

Chemical Kinetics

PURPOSE

To determine the rate law for the reaction $2 \text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{I}_2 + 2 \text{SO}_4^{2-}$.

GOALS

- To relate changes in reactant concentrations to changes in reaction rate.
- To calculate a rate constant from experimental data.

INTRODUCTION

Chemical kinetics deals with the speed, or rate, of a reaction and the mechanism by which the reaction occurs. We can think of the rate as the number of events per unit time. The rate at which you drive (your speed) is the number of miles you drive in an hour (mi/hr). For a chemical reaction the rate is the number of moles that react in a second. In practice, we usually monitor how much the concentration (the number of moles in a liter) changes in a second. Reaction rates are usually expressed in units of moles per liter per second, or molarity per second (M/s).

Reaction Rates

The reaction to be studied in this experiment is a redox reaction between iodide ions and persulfate anions.



Our definition of reaction rate is the change in concentration with time, but the concentration of which chemical species? The answer is, any of them. For example, we could measure the rate at which I_2 is formed. Then the rate would be:

$$\text{Rate} = \frac{\Delta[\text{I}_2]}{\Delta t}. \quad (2)$$

This equation states that the rate is equal to the change in I_2 concentration divided by the change in time. The units are M/s . We could also measure the rate at which $\text{S}_2\text{O}_8^{2-}$ is used up. Then the rate would be:

$$\text{Rate} = - \frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t}. \quad (3)$$

Note the negative sign in equation 3. Reaction rates are always given positive values, but the $\text{S}_2\text{O}_8^{2-}$ concentration is decreasing as the reaction proceeds.

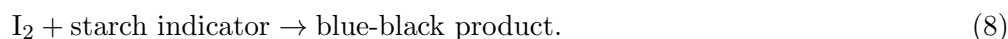
$$\Delta[\text{S}_2\text{O}_8^{2-}] = [\text{S}_2\text{O}_8^{2-}]_{\text{final}} - [\text{S}_2\text{O}_8^{2-}]_{\text{initial}} < 0 \quad (4)$$

Hence, there is a negative sign to make the reaction rate positive. We could also measure the disappearance of I^- . In the chemical equation, two iodide ions react with each $\text{S}_2\text{O}_8^{2-}$ ion. Therefore, I^- disappears twice as fast as $\text{S}_2\text{O}_8^{2-}$. The reaction rate based on disappearance of I^- would be expressed as:

$$\text{Rate} = -\frac{\Delta[\text{I}^-]}{2\Delta t} \quad (5)$$

The Chemical System Being Studied

The three reactions of importance in this experiment are:



The purpose of the experiment is to measure the rate of reaction 6. A product of this redox reaction between iodide ions and persulfate ions ($\text{S}_2\text{O}_8^{2-}$) is elemental iodine. Iodine, in the presence of thiosulfate ions ($\text{S}_2\text{O}_3^{2-}$) will reform iodide ions (reaction 7). Iodine can also, in the presence of starch, form a blue-black product (reaction 8). Reaction 7 is faster than reaction 8, and occurs preferentially if $\text{S}_2\text{O}_3^{2-}$ is present. However, if no $\text{S}_2\text{O}_3^{2-}$ is present, *or if it is used up*, reaction 8 occurs and the dark color of the indicator appears.

Method of Initial Rates

The change in concentration of a chemical species usually depends on the concentration of that species when the reaction begins. At the beginning of the reaction, its concentration is high, and a substantial amount of reactant will disappear in a second. Near the end of the reaction, its concentration is low, and a much smaller amount of reactant will disappear in a second. A standard way to compare reaction rates under different conditions is to measure the time it takes for the first small percentage of reaction to occur. This gives the initial rate.

