

CHEMISTRY 111 LAB PREPARATION FORM
Experiment 5: Chemical Kinetics - The Iodine Clock

Name _____

Lab Section _____

Purpose of Experiment:

Objectives:

Key Terms:

Chemical Kinetics-

Rate of Reaction-

Rate Law-

Method of Initial Rates –

Calculations:

Safety Warnings:

Procedure Notes:

Questions before starting experiment?

Comments from Briefing:

Experiment 5: Chemical Kinetics - The Iodine Clock

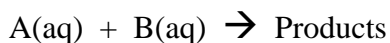
PRELAB EXERCISE

Name _____ Lab Section _____

1. What is the concentration of $\text{S}_2\text{O}_3^{2-}$ (aq) in a solution prepared by mixing 10.00 mL of 0.0050 M $\text{Na}_2\text{S}_2\text{O}_3$ (aq) with enough 0.200 M KCl (aq) to make 50.0 mL of solution? (Assume volumes are additive and that there is no chemical reaction between the compounds involved.)

2. If all the $\text{S}_2\text{O}_3^{2-}$ (aq) in the solution above is completely reacted with another substance over a 35.0 second period, what is the rate of decrease of the $\text{S}_2\text{O}_3^{2-}$ (aq) in solution? (Assume no volume change occurs.)

Use the following data set for questions for questions 3 and 4:



Rxn #	[A], M	[B], M	Rate of Loss of A, M/s
1	0.25	0.25	9.0×10^{-3}
2	0.25	0.50	3.6×10^{-2}
3	0.50	0.25	1.8×10^{-2}

3. Determine the orders of reaction (m and n) for reactants A and B.

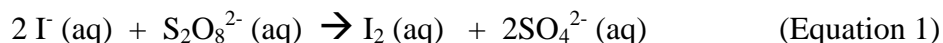
4. Determine the rate constant (k) for the reaction above .

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Introduction:

The determination and study of rates of reactions is referred to as **chemical kinetics**. It is frequently very difficult to determine when a reaction has gone to completion, so the study of the kinetics of a reaction is usually concerned with initial rates, i.e., the average rate of a reaction over the first few seconds, or at most a few minutes, during which time the reactant concentrations have varied only slightly from their original values.

The peroxodisulfate ion, $\text{S}_2\text{O}_8^{2-}$, oxidizes iodide ion reasonably slowly at room temperature in accord with the equation:



The **rate of reaction** can be expressed simply in terms of the decrease of any one of the reactants with respect to time or the increase of one of the products with respect to time and can be written arithmetically:

$$\text{Rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = -\frac{[\text{I}^-]}{2\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t} = \frac{[\text{SO}_4^{2-}]}{2\Delta t} \quad (\text{Equation 2})$$

Thus, the first equality, above, states that the reaction rate is equal to the decrease in peroxodisulfate ion concentration for a given time interval. Since the stoichiometry (Eqn 1) indicates that two iodide ions are used for every peroxodisulfate ion that reacts, the second equality, involving the iodide ion, shows this fact, etc.

One of the main purposes of a kinetics experiment is to find the **rate law** for the reaction, i.e., the algebraic expression that relates rate to the concentration(s) of the reactant(s). In the above reaction the rate depends both on the concentration of I^- and $\text{S}_2\text{O}_8^{2-}$ ions and takes the general form:

$$\text{Rate} = k[\text{I}^-]^m[\text{S}_2\text{O}_8^{2-}]^n \quad (\text{Equation 3})$$

where k is the **rate constant** and m and n are the **reaction orders**.

In this experiment you will study the kinetics of the reaction of iodide ion with peroxodisulfate ion and determine the rate law. Our method for measuring the rate of

reaction involves what is frequently called a "clock" reaction. This is a second reaction (or set of rapid consecutive reactions) that gives a signal, such as a color change, when a particular quantity of one of the reactants (here, I^- or $S_2O_8^{2-}$) has been consumed. Our "clock" will be based on the facts that (i) thiosulfate ion, $S_2O_3^{2-}$, reacts rapidly and quantitatively with iodine, I_2 :



