurately and <b>add the last reagent, 0.10 M <math>\text{K}_2\text{S}_2\text{O}_8</math>, to the flask and start timing at same time.</b> Immediately stopper the flasks with the cork provided, swirl the solution in the flask for 20 s, and then leave the flask on benchtop.  Note 1: The operation shall keep consistent to raise the precision.  Note 2: Refer to the experimental skills videos to	 

	learn how to use a graduated pipet.																													
4.	<p>Once the solution changes color, stop timing and record the reaction time. (At this moment, the timing reagent <math>\text{Na}_2\text{S}_2\text{O}_3</math> has been consumed completely; <math>\text{I}_3^-</math> and starch indicator form a blue-black complex.)</p> <p>Note: The blue-black color appears within 2 min mostly. The whole solution should change color abruptly at the same time. If it does not, the solution has not been mixed thoroughly.</p>																													
5.	Repeat each experiment twice to check the consistency. If two tests show a time difference more than 3 s, the test should be repeated again.	<table border="1"> <thead> <tr> <th>Trial No.</th> <th>NaI (mL)</th> <th>NaCl (mL)</th> <th><math>\text{Na}_2\text{S}_2\text{O}_3</math> (mL)</th> <th>Starch (mL)</th> <th><math>\text{K}_2\text{SO}_4</math> (mL)</th> <th><math>\text{K}_2\text{S}_2\text{O}_8</math> (mL)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>2.0</td> <td>2.0</td> <td>1.0</td> <td>1.0</td> <td>2.0</td> <td>2.0</td> </tr> <tr> <td>2</td> <td>2.0</td> <td>2.0</td> <td>1.0</td> <td>1.0</td> <td>0</td> <td>4.0</td> </tr> <tr> <td>3</td> <td>4.0</td> <td>0</td> <td>1.0</td> <td>1.0</td> <td>2.0</td> <td>2.0</td> </tr> </tbody> </table>	Trial No.	NaI (mL)	NaCl (mL)	$\text{Na}_2\text{S}_2\text{O}_3$ (mL)	Starch (mL)	$\text{K}_2\text{SO}_4$ (mL)	$\text{K}_2\text{S}_2\text{O}_8$ (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
Trial No.	NaI (mL)	NaCl (mL)	$\text{Na}_2\text{S}_2\text{O}_3$ (mL)	Starch (mL)	$\text{K}_2\text{SO}_4$ (mL)	$\text{K}_2\text{S}_2\text{O}_8$ (mL)																								
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6.	Calculate m, n, and k values of the rate law.	$\text{rate} = k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}^-]^n$																												
7.	<p>The instructor will assign a specific <math>\Delta t</math> value (time taken for color change) to each group. Substitute the value into the rate law obtained and design a set of reagents that will change color at given time interval <math>\Delta t</math>. Carry out the test based on the designed set of reagents and measure the actual time taken for color change. Compare the time with the assigned <math>\Delta t</math> to check its accuracy.</p> <p>Note: In order to simplify calculations, fix the volume for <math>\text{I}^-</math> (i.e. 2.0 or 4.0 mL), and then calculate the volume needed for <math>\text{S}_2\text{O}_8^{2-}</math>.</p>	$\frac{\text{rate X}}{\text{rate 1}} = \frac{\Delta t_1}{\Delta t_x} = \frac{(x \cdot 0.10 / 10.0)^m}{(2.0 \times 0.10 / 10.0)^m} = \left(\frac{x}{2.0}\right)^m$ $\frac{\text{rate Y}}{\text{rate 3}} = \frac{\Delta t_3}{\Delta t_y} = \frac{(y \cdot 0.10 / 10.0)^m}{(2.0 \times 0.10 / 10.0)^m} = \left(\frac{y}{2.0}\right)^m$																												
8.	<p>Play iodine-clock symphony:</p> <p>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 reaction mixtures prepared will change color on the correct beats of the music.</p>																													

## 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.