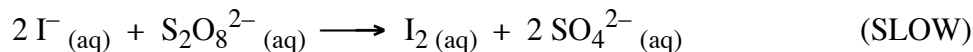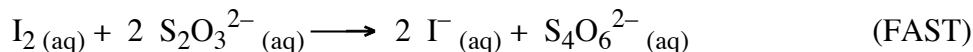# 5

Rate of Reaction

Introduction

This experiment will allow you to study the effects of concentration, temperature, and catalysts on a reaction rate. The reaction whose rate you will study is the oxidation of iodide ion by the strong oxidizing agent peroxydisulfate ion ($S_2O_8{}^{2-}$).

$$2\,I^-{}_{(aq)} + S_2O_8{}^{2-}{}_{(aq)} \longrightarrow I_{2\,(aq)} + 2\,SO_4{}^{2-}{}_{(aq)} \qquad\qquad \text{(SLOW)}$$

This reaction is slow enough to be convenient to study, unlike most common reactions involving ions in water which occur almost instantaneously.

Measuring a reaction rate entails measuring some unique property of one of the products or reactants. In this experiment, the unique property you will look for is the color produced by the I_2 formed in the reaction. This color is intensified by allowing the I_2 to react with starch to form a deep blue complex. Starch is therefore included in the reaction mixture as in indicator for I_2. It reacts only with the product I_2 and not with the reactant I^- (iodide ion).

The starch-iodine color is so intense that it becomes visible when only an extremely low concentration of I_2 has been produced. The intensity of the color increases as the concentration of I_2 increases, but to accurately measure the change in intensity of the color as I_2 builds up would require the use of a spectrophotometer. A simpler method is to resort to a sort of chemical "trick." An additional reactant is introduced that will remove the first 2.5×10^{-5} moles of I_2 formed in the reaction. The additional reactant is thiosulfate ion, $S_2O_3{}^{2-}$, which reacts with I_2 by the very fast reaction below:

$$I_{2\,(aq)} + 2\,S_2O_3{}^{2-}{}_{(aq)} \longrightarrow 2\,I^-{}_{(aq)} + S_4O_6{}^{2-}{}_{(aq)} \qquad\qquad \text{(FAST)}$$

Only a small amount of thiosulfate is added: 5.0×10^{-5} moles, or enough to react with 2.5×10^{-5} moles of I_2. Once the reaction has produced more than this amount of I_2, no more thiosulfate remains to react with it, and the starch-iodine color appears. No color appears until the reaction has produced 2.5×10^{-5} moles of I_2, because the I_2 initially formed immediately reacts with thiosulfate.

Once all the thiosulfate has been used up, the color appears very suddenly and sharply. Its appearance can be used as a <u>signal</u> to measure the rate of the reaction. The time from mixing the reactants to the appearance of color can easily be measured. This length of time is the time required by the slow reaction to produce 2.5×10^{-5} moles of I_2. As the experiment will show, the time required varies with the concentrations of the reactants, with temperature, and with the presence of catalysts.

The time is also a measure of the <u>rate of the reaction</u>. Reaction rate is formally defined as the change of <u>concentration</u> of reaction products per unit of time—in other words, at what rate, in moles per liter per second, does the concentration of the product increase as the reaction proceeds. In this experiment, the reaction will be performed in a total volume of 50 mL. Therefore, producing 2.5×10^{-5} moles of I_2 corresponds to bringing the concentration of I_2 from 0 (at the start of the reaction) to

$$(2.5 \times 10^{-5} \text{ moles}) / (0.050 \text{ liters}) = 5.0 \times 10^{-4} \text{ moles per liter.}$$

Knowing the amount of time required to increase the concentration of I_2 from 0 to 5.0×10^{-4} M indicates the average rate of the reaction during this time.

