

14. The Rate of an Iodine Clock Reaction

Introduction

Some reactions, including most of the ones that you have seen in this manual, occur so rapidly that they are over as soon as the reactants are mixed. There are many more reactions, however, that are slower; they may require minutes, hours, days, or even years to reach completion. A few chemical reactions are so slow that it is difficult to show that they happen at all.

Why are there wide differences in reaction rates? They are largely due to the differing molecular characteristics of the reactants. However, there are other factors that also affect the rate of any given reaction (Ebbing/Gammon, Chapter 14). Three of these factors are the concentrations of the reactants, the concentration of a catalyst, and the temperature at which the reaction occurs.

Purpose

In the quantitative part of this experiment, you will determine the rate law for an iodine clock reaction and the influence of temperature on that reaction. In the qualitative part, you will evaluate the effect of a catalyst on the rate of this reaction.

What is an iodine clock reaction?

There are actually several different iodine clock reactions. All of them, however, have a common feature: The completion of any one of them is signaled by the *sudden* appearance of the dark color that is characteristic of the interaction of molecular iodine (I_2) with starch. When the reaction is handled correctly, this color appears so abruptly that it can be as startling as the sudden sound of the alarm bell of a clock.

The rate of an iodine clock reaction depends on the concentrations of the reactants, as you would expect. As a result, the time required for the appearance of the dark color can be adjusted by adjusting the concentrations of the reactants. Hence it is possible to set the color alarm on a clock reaction just as you can set the sound alarm on a clock.

Concept of the experiment

You will study the rate of the reduction of potassium persulfate ($K_2S_2O_8$) with sodium iodide (NaI). The net ionic equation for this reaction is



One of the purposes of this experiment is to determine the rate law for this reaction. The rate law's general form will be (Ebbing/Gammon, Section 14.3)

$$\text{Rate} = k[\text{S}_2\text{O}_8^{2-}]^q[\text{I}^-]^r$$

and you will need to determine values for the rate constant k and the exponents q and r . Remember that the exponents must be determined experimentally; they cannot be obtained simply by looking at the balanced equation.

The rate law will be deduced by the initial-rate method (Ebbing/Gammon, Section 14.3), using three experiments. Experiment 1 will be the reference with which the other two will be compared. In Experiment 2, the initial concentration of the $\text{S}_2\text{O}_8^{2-}$ ions will be twice that in Experiment 1, but the concentration of I^- ions will be unchanged. The general form of the rate law for each of these experiments will be

$$\text{Experiment 1: Rate}_1 = k[\text{S}_2\text{O}_8^{2-}]^q[\text{I}^-]^r$$

$$\text{Experiment 2: Rate}_2 = k(2[\text{S}_2\text{O}_8^{2-}])^q[\text{I}^-]^r = 2^q \times \text{rate}_1$$

The rate in the second experiment will be 2^q times the original rate. In Experiment 3, the initial concentration of $\text{S}_2\text{O}_8^{2-}$ ions will be the same as that in Experiment 1, but the concentration of I^- ions will be doubled. The rate law will be

$$\text{Experiment 3: Rate}_3 = k[\text{S}_2\text{O}_8^{2-}]^q(2[\text{I}^-])^r = 2^r \times \text{rate}_1$$

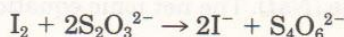
The rate in this experiment will be 2^r times the original rate.

You can *deduce* the true values of q and r from the ratios $\text{rate}_2/\text{rate}_1$ and $\text{rate}_3/\text{rate}_1$. After you have evaluated the exponents, you will know the general form of the rate law, but the value of the rate constant will be unknown. You can obtain it from the rate law and any one of the three rates. Each rate should yield the same rate constant within experimental error.

Because the rate of the reaction is given by

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

you will need to know or measure $\Delta[\text{S}_2\text{O}_8^{2-}]$, the initial change in the concentration of $\text{S}_2\text{O}_8^{2-}$ ions, and Δt , the time elapsed during that change, as well as the initial concentrations of $\text{S}_2\text{O}_8^{2-}$ and I^- ions. An easy way to obtain $\Delta[\text{S}_2\text{O}_8^{2-}]$ is by coupling another reaction to the one we are studying. The new reaction is the reduction of I_2 by $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulfate). The net ionic equation for this reaction is



where $\text{S}_4\text{O}_6^{2-}$ is the tetrathionate ion. *It is important to remember that this reaction is used only as a means of studying the rate of the first reaction.*

The new reaction is fast. As a result, I_2 is consumed in this reaction as fast as it is formed in the first reaction. Essentially there can be no I_2 present as long as there are $S_2O_3^{2-}$ ions present. However, these ions are being consumed because of the second reaction. As soon as all the $S_2O_3^{2-}$ ions have reacted, I_2 from the first reaction begins to accumulate in the solution. You can detect the sudden presence of I_2 by the sudden appearance of the dark color from the interaction of I_2 with starch, which will be used as an indicator.

