
The Kinetics of the Dissociation of Hydrogen Peroxide

Theory

Kinetics is the study of the rate of chemical reactions. The study of kinetics is a key aspect of chemistry because it provides a great deal of insight into the step-by-step mechanism by which chemical reactions occur.

One could generalize by stating that there are three things which affect the rate of chemical reactions. These are:

1. Temperature
2. Concentration of reactants
3. The presence of a catalyst

To explain these effects, a simple model known as a reaction coordinate diagram can be used (see your text for an illustration). The reaction coordinate diagram provides a model for a chemical reaction. For example, for one could study a generic reaction such as;



In order for a reaction to occur, molecule A must collide with molecule B with sufficient kinetic energy to allow the activated complex to surpass the barrier known as the activation energy (E_a). Raising the temperature increases the rate of a chemical reaction by increasing the average kinetic energy available in any single collision. It also increases the rate of a chemical reaction by increasing the number of collisions per second.

Increasing the concentration of the reactants in a chemical reaction increases the rate of that reaction because it increases the number of collisions between reactant molecules per unit time. The greater the number of collisions per second, the greater the number of successful collisions leading to product, and the faster the reaction.

Adding a catalyst to a chemical reaction increases the rate of the reaction by decreasing the size of the activation energy. The catalyst changes the mechanism of the reaction in some way which provides an alternative path for the reaction such that the energy needed to produce product, the activation energy is lowered. Therefore, at a given temperature, more molecules will have sufficient

energy to get over the activation energy barrier, and the rate of the reaction is increased. In this laboratory, you will be studying all three of the things which affect the rate of a chemical reaction-- temperature, concentration of reactant, and the presence of a catalyst.

The basic unit in a kinetic study is the rate law. For the generic reaction used as an example above, the generic rate law will be:

$$\text{rate} = k[A]^x[B]^y \quad (\text{EQ 5.2})$$

where k is the rate constant. The rate constant is not a true constant, as its value depends on temperature. However, for a given temperature, it will have a constant value. In the above equation, x and y are the order of the reaction with respect to A and B. One of the goals of this laboratory is to determine the value of the rate constant and the order with respect to the reactants in a reaction.

If there is a catalyst affecting the rate of the reaction, it will in general enter into the rate law. For example if the substance E is a catalyst for the reaction above, then the rate law will be:

$$\text{rate} = k[A]^x[B]^y[E]^z \quad (\text{EQ 5.3})$$

for the reaction,



In this laboratory, you will be determining the order of a particular reaction with respect both to a reactant and to a catalyst. You will be using the method of initial rates to determine the order of the reaction with respect to the relevant chemical species. The details of this method will be given by your instructor, but in essence, the method of initial rates involves doing two or more runs of the chemical reaction to be studied. In the two runs, all the parameters are kept constant (temperature, and the concentration of any reactants and/or catalyst) except one varies the concentration of the species whose order is to be determined. For example, in the reaction above, if one wanted to determine the order of the reaction with respect to the species A, one would do two runs. In the first run, convenient values of temperature, and concentration of A, B and E would be chosen and the initial rate would be measured. In the second run, one would keep the initial concentration of B and of E, as well as the temperature constant, but double the concentration of the reactant A. If the one doing the experiment were to then measure the rate of both the runs, he or she would be able to determine from the ratio of the rate of the two runs the value of x , the order of the reaction with respect to A. If the one doing the kinetic study is able to determine x , y and z , then he or she can use the measured rate of any of the reaction runs to solve for the rate constant. In this case, k would be given by the equation;

$$k = \frac{\text{rate}}{[A]^x[B]^y[C]^z} \quad (\text{EQ 5.5})$$

In the experiment on the decomposition of hydrogen peroxide, you will also measure the effect of temperature. You will repeat one of your earlier runs, with the identical concentrations as before, only performing the reaction at both increased and at decreased temperatures. Of course, this will change the rate of the reaction, because it will change the value of the rate constant. In this case, you will measure the rate constant of the reaction at all four temperatures. These values will allow you to calculate the activation energy (E_a) for the reaction by using the Arrhenius method. According to the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \quad (\text{EQ 5.6})$$

or, taking the natural log:

$$\ln k = \ln A - E_a/RT \quad (\text{EQ 5.7})$$

Using this second equation, it can be seen that if one can collect data for a particular reaction of the rate constant at various temperatures then a graph of the natural log of the rate constant for a reaction versus the inverse of the temperature ($\ln k$ vs $1/T$), the graph will be a straight line with a slope of E_a/R , R being the universal gas constant. The y -intercept of the graph will equal $\ln A$.