and (ii) an intense blue-black coloration is formed almost instantly when exceedingly small traces of I_2 are in the presence of starch and I^- (hence, an indicator that detects iodine). Thus, the reaction of peroxodisulfate ion with iodide ion is started in the presence of a known trace amount of thiosulfate ion and the starch indicator. As the reaction progresses, the iodine, as it is formed, immediately reacts with the thiosulfate and the reaction mixture remains colorless. When the trace quantity of thiosulfate is used up, iodine produced by the oxidation of iodide ion now remains in solution and causes the starch indicator to turn blue-black in color. Therefore, at time t , the time after mixing when the solution turns blue-black, for every mole of thiosulfate originally present, 1/2 mole of iodine has been produced and used up, and 1/2 mole of peroxodisulfate also has been used up. At this point, the change in concentration of $S_2O_8^{2-}$ must be equal to half the original $S_2O_3^{2-}$ concentration, and thus, where a rate has been expressed in terms of $-\Delta[S_2O_8^{2-}]/\Delta t$, or

$$\text{Rate} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{1[S_2O_3^{2-}]_{\text{orig}}}{2 \Delta t} \quad (\text{Equation 5})$$

The calculation of the **rate constant** (k) and the **orders of the reaction** (m and n) with respect to I^- and $S_2O_8^{2-}$ follow from the dependence of the reaction rate on reactant concentrations. (Compare equations 3 and 5.)

Experimental:

Uncatalyzed Reactions

The Preparation Table below shows the reaction mixtures #1-5 to be studied in order to determine the rate constant and reaction orders for the reaction of iodide ion with peroxodisulfate ion. **The KI and $(NH_4)_2S_2O_8$ solutions should be carefully measured with graduated cylinders, and $Na_2S_2O_3$ solutions should be dispensed with a buret (or a 10.00 mL volumetric pipet);** the KCl and $(NH_4)_2SO_4$ solutions may be measured out in graduated cylinders.

Table for the Preparation of Experimental Runs

Rxn #	mL 0.200M KI	mL 0.200M KCl	mL 0.100M (NH ₄) ₂ S ₂ O ₈	mL 0.100M (NH ₄) ₂ SO ₄	mL 0.0050M Na ₂ S ₂ O ₃
1	20.0	0	20.0	0	10.0
2	10.0	10.0	20.0	0	10.0
3	20.0	0	10.0	10.0	10.0
4	20.0	0	5.0	15.0	10.0
5	15.0	5.0	15.0	5.0	10.0
1A	20.0	0	20.0	0	10.0

Carefully measure out the KI into a 50-mL beaker (I) and the (NH₄)₂S₂O₈ into a similar beaker (II) for Rxn #1. The 10.00mL of Na₂S₂O₃ solution and 3-4 drops of starch solution are placed in a 250-mL erlenmeyer flask (along with the required volumes of KCl and (NH₄)₂SO₄ solutions in Rxns # 2-5). These last two components are added merely to dilute each reaction mixture to a total volume of 50.0mL while keeping the ionic strength constant. Start the reaction by simultaneously pouring the solution from beakers I and II into the erlenmeyer flask and swirling thoroughly. At the instant the reactants are mixed, the stop watch should be started. Stop timing when the first sudden appearance of the blue-black color occurs. Record the time required for the reaction. Also, record the final temperature of the reaction mixture. Repeat the procedure above for each of the four other reaction mixtures.

Catalyzed Reaction

Metallic cations have a pronounced effect on the rate of this reaction, i.e., they may act as catalysts. You may observe this by carrying out Rxn 1A, which is a duplicate of Rxn. 1 except that you are to add one drop of 0.1 M CuSO₄ (aq) to the ammonium peroxodisulfate solution in beaker II. Stir beaker II for few seconds to mix the catalyst and then mix the solutions together in the 250-mL erlenmeyer flask to determine the time when the color change occurs. Compare this with Rxn 1.

Record the time data for each your runs on the blackboard to be compared with the data from other groups.

Calculations:

For the rate law,

$$\text{Rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = k_T[\text{I}^-]^m[\text{S}_2\text{O}_8^{2-}]^n \quad (\text{Equation 6})$$

use the **method of initial rates** (as described in class and below) to evaluate and record both the reaction "orders" (m and n) and evaluate and record the apparent rate constants (k_T) from the data of Rxns No. 1-5. Report the average value of k_T and show its units. Also, comment on the results of the catalyzed Rxn No. 1A relative to No.1.

