Experiment 3
Kinetics - Iodine Clock Reaction

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Name:

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Date:

Key Objectives

1. Use the Method of Initial Rates to calculate rate law exponents (m, n) and rate constant (k)
2. Use the Arrhenius Equation to calculate the Activation Energy (E_a)
3. Review $M_1V_1 = M_2V_2$

Discussion

A complete discussion of Kinetics can be found in McMurry Chapter 12 or in your OER textbook Chapter 17.

The reaction examined in the laboratory is the reduction of potassium persulfate ($K_2S_2O_8$) by sodium iodide (NaI) in an aqueous solution. The net reaction is given below:

$$S_2O_8{}^{-2}(aq) + 2I^-(aq) \longrightarrow 2SO_4{}^{-2}(aq) + I_2(aq) \tag{10}$$
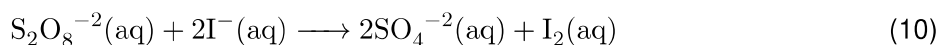
The general form of the rate law is then:

$$\text{Rate} = k[S_2O_8{}^{-2}]^m[I^-]^n \tag{11}$$

The goal of the experiment is to determine the exponents m and n and the value of the rate constant k by using the method of initial rates (see McMurry, Chapter 12.2-12.3).

Method of Initial Rates

The rate law can be determined experimentally by measuring the initial rate of a reaction for a series of different reactant concentrations. We will specifically measure disappearance of the thiosulfate anion over time.

$$-\frac{\Delta[S_2O_8{}^{-2}]}{\Delta t} = -\frac{[S_2O_8{}^{-2}]_2 - [S_2O_8{}^{-2}]_1}{t_2 - t_1} \tag{12}$$

The method of initial rates will be determined by comparing the results of three different trials where Trial 1 will be the reference solution, and in Trial 2 the $[S_2O_8{}^{-2}]$ will be doubled while the $[I^-]$ will be kept the same. Trial 3 will keep the $[S_2O_8{}^{-2}]$ while doubling the $[I^-]$. To differentiate the trials the concentrations will be given subscripts, thus $[S_2O_8{}^{-2}]_1$ would refer to the concentration for Trial 1.

Using the method of initial rates we can compare Trial 1 and Trial 2 and cancel out the terms that are the same on the top and bottom of the ratio, and determine the m exponent.

$$\frac{\text{Rate Trial 1}}{\text{Rate Trial 2}} = \frac{k[S_2O_8^{-2}]_1^m[I^-]_1^n}{k[S_2O_8^{-2}]_2^m[I^-]_2^n} = \frac{k[2.0]_1^m[2.0]_1^n}{k[4.0]_2^m[2.0]_2^n} = (1/2)^m \tag{13}$$

By comparing Trial 1 and Trial 3 a similar equation can be written to determine the n exponent.

Measuring the Initial Rate

Measuring initial rates can be easy if a visible change occurs but becomes more complicated if there is no visible change when the reaction occurs. Unfortunately the reaction in this experiment falls into the second category and while it will be easy to measure the initial rate, understanding the chemistry behind it will be a bit more complicated.
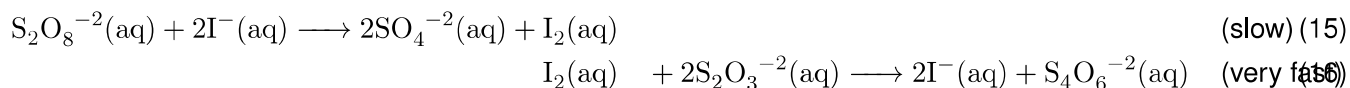
To obtain the initial rate you must measure the initial $[S_2O_8^{-2}]$ which is easy as you will prepare solutions of known concentration. Harder is to measure the $[S_2O_8^{-2}]$ after a given amount of time since the reaction does not have any physical change (color, pressure, temperature etc.) to monitor.

To determine the concentration of $S_2O_8^{-2}$ after a specific amount of time has passed we will need to couple the reaction to a second reaction that does change color. The new reaction is the reduction of I_2 by sodium thiosulfate ($Na_2S_2O_3$) to form iodine ions (I^-) and the tetrathionate ion ($S_4O_6^{-2}$) shown below.

$$I_2(aq) + 2S_2O_3^{-2}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{-2}(aq) \tag{14}$$
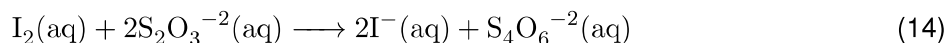
The new reaction is very fast compared to the rate of the reaction we are studying so it will have no effect on the rate of the slower reaction.