In summary, then, the rate of the reaction between iodide ion and peroxydisulfate ion will be studied in this experiment. In order to study the rate of this reaction, it will have to be performed in a system in which two other reactions take place: the reaction of the product I_2 with thiosulfate ion to remove the initially formed 2.5×10^{-5} moles of I_2, and the reaction of I_2 with starch to make the appearance of I_2 immediately visible. Both of these other reactions have very fast rates. The time required for these reactions to occur is completely negligible in comparison to the time required for the slow reaction. The rate of the entire process is therefore completely determined by the slow reaction, and this is the rate to be measured.

Part I.
Effect of Concentration on Rate

In this part of the experiment, the reaction will be carried out with the reactants at several different initial concentrations. This will be done by varying the amount of either iodide ion or peroxydisulfate ion added to the reaction mixture. The reaction is carried out by simultaneously mixing three different solutions: one containing iodide, one containing peroxydisulfate, and one containing thiosulfate and starch solution. The total volume when the solutions are combined will be 50 mL in each case, but the initial concentrations of the two reactants iodide and peroxydisulfate will be varied. The reactants will first be mixed using 20 mL of iodide solution, 20 mL of peroxydisulfate solution, and 10 mL of thiosulfate solution. Then the reaction will be repeated using a smaller volume of either the iodide solution or the peroxydisulfate solution.

In order to keep the total volume 50 mL, either the iodide solution or the peroxydisulfate solution must be diluted. The dilution will not be done with water but

with solutions of other ionic compounds that do not participate in the reaction. The ammonium peroxydisulfate solution will be diluted with ammonium sulfate solution, and the potassium iodide solution will be diluted with potassium nitrate solution. These solutions are used instead of water so that the total concentration of all ions in the solution—the ionic strength of the solution—will remain constant even when the reactants are diluted. The rate of the reaction depends on the ionic strength of the solution in which it is performed, so this should be kept constant.

Experimental Procedure for Part I

SAFETY PRECAUTIONS: Wear your SAFETY GOGGLES.

WASTE DISPOSAL: All waste from this experiment should be poured into the INORGANIC WASTE containers in the fume hood.

The experiment should be performed by two people working together. During each run, one person can watch the reaction mixture and the other can watch the clock.

Table 5.1 shows the volumes of solutions that will be required for each reaction.

Table 5.1. Reaction Mixtures for Experiment 5 — Part I.

Reaction #	Volume of solution in first graduated cylinder. (I^-)	Volume of solution in second graduated cylinder $(S_2O_8^{2-})$	Volume in beaker $(S_2O_3^{2-})$
1	20 mL 0.20 M KI	20 mL 0.10 M $(NH_4)_2S_2O_8$	10 mL $Na_2S_2O_3$ 5 drops starch
2	15 mL 0.20 M KI 5 mL 0.20 M KNO_3	20 mL 0.10 M $(NH_4)_2S_2O_8$	10 mL $Na_2S_2O_3$ 5 drops starch
3	10 mL 0.20 M KI 10 mL 0.20 M KNO_3	20 mL 0.10 M $(NH_4)_2S_2O_8$	10 mL $Na_2S_2O_3$ 5 drops starch
4	5 mL 0.20 M KI 15 mL 0.20 M KNO_3	20 mL 0.10 M $(NH_4)_2S_2O_8$	10 mL $Na_2S_2O_3$ 5 drops starch
5	20 mL 0.20 M KI	15 mL 0.10 M $(NH_4)_2S_2O_8$ 5 mL 0.10 M $(NH_4)_2SO_4$	10 mL $Na_2S_2O_3$ 5 drops starch
6	20 mL 0.20 M KI	10 mL 0.10 M $(NH_4)_2S_2O_8$ 10 mL 0.10 M $(NH_4)_2SO_4$	10 mL $Na_2S_2O_3$ 5 drops starch
7	20 mL 0.20 M KI	5 mL 0.10 M $(NH_4)_2S_2O_8$	10 mL $Na_2S_2O_3$

