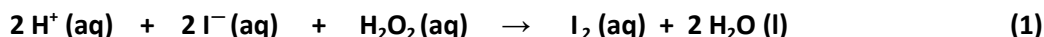


Determination of a Rate Law

Introduction

In this experiment you will determine the Rate Law for the following oxidation-reduction reaction:



The rate or speed of the reaction is dependent on the concentrations of iodide ion (I^-) and hydrogen peroxide, H_2O_2 . (The spectator ions are left off the reaction.) Therefore, we can write the Rate Law (concentration dependence) for the reaction as:

$$\text{Rate} = k [\text{I}^-]^x [\text{H}_2\text{O}_2]^y \quad (2)$$

Where: x is the order of the reaction in I^- , y is the order of the reaction in H_2O_2 , and k is the rate constant.

The temperature dependence of the rate is seen in k – that is, there is a separate value of k for each temperature at which the reaction takes place. The temperature must therefore be held constant to accurately calculate x , y and k . Since the Rate Law is empirical, we have to go to the lab to make measurements that will enable these values to be calculated. The rate will be measured for the reaction near time = 0, so that few products have been formed and there will be no reverse reaction. The concentrations of iodide and hydrogen peroxide will be varied and the rates compared to find each order (i.e., the exponents x and y). This is the Method of Initial Rates and it will be used to find x , y and k .

As with a lot of kinetics, the concentration of reactants or products at any instant is difficult to measure directly, so in this lab the rate will be determined indirectly. We have a very handy test for the presence of one of the products, iodine (I_2), namely starch. Starch reacts with iodine to form a blue/black colored complex. Unfortunately as soon as any iodine is produced it will react to make the complex and the solution will turn blue/black instantaneously. Thus, using starch as an indicator by itself would not be of much help. It confirms that some amount of I_2 is being formed, but it tells us nothing about what we are trying to measure - the rate (how long it takes to produce a given quantity of I_2 .)

To get around this problem we will introduce a side reaction that will remove the initial I_2 that is produced by our main reaction. This will prevent the solution from turning black long enough so that we can make some time measurements. We will use the following side reaction:



$\text{S}_2\text{O}_3^{2-}$, thiosulfate ion, reacts with I_2 which prevents the solution from turning blue/black. How will this help? Since we have carefully measured the amount of thiosulfate (a small amount that will run out fairly quickly), we know exactly how much iodine it will take to react with this thiosulfate. Once the small amount thiosulfate has completely reacted, I_2 will start to build up in the solution. As soon as the thiosulfate runs out, I_2 will react with the starch and the solution will turn blue/black. By putting in this "time delay", we can now calculate the rate at which I_2 is being formed.

The rate of reaction is equal to the change in concentration divided by the change in time. The change in time will be the time it takes for the solution to turn dark. We will calculate the change in concentration in I_2 based on the amount of thiosulfate added. Using the known volume and molarity, we can calculate moles of thiosulfate ($\text{S}_2\text{O}_3^{2-}$). Based on stoichiometry, we can calculate the moles of I_2 : according to equation (3), 2 moles of thiosulfate react with every 1 mole of I_2 , this gives us the change in moles, however for the rate formula we need change in concentration. Divide the moles of I_2 reacted by the total volume to find the change in molarity.

$$\text{Rate} = [\Delta \text{I}_2] / \Delta t \quad (4)$$

Equipment

Three 125 or 250 mL Erlenmeyer flasks
10 ml and 5 ml Pipettes
Stop watch or other time keeper

Three 100 or 150 mL beakers
Thermometer

One bin of chemicals per group that will contain:

0.050 M KI	0.050 M NaCl	0.010 M $\text{Na}_2\text{S}_2\text{O}_3$
1.0 M H_2SO_4	1% starch solution	0.050 M H_2O_2

Disposal: All mixtures Spill/Disposal B1 (down the sink)

Procedure:

1. **Before coming to lab, complete the initial concentration table below showing all work.** Initial concentrations are not the concentration of the solutions you start with (i.e. not 0.050M for I^- and H_2O_2). Initial concentrations are the concentration of species in the final total volume of contents of the Erlenmeyer plus beaker for each run (**see tables in steps 4 & 6**). Determine initial concentrations using the formula $M_1V_1 = M_2V_2$. M_1 and V_1 are the molarity and volume of the solutions added, V_2 is the total volume of the Erlenmeyer plus beaker. Copy these initial values onto the table in the data sheet.

Run	$[\text{I}^-]$ (initial)	$[\text{H}_2\text{O}_2]$ (initial)
1 (Flask 1 + beaker 1)	$(15.0 \text{ mL})(0.050\text{M}) = (42.5 \text{ mL})(M_2)$ Solving for M_2 , we get $[\text{I}^-]$ (initial)= 0.018 M	
2 (Flask 2 + beaker 2)		
3 (Flask 3 + beaker 3)		

2. Clean and mostly dry three Erlenmeyer flasks. Label them 1, 2 and 3.
3. Obtain a bin of chemicals for your group. Use only these chemicals for all of your runs. Use fresh pipettes for each solution. Rinse pipette twice with the solution that you will be measuring and keep this prepared pipette with the corresponding solution.
4. Add the amounts of the solutions below to prepare each flask. The chemicals must be added in the order listed (top to bottom).

	Flask #1	Flask #2	Flask #3
0.050 M KI	15.0 mL	15.0 mL	7.5 mL
1% Starch	5.0 mL	5.0 mL	5.0 mL
0.010 M $\text{Na}_2\text{S}_2\text{O}_3$	2.5 mL	2.5 mL	2.5 mL
1 M H_2SO_4	5.0 mL	5.0 mL	5.0 mL
0.050 M NaCl	0	0	7.5 mL

Note: The NaCl solution is added so that the ionic strength of and volume of each solution is the same.