You will know $\Delta[S_2O_3^{2-}]$ at the instant that this dark color appears. How? As you will show in the Prelaboratory Assignment, the stoichiometry and relative rates of the coupled reactions require the following relationship between $\Delta[S_2O_8^{2-}]$ and $\Delta[S_2O_3^{2-}]$:

$$\Delta[S_2O_8^{2-}] = (1/2)\Delta[S_2O_3^{2-}]$$

where

$$\Delta[S_2O_3^{2-}] = \text{initial } [S_2O_3^{2-}] - \text{final } [S_2O_3^{2-}]$$

Essentially all the $S_2O_3^{2-}$ ions will have reacted when the dark color appears, so the final concentration of these ions is essentially zero, and $\Delta[S_2O_3^{2-}]$ becomes

$$\Delta[S_2O_3^{2-}] = \text{initial } [S_2O_3^{2-}]$$

If we keep the initial concentration of $S_2O_3^{2-}$ ions at a small value, $\Delta[S_2O_3^{2-}]$ will be small and $\Delta[S_2O_8^{2-}]$ will be even smaller. As a consequence, there will be little change in the concentration of the reactants during the elapsed time Δt . This is a necessary condition for the initial-rates method.

The time required for the appearance of the dark color is affected by the concentration of the reactants, as you would expect from the general form of the rate law. The time is also affected to a degree by the overall concentration of ions and their charges. This influence, which is well known, cannot be predicted from the rate law. You will maintain a constant concentration of ions and charges by adding, where required, ionic substances that will not react. Thus Experiment 1 has one-half the amount of $K_2S_2O_8$ found in Experiment 2. The deficiency is overcome by the addition of inert K_2SO_4 . Similarly, Experiment 1 has one-half the amount of NaI found in Experiment 3. The addition of inert $NaCl$ keeps the total concentration of ions and charges at a constant value.

To demonstrate the influence of the temperature on the rate of this reaction, you will redo Experiment 1 at an increased temperature. The mathematics required here is straightforward. The rate law will have the same general form at the higher and lower temperatures. As a result, q and r will not change when the temperature is varied. A new rate constant, however, will need to be evaluated at the higher temperature. The activation energy for the reaction can be calculated via the Arrhenius equation (Ebbing/Gammon, Section 14.6).

Finally, you will repeat Experiment 1 one more time to explore the effect of a catalyst in qualitative terms. The catalyst will be the $Cu(II)$ ions in $CuSO_4$. No mathematical treatment will be required.

Procedure

Getting started

1. Work with a partner.
2. Obtain 3 large test tubes with 3 rubber stoppers, a Mohr pipet, and a thermometer.
3. Obtain directions for discarding the solutions that you will use in this experiment.

Completing the first series of experiments

1. Note and record the temperature of the laboratory to the nearest tenth of a degree.
2. Mark each of the test tubes with an identification number (1, 2, and 3).
3. Rinse the pipet with two 1-mL portions of the NaI solution. Each of these portions should be discarded.
4. Pipet the required volume of the NaI solution into each test tube. These volumes can be found in Table 14.1.

Table 14.1 Volumes (mL) of Solutions

Experiment	0.20 M NaI	0.20 M NaCl	0.010 M $\text{Na}_2\text{S}_2\text{O}_3$	2% Starch	0.20 M K_2SO_4	0.20 M $\text{K}_2\text{S}_2\text{O}_8$
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