The reactions are **coupled** because I_2 is produced in the first reaction, and consumed in the second reaction. Since the rate of the second reaction is very fast compared to the rate of the first reaction any I_2 is immediately consumed by the second reaction and has no effect on the rate of the first reaction (the one we are studying).

$$S_2O_8^{-2}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{-2}(aq) + I_2(aq) \qquad \text{(slow) (15)}$$
$$I_2(aq) \quad + 2S_2O_3^{-2}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{-2}(aq) \quad \text{(very fast) (16)}$$

By controlling the concentration of thiosulfate ions ($S_2O_3^{-2}$) in the second reaction we can control when I^- in the first reaction stops being used by the second reaction. When this occurs, I_2 from the first reaction will form. The presence of I_2 can be detected easily by a reaction with starch to form a dark blue, almost black color. Thus, if the concentration of thiosulfate ions ($S_2O_3^{-2}$ is kept constant in each Trial, the final concentration of persulfate ion ($S_2O_8^{-2}$) is known. The sudden change in color (clear to dark blue, almost black) than allows the calculation of Δt.

The relationship between the ions in the reaction is given by the coefficients in the balanced reaction. Thus for every persulfate ion ($S_2O_8^{-2}$) that is reduced, two thiosulfate ions ($S_2O_3^{-2}$) are oxidized. Thus, the concentration change for $S_2O_8^{-2}$ is one-half the concentration change for $S_2O_3^{-2}$.

$$-\frac{\Delta[S_2O_8^{-2}]}{\Delta t} = \frac{1}{2}\frac{\Delta[S_2O_3^{-2}]}{\Delta t} \tag{17}$$

In the experiment we will control the $[S_2O_3^{-2}]$ keeping it constant, thus the $\Delta[S_2O_8^{-2}]$ consumed in the reaction will be kept constant for all trials, meaning that the appearance of the color change gives us Δt for the reaction.

The Effect of Ion Concentration on Reaction Rates

An important consideration often overlooked when discussing reaction rates is the effect of the total concentration of ions in a reaction. The effect is small and not easily measured, but can effect the measurements in this experiment. To control for this effect, it is very important to keep the overall concentration of ions constant in the reaction. This will is done by adding inert ionic substances to the reaction. In the experiment K_2SO_4 and $NaCl$ will be used for this purpose.

The Effect of Temperature

Reaction rates are also effected by temperature in that the rate constant k changes with temperature. A complete discussion of the topic can be found in McMurry Chapter 12.11-12.12.

As reactants are converted to products in a reaction, they undergo an intermediate state or **transition state** that is 1/2 way between the reactants and products. This state is higher in energy than either the Reactants or Products, therefore, there is an energy barrier that must be overcome. The height of the barrier (the amount of energy needed for the reaction to occur) is termed the **Activation Energy (E_a)**. This is illustrated in Figure 3.1.
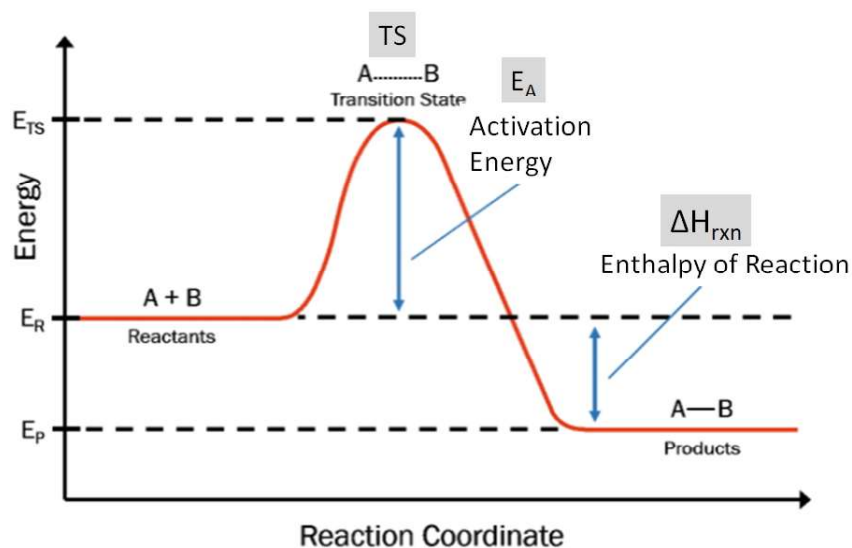

