

EXPERIMENT

25 Rates of Chemical Reactions

Objective

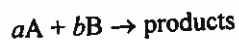
The study of the *speed* with which a chemical process takes place is crucial. Chemists and chemical engineers want reactions to take place quickly enough that they will be useful, but not so quickly that the reaction cannot be studied or controlled. Biologists use the study of reaction rates as an indication of the mechanism by which a biochemical process takes place. This experiment examines how varying the concentration of the reactants in a process 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 often 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 (and may bear no obvious relationship to the stoichiometric coefficients). 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 is *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

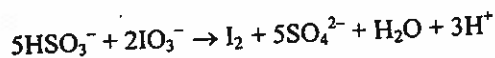
$$1 + 2 = 3 \text{ (third order)}$$

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. Although 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 appropriate reactant molecules or ions actually *collide* with each other 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

$$\log_{10} k = -E_a/2.3RT + \text{constant}$$

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 $\log_{10} k$ 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 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. It would be difficult to detect the first appearance of iodine itself (since the solution would be colored only a very pale yellow), but 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 with the right orientations and energies for reaction. It is much more likely that one or two of these molecules will first interact with each other, forming some sort of *intermediate* perhaps, and that this intermediate will react 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, you will determine the exponent of iodate ion in the rate law.

Safety Precautions

- Protective eyewear approved by your institution must be worn at all times while you are in the laboratory.
- Sodium hydrogen sulfite (sodium bisulfite) is harmful to the skin and releases noxious sulfur dioxide (SO_2) gas if acidified. Use with adequate ventilation in the room. Keep the solution covered with a watch glass when not in use.
- Potassium iodate is a strong oxidizing agent and can damage skin. Wash after handling. Do not expose KIO_3 to any organic chemical substance or an uncontrolled oxidation may result.
- Elemental iodine may stain the skin. The stains are generally not harmful at the concentrations used in this experiment, but will require several days to wear off. Iodine will stain clothing.

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 *not be 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

Run	mL Solution 1	mL distilled water	mL Solution 2
A	10.0	80.0	10.0
B	20.0	70.0	10.0
C	30.0	60.0	10.0
D	40.0	50.0	10.0
E	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 by performing two determinations of run A in the table at a temperature approximately 10°C *higher* than the temperature used previously, and then again at a temperature approximately 10°C *lower* than that used in the original determinations.

To perform the reactions at the higher temperature, set up a metal trough half filled with water on a hotplate. Adjust the controls of the hotplate so as to warm the water in the trough to approximately 10°C above room temperature. Once the temperature of the water in the trough has stabilized and no longer rises or decreases, add the two beakers of the reagents for run A, and allow them to stand in the warm water bath for 5 minutes so that they come to the temperature of the water bath. Then combine the reagents, keeping them still in the warm-water bath during the reaction. Record the time required for the iodine color to appear. Repeat the determination.

To perform the reactions at the lower temperature, set up a trough or basin half filled with water and add ice to the water in the trough/basin until the temperature is approximately 10°C below room temperature. Add ice as necessary to maintain the temperature as constant as possible at the lower temperature.

Once the temperature of the water in the trough has stabilized and no longer rises or decreases, add the two beakers of the reagents for run A, and allow the beakers to stand in the cold-water bath for 5 minutes. Add ice as needed to maintain the temperature of the cold-water bath.

Combine the reagents, keeping them still in the cold-water bath during the reaction, adding ice as needed to maintain the temperature. Record the time required for the iodine color to appear. Repeat the determination.

Does the "rule of thumb" seem to hold true? Explain.