5. Rinse the pipet with distilled water.
6. Using the NaCl solution instead of the NaI solution, repeat Steps 3 through 5.
7. Using the $\text{Na}_2\text{S}_2\text{O}_3$ solution instead of the NaI solution, repeat Steps 3 through 5.
8. Using the starch solution instead of the NaI solution, repeat Steps 3 through 5.
9. Using the K_2SO_4 solution instead of the NaI solution, repeat Steps 3 through 5.
10. Read Steps 11 and 12 completely before doing them.
11. Note and record the time just as you begin to pipet the required amount of the $\text{K}_2\text{S}_2\text{O}_8$ solution for Experiment 1 into test tube 1. Quickly insert a rubber stopper in the test tube. Mix the solution by inverting the test tube about 15 times while shaking it simultaneously. *A completely homogeneous solution is required.*
12. Note and record the exact time at which the dark color appears. Be alert. This color should appear suddenly throughout the solution at one time. If it does not, you have not mixed the solution thoroughly enough. Calculate the elapsed time. Experiment 1 should require less than 4 min.
13. Repeat Steps 11 and 12 with test tubes 2 and 3, using the quantities of the $\text{K}_2\text{S}_2\text{O}_8$ solution specified for Experiments 2 and 3 in Table 14.1.

14. Wash, rinse, and dry the test tubes and rubber stoppers.
15. Perform a second trial by repeating Steps 3 through 14.
16. If the elapsed times of the two trials of an experiment differ by more than 10 s, repeat the experiment until agreement is achieved.

Completing the second series of experiments

1. Renumber the test tubes (4, 5, and 0).
2. Prepare a beaker of water whose temperature is about 35°C by adding hot water to cold water.
3. The volumes of the solutions used in Experiment 4 will be the same as those used in Experiment 1.
4. Pipet the required volumes of the NaI, NaCl, Na₂S₂O₃, starch, and K₂SO₄ solutions into test tube 4. Place this test tube in the water bath.
5. Place about 5 mL of the K₂S₂O₈ solution in the clean, dry test tube whose number is 0. Put this test tube in the water bath.
6. Allow each test tube to remain in the water bath for about 5 min. Add small amounts of hot water to the bath during this time to maintain the temperature at about 35°C.
7. Initiate the reaction by pipeting the required volume of the warm K₂S₂O₈ solution into the other test tube in the water bath. Note and record the time.
8. Insert a rubber stopper, remove the test tube from the bath, and shake the test tube as vigorously as you can for a few seconds. Replace the test tube in the bath. Be alert.
9. Note the time at which the dark color appears. Remove the stopper, and measure and record the temperature of the solution to the nearest tenth of a degree. Calculate the elapsed time.
10. The volumes of the solutions used in Experiment 5 will be the same as those used in Experiment 1, but do not heat the solutions. Add 1 drop of 0.2 M CuSO₄ and shake the test tube gently before you initiate the reaction with the required volume of the K₂S₂O₈ solution.

The Rate of an Iodine Clock Reaction

Date:

Student name:

Course:

Team members:

Section:

Instructor:

Prelaboratory assignment

1. What factors affect the rate of any given reaction?

2. a. Give the chemical equation for the reaction whose rate is being studied.

b. Give the chemical reaction that will enable you to know $\Delta[\text{S}_2\text{O}_8^{2-}]$.

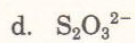
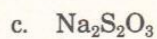
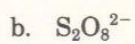
c. Why are these coupled reactions called an iodine clock reaction?

d. What interaction is responsible for the dark color?

- e. Why does the dark color appear suddenly, rather than a gradual darkening?
- f. When the dark color appears, $\Delta[\text{S}_2\text{O}_8^{2-}] = (1/2)\Delta[\text{S}_2\text{O}_3^{2-}]$, where $\Delta[\text{S}_2\text{O}_3^{2-}]$ equals the initial concentration of $\text{Na}_2\text{S}_2\text{O}_3$. Why?
3. Consider the composition of the solutions in Table 14.1. In which experiment will the longest time probably elapse before the appearance of the dark color? Why?
4. What catalyst will be used? In which experiment will it be used?

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5. Give names for the following substances:



The Rate of an Iodine Clock Reaction

Date: Student name:
 Course: Team members:
 Section:
 Instructor:

Results

Laboratory temperature: °C

Experiment	Trial	Start	End	Elapsed Time(s)
1	1
	2
2	1
	2
3	1
	2
4	1
5	1

Temp.: °C

Student name: Course/Section: Date:

c. What is the correct rate equation?

d. Calculate the initial concentrations of the $\text{S}_2\text{O}_8^{2-}$ and I^- ions in Experiments 1, 2, and 3. Remember that dilution occurred when the solutions were prepared.

e. Calculate the rate constant in Experiments 1, 2, and 3, and obtain the mean. Give the correct units.

2. a. Calculate the rate constant at the higher temperature used in Experiment 4.

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- b. Calculate the activation energy for the reaction.

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