

1. Rates of Chemical Reactions

Objective

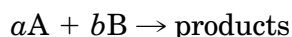
The study of the *speed* with which a chemical process takes place is crucial. Chemists or chemical engineers want reactions to take place quickly enough that they will be useful, but not so quickly that the reaction cannot be studied or controlled. Biologists use the study of reaction rates as an indication of the mechanism by which a biochemical process takes place. In this experiment, the effect of varying the concentration of the reactants in a process will be investigated as to how this affects the measured rate of the reaction. The effect of temperature in speeding up or slowing down reactions will also be examined briefly.

Introduction

The rate at which a chemical reaction occurs depends on several factors: the *nature* of the reaction, the *concentrations* of the reactants, the *temperature*, and the presence of possible *catalysts*. Each of these factors can influence markedly the observed speed of the reaction.

Some reactions at room temperature are very slow. For example, although wood is quickly oxidized in a fireplace at elevated temperatures, the oxidation of wood at room temperature is negligible. Many other reactions are essentially instantaneous. The precipitation of silver chloride when solutions containing silver ions and chloride ions are mixed is an extremely rapid reaction, for example.

For a given reaction, the rate typically *increases* with an increase in the concentrations of the reactants. The relation between rate and concentration is a remarkably simple one in many cases. For example, for the reaction



the rate can usually be expressed by the relationship

$$\text{Rate} = k [A]^m [B]^n$$

in which m and n are usually small whole numbers. In this expression, called a **rate law**, $[A]$ and $[B]$ represent, respectively, the concentration of substances A and B, and k is called the **specific rate constant** for the reaction (which provides the correct numerical proportionality). The exponents m and n are called the **orders** of the reaction with respect to the concentrations of substances A and B, respectively. For example, if $m = 1$, the reaction is said to be *first order* with respect to the concentration of A. If $n = 2$, the reaction would be *second order* with respect to the concentration of B. The so-called *overall order* of the reaction is represented by the *sum* of the individual orders of reaction. For the examples just mentioned, the reaction would have overall order

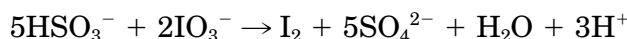
$$1 + 2 = 3 \text{ (third order).}$$

The rate of a reaction is also significantly dependent on the *temperature* at which the reaction occurs. An increase in temperature increases the rate. A rule of thumb (which does have a theoretical basis) states that an increase in temperature of 10 Celsius degrees will double the rate of reaction. While this rule is only approximate, it is clear that a rise in temperature of 100°C would affect the rate of reaction appreciably. As with concentration, there is a quantitative relationship between reaction rate and temperature; but here the relationship is less straightforward. The relationship is based on the idea that, in order to react, the reactant species must possess a certain minimum amount of energy at the time the reactant molecules actually collide during the rate-determining step of the reaction. This minimum amount of energy is called the **activation energy** for the reaction and generally reflects the kinetic energies of the molecules at the temperature of the experiment. The relationship between the specific rate constant (k) for the reaction, the absolute temperature (T), and the activation energy (E_a) is

$$\log k = -E_a/2.3RT + \text{constant}$$

In this relationship, R is the ideal gas constant, which has value $R = 8.31 \text{ J/mol K}$. The equation therefore gives the activation energy, E_a , in units of *joules*. By experimentally determining k at various temperatures, the activation energy can be calculated from the *slope* of a plot of $\log k$ versus $1/T$. The slope of such a plot would be $(-E_a/2.3R)$.

In this experiment, you will study a reaction called the “iodine clock.” In this reaction, potassium iodate (KIO_3) and sodium hydrogen sulfite (NaHSO_3) react with each other, producing elemental iodine



This is an oxidation/reduction process, in which iodine(V) is reduced to iodine(0), and sulfur(IV) is oxidized to sulfur(VI). Because elemental iodine is *colored* (whereas the other species are colorless), the rate of reaction can be monitored simply by determining the *time required* for the appearance of the *color* of the iodine. As usual with other reactions in which elemental iodine is produced, a small quantity of starch is added to heighten the color of the iodine. Starch forms an intensely colored blue/black complex with iodine. While it would be difficult to detect the first appearance of iodine itself (since the solution would be colored only a very pale yellow), if starch is present, the first few molecules of iodine produced will react with the starch present to give a much sharper color change.

