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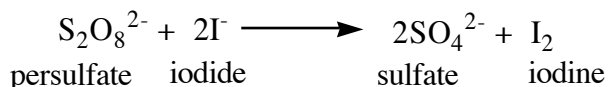
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III. Chemical Kinetics

III.1- The Iodine Clock Reaction

Introduction

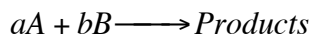
In this experiment, you will study a reaction that proceeds at an easily measured rate at room temperature:



In the first part of the experiment, the *rate equation* will be determined by investigating the effect of the concentration of the reactants on the rate of the persulfate-iodide reaction. In the second part, the *activation energy* will be calculated by studying the effects of temperature change and addition of a catalyst on the reaction system.

Background

Given the equation for a general reaction:



The dependence of the rate of the reaction on the concentration of the reactants may be expressed by a *rate equation* of the form:

$$\text{rate} = k[A]^l[B]^m$$

where, k is the rate constant (or rate coefficient); l and m are the orders of the reaction with respect to the reactants A and B, respectively; and the sum $l + m$ is the overall reaction order. Unlike the stoichiometric coefficients determined by calculation, the orders of the reaction are based on the kinetics of the reaction. The orders of the reaction are defined by the *mechanism of the reaction*, which is an account of the actual steps by which the molecules combine. Orders can only be determined experimentally.

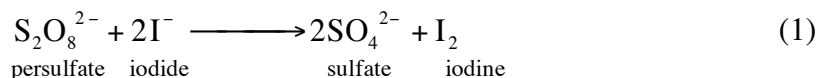
The effect of temperature on reaction rate is given by the Arrhenius equation:

$$k = A e^{-E_a/RT}$$

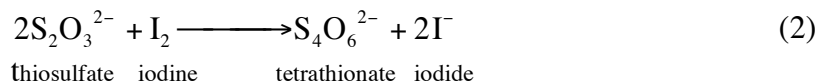
where A is the Arrhenius constant, E_a the activation energy of the reaction, T the absolute temperature, and R the universal constant of gases.

Description of the Experiment

In this experiment, we study the kinetics of the reaction between persulfate $\text{S}_2\text{O}_8^{2-}$ and iodide I^- ions:

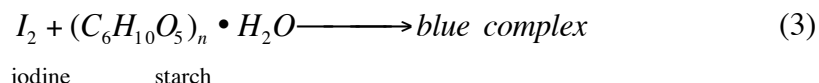


Rates of reaction are measured by either following the appearance of a product or the disappearance of a reactant. In this experiment, the rate of consumption of the iodine will be measured to determine the rate of the reaction. As reaction (1) runs, the amount of iodine (I_2) produced from it will be followed using reaction (2):



The iodine produced from the persulfate-iodide reaction (1) is immediately reduced back to iodide by thiosulfate ions (2). A known amount of thiosulfate ions will be added to the reaction vessel which will in turn consume iodine as it is produced. This continues until all the thiosulfate has been converted to tetrathionate, whereupon free iodine will start to form in the solution via reaction (1). Because we know the amount of thiosulfate we added, we can determine the amount of iodine produced from reaction (1) stoichiometrically. When all the thiosulfate is consumed, free iodine starts to form in solution. By measuring the time taken for the known amount of thiosulfate to be consumed, the rate of production of iodine during that time can be calculated.

The color of the iodine formed might be intense enough that it can act as its own indicator; however, for better results, you will add starch, which produces a deep blue starch-iodine complex:



In summary, iodide (I^-) and persulfate ions ($\text{S}_2\text{O}_8^{2-}$) react to produce iodine (I_2) and sulfate (SO_4^{2-}) in reaction (1). This iodine is immediately consumed by the thiosulfate ions ($\text{S}_2\text{O}_3^{2-}$) in a pathway described by reaction (2). As soon as all of the $\text{S}_2\text{O}_3^{2-}$ ions are consumed, the excess iodine produced in (1) is free to react with starch, turning the solution blue (3). The amount of thiosulfate ions added tells us how much iodine had been produced in the time taken for the reaction to turn blue.