5. Rinse and mostly dry 3 beakers and label as 1, 2 and 3.

6. Prepare the following solutions in clean beakers:

	Beaker #1	Beaker #2	Beaker #3
0.050 M H ₂ O ₂	15.0 mL	7.5 mL	15.0 mL
Deionized H ₂ O	0	7.5 mL	0

Note: deionized water are added so that the total volume of each run is the same. (42.5 mL)

7. Get your timer ready. Add the contents of beaker 1 to flask 1.

8. Start the stopwatch as soon as you mix the solutions. Swirl the flask to mix and note the time it takes for the color to change. This is Run 1. Record the temperature of the mixture.

9. Add the contents of beaker 2 to flask 2. Repeat procedure in step 8. This is Run 2.

10. Add the contents of beaker 3 to flask 3. Repeat procedure in step 8. This is Run 3.

The shade of color you observe should be the same in each of the three runs. If it is not, consult your instructor.

Disposal: All contents of the reaction flasks may be disposed of into the sink.

Calculations:

Review the method of initial rates in your text. You will need the values for the initial concentrations of each reactant as well as the rate.

Hypothetical data for reaction: $A + 2B \rightarrow C + 2D$

Run	[A] ₀	[B] ₀	Initial $\Delta[C]/\Delta t$ (Molarity/sec)
1	0.150 M	0.150 M	8.00
2	0.150 M	0.300 M	16.0
3	0.300 M	0.150 M	32.0

Rate = $k[A]^x[B]^y$. We need to calculate x, y and k

To get x, we have to hold [B] constant and just see how [A] affects the rate. Take the ratio of Run 3/Run 1

$$\frac{\text{Run 3}}{\text{Run 1}} = \frac{\text{Initial } \Delta[C]/\Delta t}{\text{Initial } \Delta[C]/\Delta t} = \frac{k[A]^x[B]^y}{k[A]^x[B]^y} = \frac{32.0 \text{ M/sec}}{8.0 \text{ M/sec}} = \frac{k(0.300\text{M})^x(0.150\text{M})^y}{k(0.150\text{M})^x(0.150\text{M})^y}$$

$$\text{Simplifying: } 4.0 = (0.150\text{M})^x / (0.150\text{M})^x \quad \text{or} \quad 4.0 = (0.300/0.150)^x \quad \text{or} \quad 4.0 = 2^x \quad \text{Or } x = 2$$

Do the same for B (holding [A] constant) and discover that y = 1.

You can calculate k as well. Using run 1:

$$8.00 \text{ M/sec} = k (0.150\text{M})^1 (0.150\text{M})^1 \quad \text{and solving for k, we get } k = 356 \text{ M}^{-1} \text{ s}^{-1}.$$

'k' can be calculated using any of the three runs from Part I

For your data:

Find x and y as explained above. Calculate k for each run and average the three values at the end. If your values for x and y do not turn out to be whole numbers, round to the nearest whole number. Write the Rate Law using your values for x, y and k:

$$\text{Rate} = k [I^-]^x [H_2O_2]^y$$

Name _____

CHM112 Lab – Determination of a Rate Law – Grading Rubric

Criteria	Points possible	Points earned
Lab Performance		
Initial concentrations completed before coming to lab, Safety and proper waste disposal procedures observed	3	
Lab Report		
1. Mole calculation	1	
2. Molarity calculation	1	
3. Table completed: Rate correctly calculated.	3	
4. Calculations for x and y. Rate law correctly written	3	
5. k calculations shown with units.	3	
6. Overall order	1	
7. Rate at different Molarity	1	
8. Rate logic	2	
9. Second order rate law	2	
Total	20	

Subject to additional penalties at the discretion of the instructor.

1. Show your calculations for moles of I_2 reacted: (find through moles of $S_2O_3^{2-}$)
2. Show your calculation for molarity of I_2 reacted $[\Delta I_2]$: (divide moles reacted by total reaction volume)
3. Fill in the table and show your work below!

Run	Temp(°C)	Initial $[I^-]$ M	Initial $[H_2O_2]$ M	ReactionTime (in s) Δt	Reaction Rate (in Ms^{-1}) $= [\Delta I_2] / \Delta t$
1					
2					
3					

4. Show calculations for x and y: (Include appropriate units, attach a separate sheet if necessary.)

x = _____

y = _____

Write the rate law with exponents rounded to the nearest whole number. Rate = _____

5. Calculate k for each run. Show work with units. Find the average k (include units).

k (run 1) = _____ k (run 2) = _____ k (run 3) = _____ Average k = _____

6. What is the overall order of the reaction in this lab?

7. Use your Rate Law and average k to calculate the reaction rate when $[I^-] = 0.020\text{ M}$ and $[H_2O_2] = 0.045\text{ M}$.

8. Consider the reaction $A + B \rightarrow \text{Products}$.

This reaction was experimentally determined to be first order in A and second order in B.

a. Write down the rate law for this reaction.

b. What would be the unit of rate constant 'k' for the above reaction?

c. If the concentration of A is held constant while the concentration of B is doubled, by how much will the rate of the reaction change?

9. The decomposition of a certain chemical X is found to be second order with respect to [X] and has a rate constant of $.0065 \text{ M}^{-1}\text{s}^{-1}$. If the initial concentration of X is 1.25 M, what will be the concentration after 200. seconds?