The rate law for this reaction would be expected to have the general form

$$\text{Rate} = k [\text{HSO}_3^-]^m [\text{IO}_3^-]^n$$

in which m is the order of the reaction with respect to the concentration of bisulfite ion, and n is the order of the reaction with respect to the concentration of iodate ion. Notice that even though the stoichiometric coefficients of the reaction are known, these are *not* the exponents in the rate law. The order of the reaction must be determined *experimentally*, and may bear no relationship to the stoichiometric coefficients of the balanced chemical equation. The rate

law for a reaction reflects what happens in the slowest, or *rate-determining*, step of the reaction mechanism. A chemical reaction generally occurs as a series of discrete microscopic steps, called the **mechanism** of the reaction, in which only one or two molecules are involved at a time. For example, in the bisulfite/iodate reaction, it would be statistically almost impossible for five bisulfite ions and two iodate ions to all come together in the same place at the same time for reaction. It is much more likely that one or two of these molecules first interact with each other, forming some sort of *intermediate* perhaps, and then this intermediate reacts with the rest of the ions at some later time. By careful experimental determination of the rate law for a process, information is obtained about exactly what molecules react during the slowest step in the reaction, and frequently this information can be extended to suggest what happens in all the various steps of the reaction's mechanism.

In this experiment, you will determine the order of the reaction with respect to the concentration of potassium iodate. You will perform several runs of the reaction, each time using the *same* concentration of all other reagents, but *varying* the concentration of potassium iodate in a systematic manner. By measuring the time required for reaction to occur with different concentrations of potassium iodate, and realizing that the time required for reaction is inversely proportional to the rate of the reaction, the exponent of iodate ion in the rate law should be readily evident.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Sodium hydrogen sulfite (sodium bisulfite) is harmful to the skin and releases noxious SO₂ gas if acidified. Use with adequate ventilation in the room.**
- **Potassium iodate is a strong oxidizing agent and can damage skin. Wash after using. Do not expose KIO₃ to any organic chemical substance or an uncontrolled oxidation may result.**
- **Elemental iodine may stain the skin if spilled. The stains are generally not harmful at the concentrations to be used in this experiment, but will require several days to wear off.**

Apparatus/Reagents Required

Laboratory timer (or watch with second hand), Solution 1 (containing potassium iodate at 0.024 *M* concentration), Solution 2 (containing sodium hydrogen sulfite at 0.016 *M* concentration and starch)

Procedure

Record all data and observations directly in your notebook in ink.

A. Solutions to Be Studied

Two solutions have been prepared for your use in this experiment. It is essential that the two solutions are *not mixed* in any way before the actual kinetic run is made. Be certain that graduated cylinders used in obtaining and transferring the solutions are *rinsed* with distilled water between solutions. Also rinse thermometers and stirring rods before transferring between solutions.

Solution 1 is 0.024 *M* potassium iodate. Solution 2 is a mixture containing two different solutes, sodium hydrogen sulfite and starch. Solution 2 has been prepared so that the solution contains hydrogen sulfite ion at 0.016 *M* concentration. The presence of starch in Solution 2 may make the mixture appear somewhat cloudy.

Obtain about 400 mL of Solution 1 in a clean, dry 600-mL beaker. Keep covered with a watch glass to minimize evaporation. Obtain about 150 mL of Solution 2 in a clean, dry 250-mL beaker. Cover with a watch glass.

B. Kinetic Runs

Clean out several graduated cylinders and beakers for the reactions. It is important that Solutions 1 and 2 do not mix until the reaction time is to be measured. Use separate graduated cylinders for the measurement of each solution.

The general procedure for the kinetic runs is as follows (specific amounts of reagents to be used in the actual runs are given in a table further on in the procedure):

Measure out the appropriate amount of Solution 2 in a graduated cylinder. Take the temperature of Solution 2 while it is in the graduated cylinder, being sure to rinse and dry the thermometer to avoid mixing the solutions prematurely. Transfer the measured quantity of Solution 2 from the graduated cylinder to a clean, dry 250-mL beaker.

Measure out the appropriate amount of Solution 1 using a clean graduated cylinder and transfer to a clean, dry small beaker. Again using a clean graduated cylinder, add the appropriate amount of distilled water for the run and stir to mix. Measure the temperature of Solution 1, being sure to rinse and dry the thermometer to avoid mixing the solutions prematurely.