Rate equation

The rate of the reaction *at constant temperature and ionic strength* can be expressed as the change in concentration of a reagent or product over the change in time and can be equated to the rate law expression:

$$\text{rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t} = k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}^-]^n$$

The variation in concentration of persulfate (a minus sign denotes consumption) and the variation in concentration of iodine (production) are given by:

$$\Delta[S_2O_8^{2-}] = [S_2O_8^{2-}]_{final} - [S_2O_8^{2-}]_{initial} = 0 - [S_2O_8^{2-}]_{initial} = -[S_2O_8^{2-}]_{added}$$

$\Delta[I_2] = [I_2]_{final} - [I_2]_{initial}$, but at the beginning of the reaction $[I_2]_{initial} = 0$, so:

$$\Delta[I_2] = [I_2]_{final}$$

Then:

$$rate = \frac{[I_2]}{t} = \frac{\text{moles } I_2}{\text{volume solution(L)} \times \text{time(sec)}}$$

The number of moles of iodine produced is given by the amount of thiosulfate added to the reaction vessel:

$$\text{moles } S_2O_3^{2-} = \{\text{volume of } S_2O_3^{2-} \text{ added(L)}\} \times \{\text{concentration of } S_2O_3^{2-}\}$$

The stoichiometry of reaction (2) gives:

$$rate = \frac{[I_2]}{t} = \frac{\text{moles } S_2O_3^{2-}}{2 \times \text{volume solution(L)} \times \text{time(sec)}}$$

Thus we can calculate the rate by:

$$rate = \frac{\text{vol. } S_2O_3^{2-} \text{ added (L)} \times \text{conc. } S_2O_3^{2-} \text{ (moles / L)}}{2 \times \text{volume solution(L)} \times \text{time(sec)}}$$

This reaction rate is a measure of how much iodine was produced in the time it took for the reaction to turn blue (i.e., time taken to react with all of the thiosulfate present).

Reaction Orders

In this experiment we use the **initial rate method** to find the order of the reaction with respect to persulfate (m) and the order of the reaction with respect to iodide (n). The method is based on the measurement of the rate of the reaction over a period of time. This time period is short enough for the reaction not to have proceeded significantly, but long enough to be unaffected by the time which the solutions take to mix at the start of the reaction.

The rate law equation can be written as:

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

By taking the natural log of both sides, the equation becomes:

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

For runs with different concentrations of **persulfate** and a constant concentration of iodide at a constant temperature,

$$\ln \text{ rate} = m \ln[S_2O_8^{2-}] + \text{constant}$$

The constant term in this equation is $\ln k + n \ln [I^-]$. The slope of the best fit line of a plot of $\ln \text{ rate}$ versus $\ln[S_2O_8^{2-}]$ will be equal to m , the order of reaction with respect to persulfate.

Similarly, for runs where persulfate concentration and temperature are kept constant and the amount of **iodide** is varied,

$$\ln \text{ rate} = n \ln[I^-] + \text{constant}$$

The constant term is $\ln k + m \ln[S_2O_8^{2-}]$. The slope of the best fit line of a plot of $\ln \text{ rate}$ versus $\ln[I^-]$ will be equal to n , the order of reaction with respect to iodide.

Activation energy (E_a)

Recall the Arrhenius equation:

$$k = A e^{-E_a/RT}$$

Taking natural logarithm of both sides of this equation we obtain:

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

A plot of $\ln k$ versus $1/T$ yields a straight line whose slope is $-E_a/R$ and whose y-intercept is $\ln A$, the natural logarithm of the Arrhenius constant.

Procedure

Effect of Persulfate and Iodide Concentrations on Rate

You will be provided with the following solutions:

- (i) Standardized $Na_2S_2O_3$ solution (about 0.1 M, BE SURE TO RECORD EXACT VALUE);
- (ii) 0.1M potassium persulfate, $K_2S_2O_8$; (iii) 0.2M potassium iodide, KI; (iv) 0.2M potassium chloride, KCl; (v) 0.1M potassium sulfate, K_2SO_4 .

The rate coefficient (k) of ionic reactions depends on the *ionic strength* or salinity of the solution. Potassium chloride (KCl) and potassium sulfate (K_2SO_4) are used to maintain the ionic strength of the solutions.

