Experiment 13

The Decomposition of Hydrogen Peroxide

Objectives
• To determine the general rate law of a reaction.
• To determine the rate constant for a reaction.
• To determine the activation of a reaction from two trials or multiple trials.
• To understand the functions and properties of catalysts.
• To understand dilution calculations.
• To convert between mass percent and molarity.

In the Lab
• Students will work in pairs.

Waste
• Solutions can be washed down the drain with excess water.

Safety
• The stopper in the test tube may pop out if the pressure raises enough. Do not point it at yourself or others.
Any molecule in motion possesses kinetic energy, and the faster it moves, the greater the kinetic energy it has. When molecules collide, some of the energy is converted into vibrational energy. If the vibrational energy is large, it may cause some of the chemical bonds in the molecule to break. Breaking bonds is the first step towards product formation. If the initial kinetic energies are small, the molecules will merely bounce off each other without breaking any bonds. In order to react, the molecules must have a total kinetic energy equal to, or greater than, the activation energy, $E_a$. The activation energy is the minimum amount of energy required to initiate a chemical reaction.

The energy change in a reaction is given on an energy-level diagram, or potential energy profile, as shown in Figure 13.1. The vertical axis gives the potential energy for the reaction, while the horizontal axis is a relative (i.e., time) scale that shows the progress of the reaction. The diagram indicates that there is a “hill” or energy barrier that needs to be overcome before any products can be formed. If the collision between the molecules produces enough energy to overcome the barrier, the reactant molecules are in a temporary transition state, forming an activated complex at the height of the barrier before forming the product molecules.

### Factors Influencing the Reaction Rate

The rate at which the reaction occurs depends on several factors:

1. the nature of the reaction
2. the concentration of the reactants
3. the temperature of the reaction
4. the presence of a catalyst

The change in concentration and temperature affect the rate of a chemical reaction by influencing the collisions among the molecules. An increase in concentration increases the number of molecular collisions. An increase in temperature increases the rate because the molecules move faster, increasing the kinetic energy and collisions are more frequent.

A **catalyst** is a compound that affects the rate of chemical reactions by lowering the activation energy, $E_a$. With a lower activation energy, less energy is needed to overcome the energy barrier to form the product(s). A catalyst takes part in the reaction, but is not consumed. It always returns to its original composition at the end of the reaction. Catalysts are defined as homogeneous or heterogeneous where the catalyst is either in the same phase as the reactants or in a different phase, respectively.

### Reaction Rate and Rate Laws

Consider a chemical system in which there are two reactants, $A$ and $B$, with stoichiometric coefficients $a$ and $b$, forming $c$ moles of product $C$.

$$aA + bB \rightarrow cC$$

The rate of the reaction can be defined as the change in concentration of the product as a function of the change in time:

$$\text{rate} = \frac{\Delta [C]}{\Delta t}$$
Although the rate of the reaction is constant under the conditions we set, we can vary it between trials by changing the initial concentrations of the reactants. For a given reaction, the rate typically increases with an increase in the concentration of a reactant. For our general reaction, the relationship between the rate and the concentration of the reactants is given by the rate law

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

In this rate law equation, \( k \) is a constant, called the rate constant of the reaction and should be the same for trials of the reaction at a given temperature. The superscripts, \( m \) and \( n \), are the order of the reaction with respect to \( A \) and \( B \) and are integers, such as 0, 1, 2, or 3. The values of \( m \) and \( n \) do not come from the coefficients of the balanced chemical equation, although they may occasionally have the same value. For example, if \( m \) is 1, the reaction is said to be first order with respect to reactant \( A \). The sum of orders (i.e., \( m + n \)) is the overall order of the reaction. The order of a reaction must be determined experimentally and cannot be determined from the chemical equation alone.

Determining the order of the reaction must be done using experimental data. Pairs of trials can be compared that vary only the concentration of one reactant. If changing the concentration of that reactant causes a change in the rate, then we can say that the rate is dependent to some degree on the concentration of that species. Conversely, if the rate does not change with the change in concentration of one of the reactants, the rate is not dependent on the concentration of that species.

### Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide in aqueous solution proceeds very slowly. A bottle of 3% hydrogen peroxide sitting on a grocery store shelf is stable for a long period of time. The decomposition takes place according to the reaction below.

\[
2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O} + \text{O}_2(\text{g})
\]

A number of catalysts can be used to speed up this reaction, including potassium iodide, manganese (IV) oxide, and the enzyme catalase. If you conduct the catalyzed decomposition of hydrogen peroxide in a closed vessel, you will be able to determine the reaction rate as a function of the pressure increase in the vessel that is caused by the production of oxygen gas. If you vary the initial molar concentration of the \( \text{H}_2\text{O}_2 \) solution and the catalyst (KI) concentration, the rate law for the reaction can also be determined. Finally, by conducting trials at different temperatures with the same concentrations, the activation energy, \( E_a \), can be calculated.

### Mass Percent and Molarity

The initial concentration of the hydrogen peroxide is given as 3% by mass. In order to determine the rate constant for this reaction, you'll need to convert the concentration into molarity.

\[
\text{Molarity} = \frac{\text{moles of solute}}{\text{L of solution}}
\]

\[
\text{Mass percent} = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 100
\]

Since both molarity and mass percent are concentration units, it just takes a few steps to convert one to another, using the molecular weight of the compound and the density of the solution. Since the solutions in this experiment are dilute aqueous solutions, we will assume a density of 1.00 g/mL for the \( \text{H}_2\text{O}_2 \) solution, which is the density of water.
**Example:** What is the molarity of an 85% (by mass) $\text{H}_3\text{PO}_4$ solution ($\text{M.W.} = 98.00 \text{ g/mol, } d=1.685 \text{ g/mL}$)? (An 85% solution of phosphoric acid would not be a dilute aqueous solution so the actual density of the solution is needed.)

$$M \text{olarity} = \frac{85.0 \text{ g } \text{H}_3\text{PO}_4}{100 \text{ g solution}} \times \frac{1 \text{ mol } \text{H}_3\text{PO}_4}{98.00 \text{ g } \text{H}_3\text{PO}_4} \times \frac{1.685 \text{ g } \text{H}_3\text{PO}_4}{1000 \text{ mL}}$$

$$= 14.6 \text{ M}$$

The reverse calculation, from molarity to mass percent, is also possible.

**Dilutions**

One concentration of KI and $\text{H}_2\text{O}_2$ is available for you to use. In order to determine the rate law, we must vary the concentration of both species. We can prepare solutions of lower concentration through dilution. The dilution formula

$$M_iV_i = M_fV_f$$

can only be used for dilution calculations. Do not use this formula for titration calculations. $M_i$ and $M_f$ are the concentrations and $V_i$ and $V_f$ are the volumes of the initial and final solutions, respectively. The units for this formula are not specified, you just need the same units for $M_i$ and $M_f$ and the same units for $V_i$ and $V_f$. Remember that $V_f$ is always the total volume of the solution (i.e., volume of concentrated solution plus volume of added solvent).

**Ideal Gas Law**

In this experiment, you are measuring the pressure of the gas evolved in the reaction which means we can use the ideal gas law to convert the initial rate from kPa/s (obtained from a graph of the data) to mol/L.s. The latter units are necessary to determine the rate constant of the reaction since our solutions are in units of molarity.

The ideal gas law is

$$PV = nRT$$

which can be rearranged to

$$\frac{n}{V} = \frac{P}{RT}$$

$n/V$ is in units of mol/L, which is the molarity of the solution, so we can write

$$M = \frac{P}{RT}$$

where $M$ is the molarity. Divide both sides by seconds, which will result in the molar rate constant

$$\frac{M}{s} = \frac{P}{sRT}$$

We find P/s from the graph and use the above formula to find the rate in M/s.

Looking at the units, you should see

$$\frac{\text{mol}}{\text{L s}} = \frac{\text{torr/s}}{\left(\frac{\text{L torr}}{\text{K mol}}\right)\text{K}}$$

Prove to yourself that these are equal.