		15 mL 0.10 M $(NH_4)_2SO_4$	5 drops starch

It is best to obtain the entire amount of each solution for all of the reactions before starting the experiment. This assures that your supplies will be uniform for all runs, both in concentration and in temperature. As will be seen in Part II, small changes in temperature can cause considerable changes in reaction rate. Be sure that all your beakers and graduated cylinders are spotlessly clean before obtaining any of the reagents. Incorrect reaction times will be obtained if the KI, $(NH_4)_2S_2O_8$, or $Na_2S_2O_3$ react with impurities. The following amounts should be sufficient for each reaction to be done twice and some, if necessary, three times:

300 mL of 0.20 M KI (potassium iodide)

300 mL of 0.10 M $(NH_4)_2S_2O_8$ (ammonium peroxydisulfate)

200 mL of 0.0050 M $Na_2S_2O_3$ (sodium thiosulfate)

100 mL of 0.20 M KNO_3 (potassium nitrate)

100 mL of 0.10 M $(NH_4)_2SO_4$ (ammonium sulfate)

10 mL starch solution (shaken well)

Four 25-mL graduated cylinders and one 10-mL graduated cylinder should be obtained. The 10 mL cylinder will be used only for the 0.0050 M sodium thiosulfate solution. The other cylinders will be used for the other solutions. Label each cylinder with the formula for the compound for which it is to be used.

To perform the first run—reaction #1—measure out 10 mL of sodium thiosulfate solution using the 10 mL graduated cylinder and add this to a clean, dry 100-mL beaker. Shake the starch solution well, and add 5 drops of starch. Put a thermometer in the beaker. (Be very careful with the thermometer: support it upright in the middle of a ring on a ringstand.) Collect 20 mL of KI solution in a graduated cylinder, and 20 mL of ammonium peroxydisulfate in another graduated cylinder. With one person watching the second hand of the clock, the other should simultaneously add both solutions from the graduated cylinders to the beaker. The timing starts at exactly the second when the two solutions go into the beaker. The person watching the reaction should stir the reaction gently with the thermometer. A consistent stirring rate should be used, and the same rate should be used for all the runs. Observe the temperature on the thermometer.

The reaction with thiosulfate ion is over the instant that the blue color appears. Record the amount of time required. The time for the first reaction should be less than one minute. If it is not, the chemicals have probably been mixed incorrectly.

Reaction #1 should be repeated, using the same procedure. The time required for the blue color to appear should be within a few seconds of the time required on the first run. If the two times are not close to each other, the reaction should be repeated again until two similar times are obtained. All of the other reactions in the section should be run in the same way, repeating each reaction at least twice. If the times of the two identical runs are not within 2% of each other, then the same reaction should be repeated until two times that are within 2% of each other are obtained.

Chemistry 1B Experiment 5

The procedure for the other reactions is the same as that used for Reaction #1, except that less than 20 mL of either KI or ammonium peroxydisulfate is used and a diluting solution is used to bring the total volume up to 50 mL. Add the diluting solution—KNO_3 for KI, and $(NH_4)_2SO_4$ for $(NH_4)_2S_2O_8$—to the appropriate reactant solution in its graduated cylinder. For each reaction, there should two graduated cylinders, each containing 20 mL of solution, to be poured into the 100 mL beaker containing 10 mL of 0.0050 M $Na_2S_2O_3$ solution.

Calculations for Part I

A. Calculating the Rate of Reaction

Each of the seven reactions proceeded at a different rate. The rates for the reactions can be calculated in terms of

$$\frac{\Delta[I_2]}{\Delta \text{ time}},$$

the change in iodine concentration per second. The appearance of the blue color means that $[I_2]$ has gone from 0 to 5.0×10^{-4} M by the time the color appears (actually, it means that $[I_2]$ <u>would have been</u> 5.0×10^{-4} M if the thiosulfate had not reacted with it). Therefore, the rate of each reaction is found by dividing 5.0×10^{-4} M by the time it takes for the solution to turn blue.