In summary, then, for the catalyzed decomposition of hydrogen peroxide, you will be able to determine the rate law and the rate constant at various temperatures, as well as the activation energy of the reaction.

The Experiment

The particular reaction to be studied is the decomposition of hydrogen peroxide in the presence of the catalyst iodide ion. The reaction to be studied can be represented by:



The decomposition of hydrogen peroxide is spontaneous at room temperature, but it is too slow to measure conveniently. The rate of the reaction is increased by the presence of ultraviolet light, which is why commercial hydrogen peroxide is sold in light-resistant brown bottles. The addition of iodide ion in the form of a solution of potassium iodide to the reaction will cause the reaction to occur at a rate appropriate to study on the time scale of a few minutes.

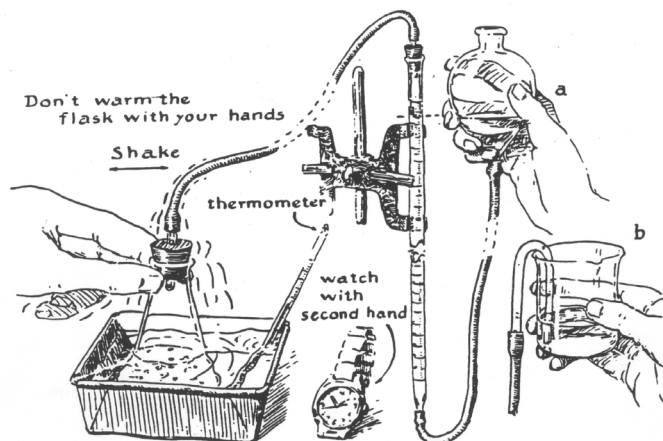
The progress of the reaction will be followed by measuring the volume of oxygen released as a function of time. For this reason, although a true rate constant will be measured, it will be in non-conventional units. The units of the rate of reaction will be in ml of O_2 per minute. The actual rate of the reaction will be determined from a graph of volume of O_2 versus time. The initial rate of the reaction will be calculated as the maximum tangent slope of the graph.

By measuring the rate of the reaction at room temperature, but with a number of different reactant concentration ratios, the "order" of the reaction with respect to both hydrogen peroxide and iodide will be determined, as well as the rate constant at room temperature. By doing one of the reaction concentration ratios at three other temperatures, and by using the Arrhenius equation, the student will be able to calculate the activation energy for the reaction.

Experimental Method

The experiment must be performed by groups of two or three (three being ideal). Begin by setting up the apparatus as illustrated below.

FIGURE 5.1



Your instructor will provide specifics, as the setup may vary somewhat. The 50-ml buret or gas tube should be filled to somewhere near the top of the readable markings. The whole system should be checked carefully for leaks. This can be done by sealing up the entire system and lowering the beaker or leveling bulb. Use a rubber stopper if you are using the bulb to seal the system. If you use a beaker, then pinch the hose to seal in order to check for leaks. If the system is sealed, the water level in the buret or gas tube will go down slightly but after that hold steady. The purpose of the beaker or leveling bulb is to assure that the pressure within the reaction vessel is the same as that in the room. If there is a pressure differential between the room and the gases in the system, the recorded volume change will be effected.

The effect of concentration of reactants on the rate of decomposition of H_2O_2 . You will be measuring the initial rate of reaction for three different concentration ratios. The three mixtures are described in the table below:

TABLE 5.1

Reagents	Mixture #1	Mixture #2	Mixture #3
0.10 M KI	15.0 ml	15.0 ml	30.0 ml
distilled H_2O	35.0	25.0	20.0
3% hydrogen peroxide	10.0	20.0	10.0
total volume	60.0	60.0	60.0

The first three reactions should be performed at room temperature. The potassium iodide solution and the water can be added to the 250-ml Erlenmeyer flask and allowed to equilibrate at room temperature in the water bath. The water in the bath should be between 4 and 8 cm deep. The hydrogen peroxide should be added to a separate container and also allowed to equilibrate to the temperature of the water bath. The solutions can be measured using graduated cylinders, but be sure to get the volumes as precise as possible. If measuring pipets or burets are available, that would be preferable.

Before performing the experiment, measure the temperature of the water in the bath. It should be very close to room temperature. This will be important, because for Mixtures 1–3, you need to do all three runs at the same temperature. Record the temperature of the bath in your lab notebooks.