Figure 3.1: Potential Energy Profile for a Reaction credit: (a) author

According to the Kinetic Molecular Theory, at higher temperatures, there are more molecules with the energy required to react as shown in Figure 3.2 The effect of temperature on the rate constant is given by the Arrhenius Equation where k = reaction rate, A = constant, E_a = Activation Energy, R = gas constant and T = Temperature (in K).
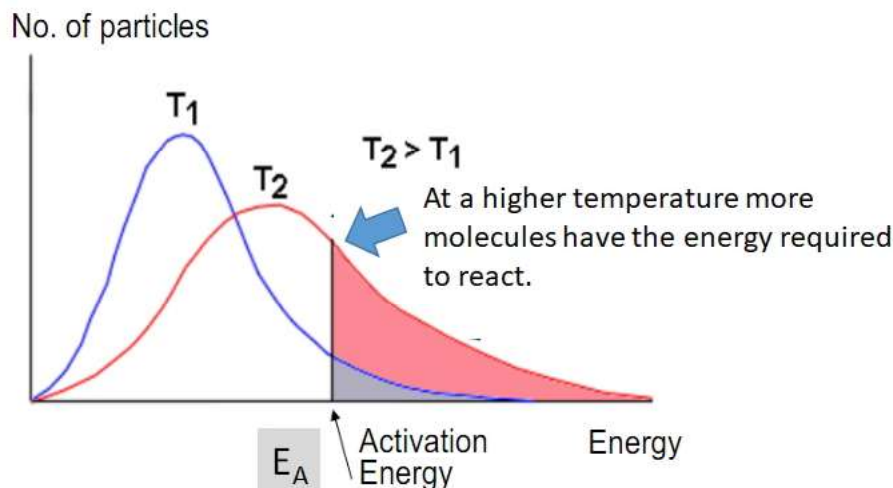

Figure 3.2: Distribution of Molecular Kinetic Energy at two different temperatures. credit: Thi, W.-F. (2015). Disk Chemistry. EPJ Web of Conferences. 102. 00012. 10.1051/epjconf/201510200012 modified by author

$$ln\ k = ln\ A - \frac{E_a}{RT} \qquad (18)$$

The equation can be rearranged into the standard form of a line ($y = mx + b$) and if a plot of $ln\ k$ versus $1/T$ is made than the slope of the line is $m = -E_a/R$.

$$ln\ k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + ln\ A \qquad (19)$$

Alternatively the equation can be used to compare the rate constant at two different temperatures.

$$ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (20)$$

The Activation Energy (E_a) will be determined by repeating Trial 1 at a different temperatures.

Effect of a Catalyst

The effect of a catalyst on the reaction will be explored by adding $CuSO_4$ to the reaction and measuring the reaction rate.

Dilutions

You will be diluting the solutions used in the experiment, don't forget that:

$$M_1V_1 = M_2V_2 \tag{21}$$

Procedure

Determining the Rate Equation

1. Obtain 10 large test tubes, and 6 disposable pipets.

2. Obtain 30 mL of each of the solutions listed in Table 3.1 below.

3. Record the temperature of the laboratory.

4. Be sure to rinse the pipets with several small portions of each solution used. Use a separate pipet for each solution.

5. Using the quantities in the table below, prepare the solution in Test Tube 1 except for adding the $K_2S_2O_8$.

6. Read the next three steps completely before proceeding.

7. Record the time at the instant you add the required amount of $K_2S_2O_8$ to the test tube. Quickly stir the solution (as demonstrated in class). It is very important that you have a homogeneous solution.

8. Observer your solution and record the exact time the appearance of the dark blue (almost black) color appears. The color should appear throughout the test tube at the same time. If it does not, your solution was not homogeneous and you should repeat the trial.

9. Each trial should take less than 5 minutes. If your trial exceeds 5 minutes inform your instructor.

10. Repeat the process above for each of the remaining test tubes in the results section. If any two trials differs by more than 15 seconds repeat until the two consecutive trials agree to within 15 seconds.

11. Dispose of all solutions in the sink.

Determining the Activation Energy

1. Set up a hot-plate and boil a large (1000 mL) beaker of water. Once the water is hot, move on to the next step.

2. Use a second 1000 mL beaker prepare 500 mL of water at about 35 °C by mixing warm water to cold water. You will have to periodically add hot water to the bath to maintain the temperature.

3. Record the temperature of the warm water solution.

4. Read the next three steps completely before proceeding.

5. Using the quantities in the table below, prepare the solution in Test Tube 4 using the same volumes as in Test Tube 1, except for adding the $K_2S_2O_8$.

6. Place the test tube into the warm water bath and allow 10 minutes for the solution to reach equilibrium. Also place a test tube containing 10 mL of $K_2S_2O_8$ into the warm water bath and allow 10 minutes for the solution to reach equilibrium.

7. Record the time at the instant you add the required amount of $K_2S_2O_8$ to the test tube. Quickly stir the solution (as demonstrated in class). It is very important that you have a homogeneous solution.

8. After mixing place the solution back in the warm water bath.

9. Observe your solution and record the exact time the appearance of the dark blue (almost black) color appears. The color should appear throughout the test tube at the same time. If it does not, your solution was not homogeneous and you should repeat the trial.