For each of the seven reaction conditions, the average of the two similar reaction times should be used to calculate the rate. Note that the more time required for the blue color to appear, the smaller the rate of the reaction is.

B. Finding the Form of the Rate Law

The rate of a reaction should be proportional to the concentration of the reactants in some way. A general method of expressing this proportionality of the reaction A + B $\rightarrow$ products is to say that:

$$\text{rate} = k\,[A]^x\,[B]^y$$

Most commonly, the exponents x and y equal 0, 1, or 2. If the rate is proportional to the concentration of a reactant to the zeroth power, then the rate does not change at all as the concentration of that reactant changes: $[A]^0 = 1$, regardless of the value of [A]. If the rate is proportional to the concentration to the first power, then the two are said to be directly proportional. If [A] doubles, the rate doubles; if [A] is reduced by a factor of 5, the rate is reduced by a factor of 5. Finally, if the rate is proportional to $[A]^2$, then the rate changes very dramatically as [A] changes. If [A] is doubled, the rate goes up by a factor of $2^2 = 4$. If [A] is decreased to 1/4 of its earlier value, then the rate is only $(1/4)^2$ = 1/16th of its earlier value.

In this experiment, you measured the rate at the beginning of the reaction. To determine the rate law, you need to calculate the concentrations of $[I^-]$ and $[S_2O_8^{2-}]$ at the beginning of each reaction. Remember that mixing the solutions dilutes their

concentrations. Use the dilution formula below to calculate the concentrations of $[I^-]$ and $[S_2O_8^{2-}]$ in each reaction mixture.

$$M_{stock} \cdot V_{stock} = M_{mixture} \cdot V_{mixture}$$

Use the total volume after all three solutions are mixed for $V_{mixture}$.

Then, by inspecting your data of rate as a function of $[I^-]$ and $[S_2O_8^{2-}]$, decide which of these exponents applies to each reactant—that is, state what the values of x and y should be in the expression:

$$\text{rate} = \frac{\Delta[I_2]}{\Delta \text{ time}} = k\,[I^-]^x\,[S_2O_8^{2-}]^y$$

Show how all seven reactions support the rate law. Do not base your decision on only three of them.
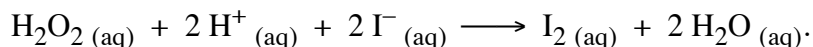
C. Calculating the Rate Constant, k

Once the form of the rate law has been determined from the experimental data, the value of the rate constant, k, can be calculated. For each of the seven reactions, both the rate and the initial reaction concentrations are known. The only unknown in the rate expression is the rate constant, k. Calculate k for each of the reaction conditions. If the values of the exponents x and y have been chosen correctly, the different values for k obtained in this way should be very similar. The value of the rate constant should not vary with concentration, but it will vary with temperature.

Calculate an average value for k from the seven individual values. This can be assumed to be the correct value for the rate constant at the temperature at which the reaction was done.

Prelab Question for Part I

Using the same procedure that you will use in this experiment, a student investigated the effect of changing reactant concentrations on the rate of the reaction:

$$H_2O_{2\,(aq)} + 2\,H^+_{\,(aq)} + 2\,I^-_{\,(aq)} \longrightarrow I_{2\,(aq)} + 2\,H_2O_{\,(aq)}.$$

The student made up four reaction mixtures with different initial concentrations of H_2O_2, H^+, and I^-, which are listed in the table below. The student measured the time it took for each reaction to produce the first 8.33×10^{-4} M of I_2. (That is, $\Delta[I_2] = 8.33 \times 10^{-4}$ M.)