Make sure you use the correct value of $R$ in the equation

$$\left(0.08206 \frac{\text{L atm}}{\text{mol K}} \times \frac{760 \text{ torr}}{1 \text{ atm}}\right) = 62.364 \frac{\text{L torr}}{\text{mol K}}$$

**Arrhenius Equation**

The Arrhenius equation, shown below, can show us how the rate constant will vary with the temperature of a reaction for trials with equal concentrations of reactants.

$$k = Ae^{-\frac{E}{RT}}$$

Taking the natural logarithm of each side results in

$$\ln k = \ln A - \frac{E}{RT}$$

which would be useful if we had data at several temperatures and could graph the data because the equation can be rearranged to

$$\ln k = \left(\frac{-E}{R}\right)\frac{1}{T} + \ln A$$

$$y = m \quad x + b$$
so the slope could be used to calculate the activation energy. With only two data points to use for the temperature comparison (only Parts I and IV have the same concentrations of reactants), graphing is a little excessive so instead we can use another form of the Arrhenius equation, shown below.

\[
\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

where \( k_1 \) and \( k_2 \) are the rate constants at two different temperatures, \( T_1 \) and \( T_2 \) (in Kelvin). The value of the activation energy, \( E_a \), is in joules per mole. Pay attention to the units and value of the gas constant, \( R \). This is not the same value of \( R \) used in the previous calculation.

Tips for Procedure

- **Record exact volumes used in each step to one digit beyond the markings on the glassware.** Volumes given in the table are approximate values.
- Allow the solutions to sit before mixing for at least two minutes for their temperatures to equilibrate.
- Be prepared to start collecting data immediately after the solutions are mixed.
- The stopper may pop out of the test tube near the end of the experiment. This is to be expected as the pressure inside the test tube increases. Use the data up to the point of the pop when completing the data analysis.
- If you don’t see an increase in pressure, repeat the trial after checking for leaks in your setup.
- \( T_2 \) should be approximately 10 degrees higher than \( T_1 \).

Suggested Materials

- MeasureNet
- gas pressure probe kit
- thermometer
- 3% hydrogen peroxide, \((\text{H}_2\text{O}_2)\), solution
- 0.5 M potassium iodide, \((\text{KI})\), solution
- two 6” test tubes
- pipets
- pipet bulb
- 400 mL beaker
- other glassware and equipment, as needed

Procedure

You must write your procedure and prepare your lab notebook to record data before coming to lab to do the experiment. Make sure that you will collect the data necessary to complete the data analysis questions. It’s better to have too much information and not need it, than to need something and not have it.

Instructions on using graduated pipets can be found in Chapter 3. Steps for using the gas pressure probe with the MeasureNet workstation are in Chapter 4.

Table 13.1. Approximate volumes for each trial.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Volume of 3.00% H$_2$O$_2$ (mL)</th>
<th>Volume of 0.500 M KI (mL)</th>
<th>Volume of Water (mL)</th>
<th>Temperature</th>
<th>File Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>$T_1$</td>
<td>001</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.5</td>
<td>0.5</td>
<td>$T_1$</td>
<td>002</td>
</tr>
<tr>
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<td>1</td>
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<td>$T_1$</td>
<td>003</td>
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<tr>
<td>4</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>$T_2$</td>
<td>004</td>
</tr>
</tbody>
</table>
**Data Analysis**

1. What is the concentration of the 3% \( \text{H}_2\text{O}_2 \) solution in units of molarity? Assume the density of \( \text{H}_2\text{O}_2 \) is 1.00 g/mL.

2. Find the concentration for the \( \text{H}_2\text{O}_2 \) and KI solutions for each trial after the solutions and/or water are mixed together.

3. Determine the initial rate in torr/s of each reaction using a graph of pressure vs. time for each part. Look at the units of the data being graphed to determine what information is needed from the graph to determine this.

4. Convert the initial rate for each part to M/s using the ideal gas law.

5. Comparing the parts done at the same temperature, look at the data for the initial concentrations of the reactants (found in question 2) and the initial rates determined in question 4 to determine the order of the reaction with respect to each reactant. Write the general rate law for the reaction.

6. Determine the value of the rate constant, \( k \), for each part using the general rate law equation from question 5. For the parts at the same temperature, report the value of \( k \) as an average with its standard deviation.

7. Use the Arrhenius equation to determine the activation energy, \( E_a \), for this reaction by comparing trials with the same concentrations of reactants at two different temperatures.