In this experiment, you will find the time it takes for the first small percentage of reaction 6 to occur. But we do it in an indirect way. The time it takes for reaction 7 to occur will actually be measured. The experiment will be set up such that the amount of thiosulfate ($\text{S}_2\text{O}_3^{2-}$) is only about one percent of the amounts of iodide and persulfate ($\text{S}_2\text{O}_8^{2-}$) ions. During the first percent or so of reaction 6, the elemental iodine produced is consumed by thiosulfate in reaction 7. No iodine is left to react with the starch indicator. When the $\text{S}_2\text{O}_3^{2-}$ is used up, reaction 6 is still going (it still has about 99% to go!), but the iodine produced then begins to react with the starch, giving a color change. Thus, the color change indicates the total consumption of thiosulfate, $\text{S}_2\text{O}_3^{2-}$.

Knowing the amount of thiosulfate that reacted and measuring the time that it takes to react gives $\Delta[\text{S}_2\text{O}_3^{2-}]/\Delta t$. This is related to the rate of reaction 6 (what we want!) by the stoichiometry of the reactions.

$$\text{Rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = -\left(\frac{1}{2}\right)\frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} \quad (9)$$

The one half in the formula arises from the 1:2 stoichiometry between $\text{S}_2\text{O}_8^{2-}$ and $\text{S}_2\text{O}_3^{2-}$ ions. The term $\Delta[\text{S}_2\text{O}_3^{2-}]$ is negative (the concentration decreases as the reaction proceeds), but the negative sign in the formula again gives a positive value for the rate.

Rate Constants and Reaction Orders

A simple question about reaction rates is this: does the rate you measure depend on the amount of reactants you start with? It seems as if it should, but this is not always the case. The answer to the question depends on the mechanism of the reaction. A reaction mechanism is the series of steps that the reaction follows. The slowest step determines the measured reaction rate, and is called the **rate-determining step**. Look again at the reaction whose rate is to be measured.



You might guess that this reaction occurs when two iodide and one persulfate ion collide together in solution. However, a collision between three species such that they meet in the correct orientations to react is very rare. Most likely, the reaction proceeds in simpler steps. Some reasonable mechanisms are these:

- 1 The rate-determining step has two iodide ions coming together. In this case, the rate depends only on the initial concentration of iodide.
- 2 The rate-determining step involves a persulfate ion decomposing. In this case, the rate depends only on the initial concentration of persulfate.
- 3 The rate-determining step has an iodide ion and a persulfate ion coming together. In this case, the rate depends on the concentrations of both ions.

All of the mechanisms are plausible. The only way to distinguish among them is by experiment.

The concentration dependencies are summarized by the **rate law**. For our reaction, the rate law can be written:

$$\text{Rate} = k[\text{I}^-]^x[\text{S}_2\text{O}_8^{2-}]^y. \quad (11)$$

Here, k is called the **rate constant**, which is unique to the reaction. (Do not confuse k , the rate constant, with K , the equilibrium constant!) The exponents x and y must be determined by experiment. We do this by measuring the reaction rate at different initial concentrations of iodide and persulfate. For example, if we double the initial $[\text{I}^-]$ and the rate does not change, then x

must be equal to zero, and the reaction is said to be **zero order** in iodide ions. If the rate doubles when $[I^-]$ is doubled, x must be one, and the reaction is **first order** in iodide ions. If the rate goes up by a factor of four when $[I^-]$ is doubled, x must be two, and the reaction is **second order** in iodide ions. Doing other experiments and varying $[S_2O_8^{2-}]$ will then allow one to determine y , the reaction order for persulfate ion. Your textbook gives an algebraic method for determining x and y , which must be used for more complicated reaction orders.

Once the reaction order for each reactant is determined, one can substitute the values for reactant concentration, order, and rate (change in concentration per unit time) for a given run into the rate law and solve for the rate constant, k . The units of k will vary with the overall reaction order, which is the sum of the individual exponents. Reaction order is an indication of the total number of species involved in the rate-determining step of the reaction mechanism.

You will do five runs of the reaction. These will enable you to determine the reaction order in each of the reactants, and calculate the rate constant. You will then determine the rate law for the reaction between iodide and persulfate ions.