Mixture	$[H_2O_2]$	$[H^+]$	$[I^-]$	time
1	5.6×10^{-2} M	1.8×10^{-5} M	8.3×10^{-3} M	185 s
2	2.8×10^{-2} M	1.8×10^{-5} M	8.3×10^{-3} M	389 s
3	5.6×10^{-2} M	1.8×10^{-5} M	1.67×10^{-2} M	99 s
4	5.6×10^{-2} M	1.8×10^{-4} M	8.3×10^{-3} M	205 s

Chemistry 1B Experiment 5

(a) For each of the four trials shown in the table, calculate the reaction rate, $\dfrac{\Delta [I_2]}{\Delta \text{ time}}$.

(b) Determine the order of the reaction with respect to each of the three reactants. That is, determine the integer values of x, y, and z in the rate law:

$$\text{Rate} = \frac{\Delta [I_2]}{\Delta \text{ time}} = k\,[H_2O_2]^x\,[H^+]^y\,[I^-]^z.$$

(c) For each of the four trials, calculate the rate constant, k.

Part II

Effect of Temperature and Catalysts on Rate

In the first section, the reaction was performed at different reactant concentrations but at constant temperature. In this section, the concentrations will be kept constant and the temperature will be varied.

A small change in temperature can cause a large change in reaction rate. For a typical reaction near room temperature, a 10°C increase in temperature doubles the rate of reaction. This is because, in a typical reaction, very few of the collisions between reactant ions or molecules take place with sufficient energy to cause reaction. The energy necessary for a collision to result in reaction is called the energy of activation, E_a, of that reaction. A small increase in temperature can have a considerable effect on the number of molecules that have this required amount of energy to undergo reaction when collision occurs. The activation energy of a reaction can be found by performing a reaction at several different temperatures. The rate constant, k, increases as the temperature increases following the relationship:

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \text{constant}$$

The value of E_a does not change with temperature. Its value can be found by preparing a graph on which the natural log of the rate constant, ln k, is plotted on the y-axis against the reciprocal of the absolute temperature of the reaction, 1/T, on the x-axis. The energy of activation can be found from the slope of this graph. Since the equation above is of the general form, y = mx + b, the slope of the graph will equal m, or -E_a/R, when y is ln k and x is 1/T.

The activation energy for the reaction can be found in joules from the slope of the graph by using the value of R = 8.314 J / mol·K.

The effect of a catalyst on reaction rate will also be studied in this section. A catalyst is a substance that can increase the rate of reaction by changing the mechanism of the reaction. Usually, a catalyzed mechanism will have a lower activation energy than an uncatalyzed mechanism. At any given temperature, there will be more molecules

having sufficient energy to react via the catalyzed mechanism than via the uncatalyzed route. Therefore, the rate of the catalyzed reaction will be faster.

In this experiment, the catalyst will be a small amount of copper (II) ions, $Cu^{+2}_{(aq)}$. Both the catalyzed and the uncatalyzed reactions will be performed at several different temperatures. In this way, the activation energy of both pathways can be found, and can be compared.

Experimental Procedure for Part II

SAFETY PRECAUTIONS: Wear your SAFETY GOGGLES.

WASTE DISPOSAL: All waste from this experiment should be poured into the INORGANIC WASTE containers in the fume hood.

In this part of the experiment, the concentrations of reactants will be the same for all runs. You will vary the temperature and measure the effect of a catalyst. Table 5.2 shows the volumes of solutions required for each reaction.

Again, you should take the entire amount of each solution you will need before starting the experiment. The following amounts should be sufficient to allow each reaction to be carried out at five or more different temperatures:

120 mL of 0.20 M KI (potassium iodide) diluted with 120 mL of purified water to make 240 mL of 0.10 M KI

120 mL of 0.10 M $(NH_4)_2S_2O_8$ (ammonium peroxydisulfate) diluted with 120 mL of purified water to make 240 mL of 0.050 M $(NH_4)_2S_2O_8$

150 mL of 0.0050 M $Na_2S_2O_3$ (sodium thiosulfate)

10 mL starch solution (shaken well)

5 mL dilute $CuSO_4$ (copper sulfate)

Table 5.2. Reaction Mixtures for Experiment 5 -- Part II.