1. Prepare a 4.0×10^{-3} M solution of sodium thiosulfate as follows: Rinse a clean 250mL volumetric flask with distilled water. Pipette an aliquot of 10 mL of the standardized thiosulfate solution into the volumetric flask and add distilled water to the mark on the neck of the flask. Stopper and invert the flask a few times to mix its contents. Transfer the diluted thiosulfate solution into a clean labeled plastic bottle. This diluted solution will be used along the experiment.

2. Label a 50mL Erlenmeyer flask "A" and a 50mL beaker "R", the reaction beaker. For each run of the reaction, make up glassware as shown in the chart below. Between runs, rinse the flasks THOROUGHLY with distilled water.

Runs	Erlenmeyer A		Reaction Beaker "R" (+ 2 drops fresh starch solution + magnetic bar)		
	0.2M KI (mL)	0.2M KCl (mL)	0.1M K ₂ S ₂ O ₈ (mL)	0.1M K ₂ SO ₄ (mL)	4.0x10 ⁻³ M*** S ₂ O ₃ ²⁻ (mL).
1	10	0	5	5	5
2	5	5	5	5	5
3	2.5	7.5	5	5	5
4	5	5	7.5	2.5	5
5	5	5	10	0	5

3. For each run, start stirring the reaction beaker. Then, dump the contents of flask "A" into it and immediately begin timing. Record the "Blue Time" (the time in seconds needed for the solution to turn blue) for each run. Deposit all waste in the liquid waste container. ***Do not add the S₂O₃²⁻ solution until you are ready to mix mixtures A and R together.

Discussion and Calculations

Prepare the following graphs:

1. $\ln \text{rate}$ versus $\ln[S_2O_8^{2-}]$, for runs where $[I^-]$ is constant (runs 2, 4 and 5).
2. $\ln \text{rate}$ versus $\ln[I^-]$, for runs where $[S_2O_8^{2-}]$ is constant (runs 1, 2 and 3).
3. $\ln k$ versus $1/T$ for runs at constant concentrations but variable temperature.

For these graphs draw a best-fit line. The slopes of graph 1 and graph 2 will give you m and n , respectively (round them to their nearest integer values). The slope of graph 3 will give you $-E_a/R$ and the intercept $\ln A$.

In your calculations, you should keep in mind that the starting concentration in the reaction vessel for each reagent is not simply what was printed on the bottle. For instance, for the first run in Part One, you used 20 mL of the 0.2M KI solution; however, when the reaction is run, the actual concentration of iodide, at start, is not 0.2M. Find the concentration of the two reagents (iodide and persulfate) used in each run (Hint: what dilutions have occurred?).

The rate for every run in this experiment can be calculated by:

$$\text{rate} = \frac{[S_2O_3^{2-}]_{\text{diluted}} \times 5}{2 \times 25 \times \text{time}} = \frac{4.0 \times 10^{-4}}{\text{time}} \text{ Ms}^{-1}$$

Since the total volume in every reaction is 25 mL and 5 mL of the dilute thiosulfate solution is used in every reaction, the only quantity in this equation that will change is the time. Be sure to account for all dilutions in the sodium thiosulfate solution concentration.

Once you have determined m and n , the rate constant k is calculated from:

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

Your final k value (at room temperature) should be the average of the k values obtained for runs 1 through 5 in Part One. Make sure to give the units for k .

Goals

- 1) Determine the experimental rate law
- 2) Propose a mechanism consistent with the experimental rate law. (Do not worry if it is the correct mechanism, only that the experimental rate law can be derived from it)
- 3) Determine the activation energy and Arrhenius constant for the reaction.

Data Sheet

Effect of Reagent Concentration Temperature of solution: _____

	KI (mL)	KCl (mL)	K ₂ S ₂ O ₈ (mL)	K ₂ SO ₄ (mL)	S ₂ O ₃ ²⁻ (mL)	Time (sec)
1	10	0	5	5	5	
2	5	5	5	5	5	
3	2.5	7.5	5	5	5	
4	5	5	7.5	2.5	5	
5	5	5	10	0	5	

Effect of Temperature (note: pick a run from above to use as room temperature run)

	KI (mL)	KCl (mL)	K ₂ S ₂ O ₈ (mL)	K ₂ SO ₄ (mL)	S ₂ O ₃ ²⁻ (mL)	Temperature (K)	Time (sec)
1							
2							
3							
4							
5							