EQUIPMENT

- 2 50 mL burets
- 2 50 mL graduated cylinders
- 4 100 mL beakers
- 4 50 mL beakers
- 1 magnetic stir plate
- 1 magnetic stir bar
- 1 10.00 mL volumetric pipet
- 1 pipet bulb
- 1 ring stand with buret clamp
- 1 deionized water squirt bottle

REAGENTS

- ~90 mL 0.200 M KI
- ~90 mL 0.100 M $(NH_4)_2S_2O_8$
- ~60 mL 0.0050 M $Na_2S_2O_3$
- ~30 mL 0.200 M KCl
- ~30 mL 0.100 M $(NH_4)_2SO_4$
- ~20 drops 3% starch solution

SAFETY

Sodium persulfate is an oxidizing agent. Oxidizing agents can supply their own source of oxygen and may react violently with organic liquids or other reducing agents. The dilute persulfate solutions used in this experiment may be handled safely with other aqueous solutions.

WASTE DISPOSAL

All of the solutions can be flushed down the sink with plenty of water.

PRIOR TO CLASS

Please read the following sections of Lab Safety and Practices:

- Good Lab Practices¹
- Measurement²
- Volumetric Glassware³

Please review the following videos under Instructional Videos:

- Pipeting Techniques⁴
- Titration⁵
- Cleaning and Conditioning a Buret⁶
- Cleaning a Buret⁷

LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

- 1 Five different solutions with similar names are used in this experiment. Label the glassware so you will not mix things up. For example,

50 mL buret for KI
100 mL beaker for obtaining KI
50 mL beaker for KI dispensed from buret
50 mL buret for $(\text{NH}_4)_2\text{S}_2\text{O}_8$
100 mL beaker for obtaining $(\text{NH}_4)_2\text{S}_2\text{O}_8$
50 mL beaker for $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dispensed from buret
10.00 mL pipet for $\text{Na}_2\text{S}_2\text{O}_3$

¹..\practices\manual.html

²..\measurements\manual.html

³..\equipment\manual.html#volumetric glassware

⁴..\movies\pipeting.html

⁵..\movies\titration.html

⁶..\movies\conditioning.html

⁷..\movies\cleaning.html

graduated cylinder for KCl
graduated cylinder for $(\text{NH}_4)_2\text{SO}_4$
100 mL beaker in which to run the reaction

Although you are using burets and pipets to measure volumes, you will be dispensing the liquids into beakers, and pouring them from the beakers as you conduct the reactions. Some loss of liquid will occur in these transfers. Therefore, it is not necessary to read the buret to 0.01 mL as you would in a titration. Read to the nearest 0.1 mL (small gradation).

- 2** The following procedure applies for *each* run. Make sure the reaction beaker is rinsed and dried between each run.
 - a** Use your KI buret to measure the appropriate amount of 0.200 *M* KI into the labeled beaker.
 - b** Use your $(\text{NH}_4)_2\text{S}_2\text{O}_8$ buret to measure the appropriate amount of 0.100 *M* $(\text{NH}_4)_2\text{S}_2\text{O}_8$ into the labeled beaker.
 - c** Use a pipet to measure 10.00 mL of $\text{Na}_2\text{S}_2\text{O}_3$ into the reaction beaker. Add 3 or 4 drops of starch solution.
 - d** Use a graduated cylinder to add KCl or $(\text{NH}_4)_2\text{SO}_4$ solution to the reaction beaker if it is required for the run. These solutions are added to maintain a constant concentration of ions in all the runs.
 - e** Add the magnetic stir bar to the reaction beaker and mix the contents of the reaction beaker.
 - f** This step needs to be carefully coordinated. While the contents of the reaction beaker are being stirred, add the KI and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solutions simultaneously to the reaction beaker. This is the initial time for the reaction.
 - g** Watch the reaction and note the time at which the blue-black color of the starch-iodine complex appears. Record the elapsed time in Table A.
- 3** Record the values from these calculations in Table B. Repeat the calculations for the other four runs.
- 4** Calculate the rate constants for the other four runs and record the rate constants in Table B.
- 5** When you are finished, rinse all of your glassware with water, dry it and return it to the set-up area where you found it.
- 6** Before leaving, enter your results in the in-lab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your lab instructor. When all results are correct, note them and log out of WebAssign. The in-lab assignment must be completed by the end of the lab period. If additional time is required, please consult with your lab instructor.