Reaction	Volume of solution in first graduated cylinder. (I^-)	Volume of solution in second graduated cylinder ($S_2O_8^{2-}$)	Volume in beaker ($S_2O_3^{2-}$)
Uncatalyzed (at 5 temps)	20 mL 0.10 M KI	20 mL 0.050 M $(NH_4)_2S_2O_8$	10 mL $Na_2S_2O_3$ 5 drops starch
Catalyzed (at 5 temps)	20 mL 0.10 M KI	20 mL 0.050 M $(NH_4)_2S_2O_8$ 4 drops $CuSO_4 (aq)$	10 mL $Na_2S_2O_3$ 5 drops starch

Both the uncatalyzed and the catalyzed reaction will be performed at five different temperatures. The procedure for the reactions will be essentially the same as in the first part. One of the reactions will be performed at room temperature, and this can be done simply by mixing the reactants at room temperature. For the other runs, the reactants should either be warmed or cooled by placing them, in graduated cylinders, inside a large beaker or plastic container filled with a warm water or cold water bath. Ice is available for preparing the cold water bath. (Use only a few ice cubes at a time. Too many ice cubes will make the temperature unstable.) If possible, the bath should contain enough water to completely cover the levels of the solutions in the graduated cylinders, but it should not be filled so high that water from the bath gets into the solutions. This would dilute the solutions, and change the rate of reaction.

The exact temperatures at which the reactions are run are not crucial, but there should be, for both the catalyzed and uncatalyzed reactions:

One (T_1) in the range 5°C to 10°C

One (T_2) in the range 10°C to 20°C

One (T_3) in the range 20°C to 30°C —the room temperature run

One (T_4) in the range 30°C to 40°C

One (T_5) in the range 40°C to 50°C

To run a reaction, fill the graduated cylinders with the solutions, immerse them in the water bath (except for the room temperature reactions) and place a thermometer in the cylinder containing the KI solution. When the temperature of this solution has reached the desired range for the reaction, it can be assumed that the temperatures of the other solutions have also.

If the reaction is to be a catalyzed one, four drops of copper sulfate solution should be added to the ammonium peroxydisulfate solution before mixing the other reactants.

To initiate the reaction, the solutions can be mixed as before, by adding the sodium thiosulfate solution to a beaker and then simultaneously adding the other two solutions. For better temperature control, an alternate procedure can be used. The sodium thiosulfate and KI solutions can both be added to an Erlenmeyer flask, and the flask can be immersed in the water bath. The ammonium peroxydisulfate solution is then added to the flask to initiate reaction. One or the other procedure should be used consistently for all runs.

During the reaction, the beaker or flask should be stirred or swirled in a uniform manner for all runs with the thermometer in the reaction mixture. The time required for the blue color to appear should be recorded. The temperature at the time the color appears should be taken as the temperature of the reaction.

Calculations for Part II

The data obtained in this section are to be used to find the energy of activation for both the uncatalyzed reaction and the catalyzed reaction. This will be done by finding the slope of the graph on which the natural logarithm of the rate constant—ln k—is plotted on the y-axis against the reciprocal of the absolute reaction temperature—1/T—on the x-axis.

A. Calculating the Rate Constants k and k_{cat}

The rate constant k is found by the same procedure used in the first part of the experiment. First, find the rate of each reaction by dividing 5.0×10^{-4} M by the number of seconds required for the blue color to appear. Find the initial concentrations of $[I^-]$ and $[S_2O_8^{2-}]$, which will be the same for each reaction mixture in this section of the expriment. Remember that you diluted the KI stock solution to 0.10 M, and the $(NH_4)_2S_2O_8$ stock solution to 0.050 M.