Determination of Rate

Since the $[\text{S}_2\text{O}_3^{2-}]_{\text{orig}}$ is the same in each of the Rxn's, and since it is assumed to be completely used up by the time (t_b) the color change occurs, the following relationship can be shown to be true (using equation 5):

$$\text{Rate of loss of reactant, } \text{S}_2\text{O}_8^{2-} = -\frac{1\Delta[\text{S}_2\text{O}_3^{2-}]}{2 \Delta t} = \frac{5.00 \times 10^{-4} \text{ M}}{t_b}$$

where t_b = time required for the clock to "tick". The value $5.00 \times 10^{-4} \text{ M}$ is the same for each beaker, because it depends on the limiting reactant, the $\text{S}_2\text{O}_3^{2-}$.

Determination of Rate Law

If you have been careful in solution preparation, the **rate law** can be determined for your reaction:

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

m and **n** are called the reaction orders for $[\text{I}^-]$ and $[\text{S}_2\text{O}_8^{2-}]$ respectively.

Determination of m and n is made by inspection (more accurately by mathematics) using the method of initial rates.

Method of Initial Rates

The **method of initial rates** measures the rate of a reaction just after the reactants are brought together and allowed to interact. To determine the orders of the reaction, individual reactions are compared to see how rate is affected by changing the initial

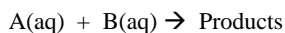
concentrations of one reactant, while holding the concentration of the other reactant constant. Consider the following simplified possibilities:

If the $[A]_{\text{init}}$ in Rxn #1 is doubled in Rxn #2 while $[B]_{\text{init}}$ is the same in Rxn's #1 and #2, the rate of the reaction may:

1. remain **unchanged**, if so the reaction order for [A] is **0**
2. be **doubled**, if so the reaction order for [A] is **1**
3. be **quadrupled**, if so the reaction order for [A] is **2**

Thus, for the purpose of this experiment, the orders of reactant (m and n) can have values of 0, 1, or 2.

	Rxn #	[A], M	[B], M	Rate of Loss of A, M/s	
Example	1	0.15	0.15	4.0×10^{-2}	Data:
	2	0.15	0.30	4.0×10^{-2}	
	3	0.30	0.15	1.6×10^{-1}	



•Between Rxn #1 and Rxn #2, [A] is **constant** while [B] is **doubled** (i.e. 0.15 M \rightarrow 0.30 M). The rate of the reaction is **unchanged**, so the order of reaction for reactant B is **n = 0**.

•Between Rxn #1 and Rxn #3, [B] is **constant** while [A] is **doubled** (i.e. 0.15 M \rightarrow 0.30 M). The rate of the reaction is **quadrupled**, so the order of reaction for reactant A is **m = 2**.

The rate law is therefore: $\text{Rate of Loss of A} = k[A]^2[B]^0$

or more simply $\text{Rate} = k[A]^2$

The rate constant (k) can be solved for by algebraic substitution into the equation: $k = \text{Rate} / [A]^2$

For example: using the data from Rxn#1 gives $k = 9.0 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$. For a given reaction, at a given temperature, k should be a constant that is independent of each of reactant concentrations.

Safety Notes:

Wear Goggles at all times.

Some of the solutions may stain hands and clothing.

All solutions may be flushed down the sink with water.

Calculation Results (Use Class Average):

Table 3. Initial Rates

Rxn #	[I ⁻]init.	[S ₂ O ₈ ²⁻]init.	Rate*, (M/s)	Rate Constant*, k
1				
2				
3				
4				
5				

Average value for k = _____

m = _____

n = _____

Rate Law : Rate =

*For rate and rate constant calculation see information in the calculations section.

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POSTLAB EXERCISE

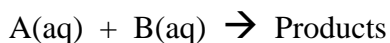
Name _____ Lab Section _____

Questions:

1. Referring to your experimental results, how does the catalyst affect the rate in Rxn 1A as compared to Rxn 1?

2. Based on your experimentally determined rate law, predict a value for rate of reaction if $[I^-]_{init.} = [S_2O_8^{2-}]_{init} = 0.50 \text{ M}$.

Use the following data set for questions for questions 3 and 4:



Rxn #	[A], M	[B], M	Rate of Loss of A, M/s
1	0.12	0.10	8.4×10^{-6}
2	0.12	0.20	1.7×10^{-5}
3	0.24	0.10	3.4×10^{-5}

3. Determine the orders of reaction (m and n) for reactants A and B.

4. Determine the rate constant (k) for the reaction above.