Prepare a table in you lab notebook to record the data. The table should look something like this:

TABLE 5.2

	Mix #1 Temp	Mix #2 Temp	Mix #3 Temp	Mix #4 Temp	Mix #5 temp	Mix #6 temp
time interval (min.)	volume reading	volume reading	volume reading	volume reading	volume reacing	volume reading
0.0						
0.5						
1.0						
1.5						
2.0						
2.5						
3.0						
3.5						
4.0						
4.5						
5.0						
5.5						
6.0						
6.5						
7.0						
7.5						
8.0						
8.5						
9.0						
9.5						
10.0						

When all is ready, pour the hydrogen peroxide into the reaction mixture, raise the beaker or leveling bulb to somewhere near the top reading on the buret or gas tube and seal up the system. Once you bring the level of the beaker or leveling bulb to the same height as the liquid in the buret, take your first reading. It is not necessary to take readings in the first few seconds, so it is more important to get a good reading than to take a reading as fast as possible. Because the water level will be moving, you will only be able to measure the volume to within ± 0.1 ml. While one member of your group is recording data, another should be swirling the Erlenmeyer flask **at as constant a rate as possible**. If mixture #1 is stirred much less rapidly than mixture #3, this will affect your results. Continue reading data every thirty seconds (being sure to equalize the water level each time) for ten minutes or until at the water level in the buret has dropped at least 35 ml. Re-measure the temperature in the bath. Your temperature will be the average of that measured before and after the experiment.

Repeat the procedure for mixture #2 and #3, being sure to record the temperature before and after the run.

The effect of changing temperature on the rate of decomposition of H_2O_2 . Repeat the procedure, using the same volumes of reagents as that used in mixture #1 at three other temperatures. The minimum temperature should not be below 5 degrees centigrade, and the maximum temperature should not be above 45 degrees. For example if your room temperature data was collected at 21.2 °C, you could do runs at 12 °C, 30 °C and 40 °C (remember to always record your temperature

to the maximum precision the thermometer allows). In these runs it is especially important to let the solutions equilibrate at the temperature of the water baths. The solutions should be allowed to equilibrate for at least three minutes. Hopefully, the cold or hot water baths will be at a fairly constant temperature. Be sure to record the temperature both before and after each run, and take an average.

Calculations

The first step in performing the calculations is to prepare plots of volume versus time for all six runs. If your graphing routine allows, you can plot all six runs on the same graph. Another option is to plot runs 1-3 on one graph and runs 4,5, and 6 on another. Be absolutely sure you know which curve corresponds to which run, and label your graph so that it is clear which is which as well.

For each of your runs, determine the maximum slope of the graph. You may do this by hand using a ruler and getting the slope from calculating the rise over the run. Alternatively, you may use VernierGraph to determine the maximum slope of the curve.

In any case, report the maximum slope of each run. This is the initial rate of the reaction. Be careful about the units of the reaction rate. It would be helpful to record the results in a table.

Next, use the method of initial rates and your room temperature data to determine the order of the reaction with respect to each of the reactants. Whatever mathematical method you use to extract these orders, **do not round off to an integer or to a half-integer at this point.**

Once you have the orders, report your rate law for the reaction you studied. At this point, go ahead and round the orders to the nearest integer or half-integer.

Now that you have the rate law, calculate the rate constant for each of your six runs. Again, be careful about units. Note that in order to calculate k , you will have to calculate the concentration of iodide ion and of hydrogen peroxide. This may be a bit trickier than it seems. For the three runs at room temperature, calculate the average rate constant and the standard deviation. Report your answer as $k = \text{###} \pm \text{###}$ (average and standard deviation)

Next, prepare a graph of natural log of k versus the inverse of temperature. Use your average value of k for the room temperature data. From a linear fit to your graph and the Arrhenius equation, determine the value of the activation energy (E_a) and the frequency factor (A).

Questions

1. What does the size of the standard deviation of k say about the precision of your measurements?
2. How linear was your Arrhenius plot? What does that say about your value of E_a ?
3. What percentage of the hydrogen peroxide has been decomposed in Mixture #1 when 20.0 ml of O_2 gas has been evolved? Assume your room temperature, 740 torr of pressure, and a density of 3% H_2O_2 of 1.00 g/ml. Do not forget to take into account the vapor pressure of water.
4. Propose a mechanism for the reaction consistent with the rate law you measured.