Then find the rate constant for each reaction from the rate law for the reaction. The rate law (i.e., the values of the exponents x and y) for the uncatalyzed reaction was determined in Part 1. For the catalyzed reaction, which follows a different mechanism from the uncatalyzed reaction, the rate law[1] is:

$$Rate = k_{cat} [I^-] [S_2O_8^{2-}]$$

In the first part of the experiment, the values obtained for the rate constant k should have been nearly the same for all the reactions. Here the values should be expected to be quite different, since the reactions were done at different temperatures.

B. Graphing ln k versus 1/T

Calculate the natural logarithm of each rate constant (ln k) and the reciprocal of the absolute temperature of each reaction (1/T, in units of K^{-1}).

Prepare a graph with ln k on the *y*-axis and 1/T on the *x*-axes.

Plot five points on the graph for the five uncatalyzed reactions. Draw the best possible single straight line that comes closest to going through all of these points. Then repeat this procedure for the five catalyzed reactions. This can be done on the same graph paper, but will produce a different straight line.

Which of the two straight lines is steeper? The steeper the line is, the more the reaction rate is changed by a change in temperature. Should the reaction pathway whose rate is affected most by temperature be the one with the larger or the smaller energy of activation?

C. Calculating the Activation Energy, E_a

The slope of each straight line is equal to

---

[1] For the catalyzed reactions, the true rate law includes the concentration of the catalyst:

Rate = k′ $[Cu^{2+}]$ $[I^-]$ $[S_2O_8^{2-}]$

The rate law we are using has the concentration of catalyst absorbed into k_{cat}. You do not need to worry about $[Cu^{2+}]$ in your calculations.

$$m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}.$$

Choose any two well-separated and easily interpolated points on the straight line as point (x_1, y_1) and (x_2, y_2). These should not be experimental data points. The line averages all of the experimental data together for you. The slope of each graph should be a negative number, since the value of 1/T goes down as the values of T, k, and ln k go up. Calculate the slope for the uncatalyzed reaction and for the catalyzed reaction.
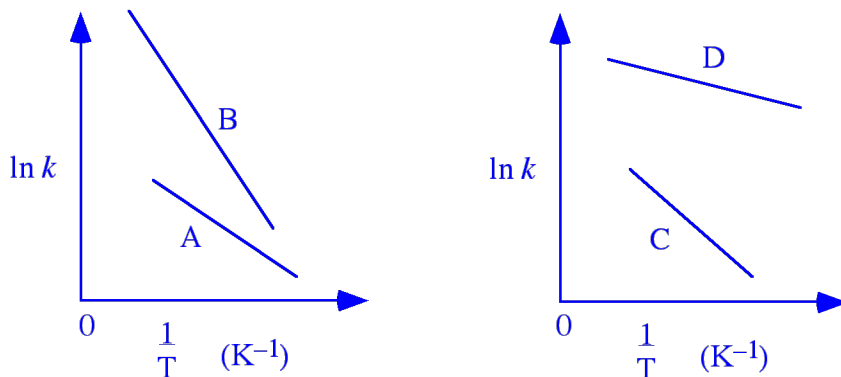
The slope of the graph, m, has units of Kelvins, and is equal to $-E_a/R$. Therefore, $E_a = -Rm$. The activation energy can be calculated from this equation in J / mol by using R = 8.314 J / mole·K. Calculate the activation energy for the uncatalyzed reaction and for the catalyzed reaction.

Calculate the percent error in the activation energy of the uncatalyzed reaction. The accepted value is 51.9 kJ / mol.

Sketch energy diagrams for the reactions, incorporating your results for the activation energy. Do your results make sense? Would you expect the faster reaction to have a higher or lower activation energy? Explain. What is uncertain about the sketches you made?