If the temperatures of Solutions 1 and 2 differ by more than one degree, wait until the two solutions come to the same temperature.

When the two solutions have come to the same temperature, prepare to mix them. Have ready a clean stirring rod for use after mixing the solutions.

Noting the time (to the nearest second), pour Solution 1 into the beaker containing Solution 2 and stir for 15–30 seconds. Watch the mixture carefully, and record the time the blue/black color of the starch/iodine mixture appears.

Repeat the same run, using the same amounts of Solutions 1 and 2 before going on to the next run.

The table that follows indicates the amounts of Solution 1, distilled water, and Solution 2 to be mixed for each run. Distilled water is added in varying amounts to keep the total volume the same for all the runs.

Table of Kinetic Runs

<i>Run</i>	<i>mL Solution 1</i>	<i>mL distilled water</i>	<i>mL Solution 2</i>
<i>A</i>	10.0	80.0	10.0
<i>B</i>	20.0	70.0	10.0
<i>C</i>	30.0	60.0	10.0
<i>D</i>	40.0	50.0	10.0
<i>E</i>	50.0	40.0	10.0

From the time required for the appearance of the blue/black color, and the concentration of potassium iodate used in each kinetic run, determine the *order* of the reaction with respect to iodate ion concentration.

Construct a plot of *time required for reaction* (vertical axis) versus *concentration of iodate ion* (horizontal axis). Construct a second plot, in which you plot the *reciprocal* of the time required for reaction on the vertical axis versus the concentration of iodate ion. Why is the reciprocal graph a straight line?

C. Temperature Dependence

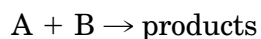
A rule of thumb indicates that the rate of reaction is *doubled* for each 10°C temperature increase. Confirm this qualitatively by performing two determinations of run A in the table at a temperature approximately 10°C *higher* than the temperature used previously. Repeat the procedure, making two determinations of run A, at a temperature approximately 10°C *lower* than the original determinations.

Rates of Chemical Reactions

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

Prelaboratory Questions

1. Given the following data, determine the *orders* with respect to the concentrations of substances A and B in the reaction



$[A]_{\text{initial}}$	$[B]_{\text{initial}}$	Time for reaction
0.10 M	0.10 M	262 s
0.20 M	0.10 M	131 s
0.30 M	0.10 M	87 s
0.20 M	0.20 M	66 s
0.10 M	0.20 M	131 s

2. What must be the *units* of the specific rate constant in Prelaboratory Question 1, given that the rate of reaction would be measured in M/s ?
3. Why is it not possible to predict the *form* of the rate law for a reaction from a knowledge of the overall stoichiometry of a reaction?

Rates of Chemical Reactions

Date: Student name:
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Results/Observations

Kinetic Runs

Time required for I ₂ color to appear	First trial	Second trial
Run A (10 mL Solution 1)
Run B (20 mL Solution 1)
Run C (30 mL Solution 1)
Run D (40 mL Solution 1)
Run E (50 mL Solution 1)

Based on your results, what is the *order* of the reaction with respect to potassium iodate concentration? Explain your reasoning.

Temperature Dependence

What higher temperature did you use?

What time was required for reaction?

What lower temperature did you use?

What time was required for reaction?

Do these times confirm the rule of thumb?

Questions

1. In this experiment you determined the dependence of the reaction rate on the concentration of potassium iodate. Devise an experiment for determining the dependence of the rate on the concentration of sodium sulfite.
2. Why was it necessary to keep the total volume of the reagents after mixing constant in all the kinetic runs (i.e., why was it necessary to add distilled water in inverse proportion to the quantity of Solution 1 that was required)?
3. Why was it necessary that the two solutions to be mixed be at the same temperature before mixing? What error would have been introduced if the solutions were not at the same temperature?
4. A term that is often used by kineticists is the **molecularity** of a reaction. Use a scientific dictionary or chemical encyclopedia to write a definition of molecularity and explain how this term differs from the order of a reaction as discussed earlier.
5. Determination of the rate law for a reaction is often the first step in elucidating the *mechanism* of the reaction. Write a specific definition for what is meant by a reaction mechanism.