10. Dispose of all solutions in the sink.

Effect of a Catalyst on the Reaction Rate

1. Prepare Test Tube 5 using the same amounts as in Test Tube 1, however, before adding the $K_2S_2O_8$ add 1 drop of 0.2 M $CuSO_4$ and mix the test tube until the solution is homogeneous.

2. Dispose of all solutions in the sink.

Test Tube #	0.20 M NaI (mL)	0.20 M NaCl (mL)	0.010 M $Na_2S_2O_3$ (mL)	2%-Starch (mL)	0.20 M K_2SO_4 (mL)	0.20 M $K_2S_2O_8$ (mL)
1	2.0	2.0	2.0	1.0	2.0	2.0
2	2.0	2.0	2.0	1.0	0	4.0
3	4.0	0	2.0	1.0	2.0	2.0

Table 3.1: Solutions Needed for the Experiment.

Name: _____   Class: _____   Date: _____

Results

Test Tube #	Temp. (℃)	Trial #	Start (sec)	Final (sec)	Δt (sec)
1		1			
		2			
		3			
		4			
2		1			
		2			
		3			
		4			
3		1			
		2			
		3			
		4			
4		1			
		2			
		3			
		4			
5		1			
		2			

Table 3.2: Results - Experimental Data

1. Determine the average value and standard deviation of Δt for Test Tubes 1-5 and note the results in Table 3.3. Show an example calculation for Test Tube 1.

Test Tube #	Avg. Temp. (°C)	Avg. Δt (sec)	Standard Deviation	Initial Rate
1				
2				
3				
4				
5				

Table 3.3: Results - Average and Standard Deviation for Test Tubes 1-5.

2. Calculate the initial rates for the reactions in Test Tubes 1-5 using the value of $\Delta[S_2O_8^{-2}]$ that you determined in the pre-laboratory assignment and the mean elapsed times calculated from your results. Record your results in Table 3.3. Show an example calculation for Test Tube 1.

3. Calculate the initial concentrations of $S_2O_8^{-2}$ and I^- ions in solutions in test tubes 1-3. Remember that dilution occurred when the solutions were prepared. Record your results in Table 3.4. Show an example calculations for Test Tube 1.

Test Tube #	$[S_2O_8^{-2}]$	$[I^-]$
1		
2		
3		

Table 3.4: Results: Initial Concentrations for Test Tubes 1-3.

4. Calculate the exponents (m and n) in the reaction rate using the data from Test Tubes 1-3. Experimental Error will result in the exponents not being whole numbers as expected, you will have to round to the nearest hundredth. Explain.

5. From the results of the previous equation what is the correct rate equation?

6. Calculate the rate constant (k) for Test Tubes 1-3. Determine the average and standard deviation. Record your results in Table 3.5. Show an example calculation for Test Tube 1.

Test Tube #	Rate Constant (k)
1	
2	
3	
Average:	
Standard Dev:	

Table 3.5: Results - Average and Standard Deviation for Test Tubes 1-5.

7. Calculate the rate constant for Test Tube Number 4 and using the value calculate the Activation Energy for the reaction. Explain.

Rate Constant Test Tube 4: _____   Activation Energy: _____

8. What do your results demonstrate about the effect of adding a catalyst on the rate of the reaction?

9. Consider the reaction that occurred in Test Tube 1. Describe how you would alter the concentrations of each of the reactants below so that the dark color will appear in exactly 1/4 the average time you found in the experiment. The experiment must be performed at room temperature and the total volume of the reaction must be the same used in Trial 1. Explain

Test Tube #	0.2 M NaI (mL)	0.2 M NaCl (mL)	0.01 M $Na_2S_2O_3$ (mL)	2%-Starch (mL)	0.2 M K_2SO_4 (mL)	0.2 M $K_2S_2O_8$ (mL)
6						

Table 3.6: Concentration of Reactants to Cause the Reaction to Occur in 1/2 Time.

Name: _____   Class: _____   Date: _____

Prelab Questions

1. It is very important to keep track of the many different compounds used in the experiment. Fill in the missing blanks in the table below.

Name	Formula
Potassium Persulfate	
	NaI
	K_2SO_4
Sodium Chloride	
Persulfate Anion	
	$S_2O_3^{-2}$
	I_2
Iodide Anion	
	$S_4O_6^{-2}$
Suflate Anion	

Table 3.7: Compounds used in the Experiment

2. What is the purpose of the K_2SO_4 and NaCl used in the experiment?

3. What is the purpose of the $Na_2S_2O_3$ used in the experiment?

4. Write the chemical equation being studied in this experiment along with the generic rate law for the reaction.

5. Calculate the $\Delta[S_2O_8^{-2}]$ (change in the Molarity) that will occur in Test Tubes 1-3 in the reaction (Equation 17 might help you).

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