Prelab Question for Part II

The diagrams below show plots of ln k against 1 / T for four different chemical reactions: Reaction A, Reaction B, Reaction C, and Reaction D. (One of these two situations applies to this experiment.)
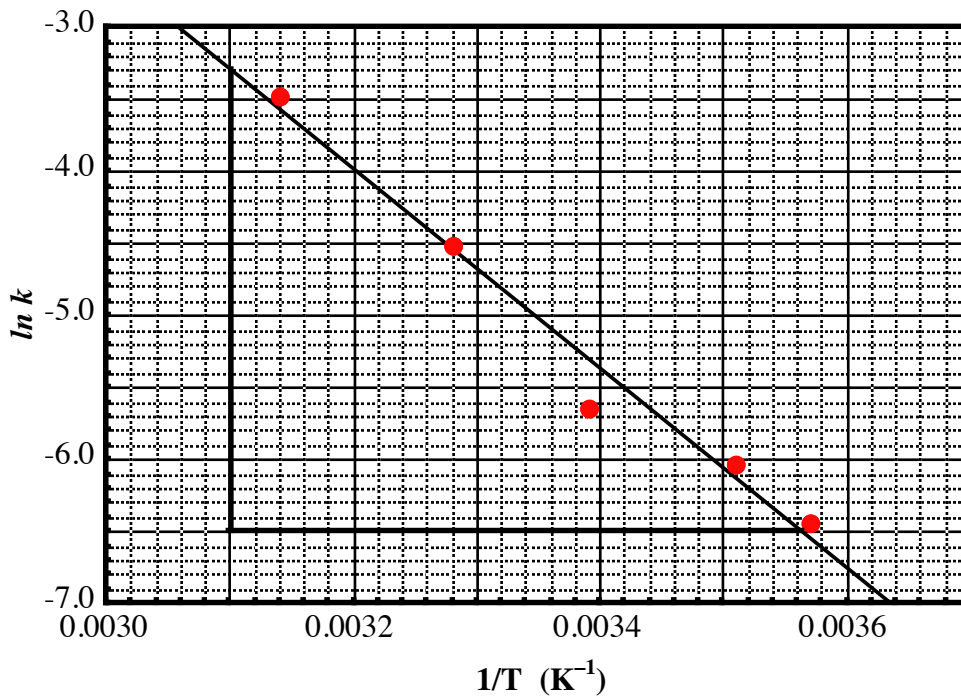

(a)   Which reaction has the larger activation energy: Reaction A or Reaction B?

(b)   Which reaction has the larger activation energy: Reaction C or Reaction D?

(c)   Reaction D is faster than reaction C (it has a higher ln k). Suggest a possible molecular-level reason why reaction D could be faster than reaction C?

(d) Reaction B is faster than reaction A. Suggest a possible molecular reason why.

Sample Calculation for Part II

The following table has been expanded from data obtained in a Laney College student's iodine clock experiment.

Temp. (°C) (experimentally determined)	T (K)	$\frac{1}{T}$ (K^{-1})	time (s) (experimentally determined)	k (L·mol^{-1}·s^{-1})	ln k
7	280	0.00357	390	1.6×10^{-3}	–6.44
12	285	0.00351	265	2.4×10^{-3}	–6.03
22	295	0.00339	180	3.5×10^{-3}	–5.65
32	305	0.00328	55	$11. \times 10^{-3}$	–4.51
45	318	0.00314	20	$31. \times 10^{-3}$	–3.47

$$m = slope = \frac{\Delta(\ln k)}{\Delta(1/T)} = \frac{-6.50 - (-3.30)}{0.003560\ K^{-1} - 0.003100\ K^{-1}} = -6.9\underline{5}7 \times 10^3\ K.$$

Since, $m = -\dfrac{E_a}{R}$,

$$E_a = -mR = -(-6.9\underline{5}7 \times 10^3\ K) \times (8.314\ J·mol^{-1}·K^{-1}) = 5.78 \times 10^4\ J·mol^{-1} = \underline{57.8\ kJ\ /\ mol}.$$