



Experiment 6.

A Rate Law and Activation Energy



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- **Objectives**
 - **Introduction**
 - **Experimental Procedure**

OBJECTIVES

- To determine the rate law for a chemical reaction
- To utilize a graphical analysis of experimental data to
 - determine the order of each reactant in the reaction
 - determine the activation energy for the reaction



INTRODUCTION

rate law : rate = $k[A]^m[B]^n$

Varying the concentration, we can determine the order of reaction rate.



Arrhenius equation:

$$k' = Ae^{-E_a/RT}$$

Comparing the rate constants at different temperature, we can calculate the activation energy



EXPERIMENTAL PROCEDURE

Overview

Measured volume of several solutions having known concentrations of reactants are mixed in a series of trials. The time required for a visible color change to appear in the solution is recorded for the series of trials. The data are collected and plotted (two plots). From the plotted data, the order of the reaction with respect to each reactant is calculated and the rate law for the reaction is derived. After the rate law for the reaction is established, the reaction rate is observed at non-ambient temperatures. The plotted data produces a value for the activation energy of the reaction.

Part A.

Determination of Reaction Times



1. Prepare solution A for the kinetic trials

Table 24.1 summarizes the preparation of the solutions for the kinetic trials. Use previously boiled, deionized water. Measure the volumes of KI and $\text{Na}_2\text{S}_2\text{O}_3$ solutions with clean pipets. Burets or pipets can be used for the remaining solutions. At the same time, prepare, all of the solutions A for kinetic trials 1–8 in either clean and labeled 20-mL vial. Trial 8 is to be of your design.

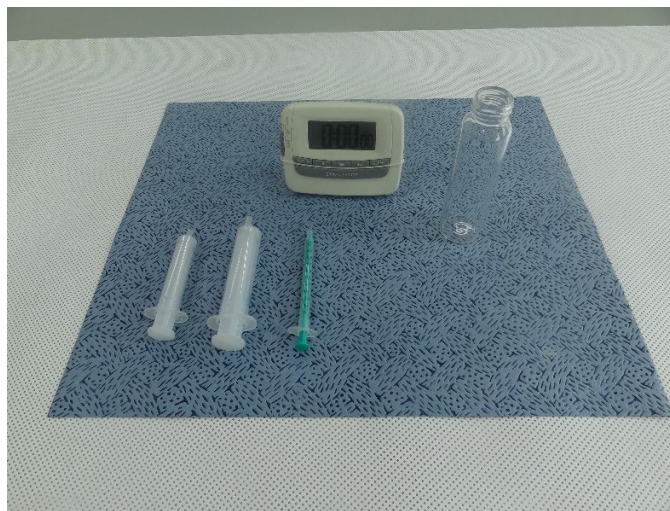
Table 24.1 Composition of Test Solutions

Kinetic Trial	Solution A					Solution B
	Distilled water	Buffer	0.3 M KI	0.02M $\text{Na}_2\text{S}_2\text{O}_3$	Starch	0.1M H_2O_2
1	4.0 mL	1.0 mL	1.0 mL	1.0 mL	5 drops	3.0 mL
2	3.0 mL	1.0 mL	2.0 mL	1.0 mL	5 drops	3.0 mL
3	2.0 mL	1.0 mL	3.0 mL	1.0 mL	5 drops	3.0 mL
4	1.0 mL	1.0 mL	4.0 mL	1.0 mL	5 drops	3.0 mL
5	2.0 mL	1.0 mL	1.0 mL	1.0 mL	5 drops	5.0 mL
6	0.0 mL	1.0 mL	1.0 mL	1.0 mL	5 drops	7.0 mL
7	5.0 mL	1.0 mL	1.0 mL	1.0 mL	5 drops	2.0 mL
8	—	1.0 mL	—	1.0 mL	5 drops	—

2. Prepare solutions for kinetic trial 4

Solution A. Stir the solution in a 50-mL vial.

Solution B. Pipet 3.0 mL of 0.1 M H_2O_2 with a 5-mL or 10-mL syringe.

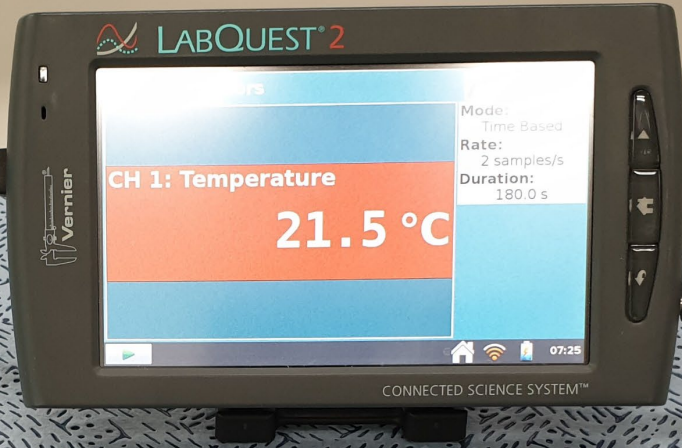


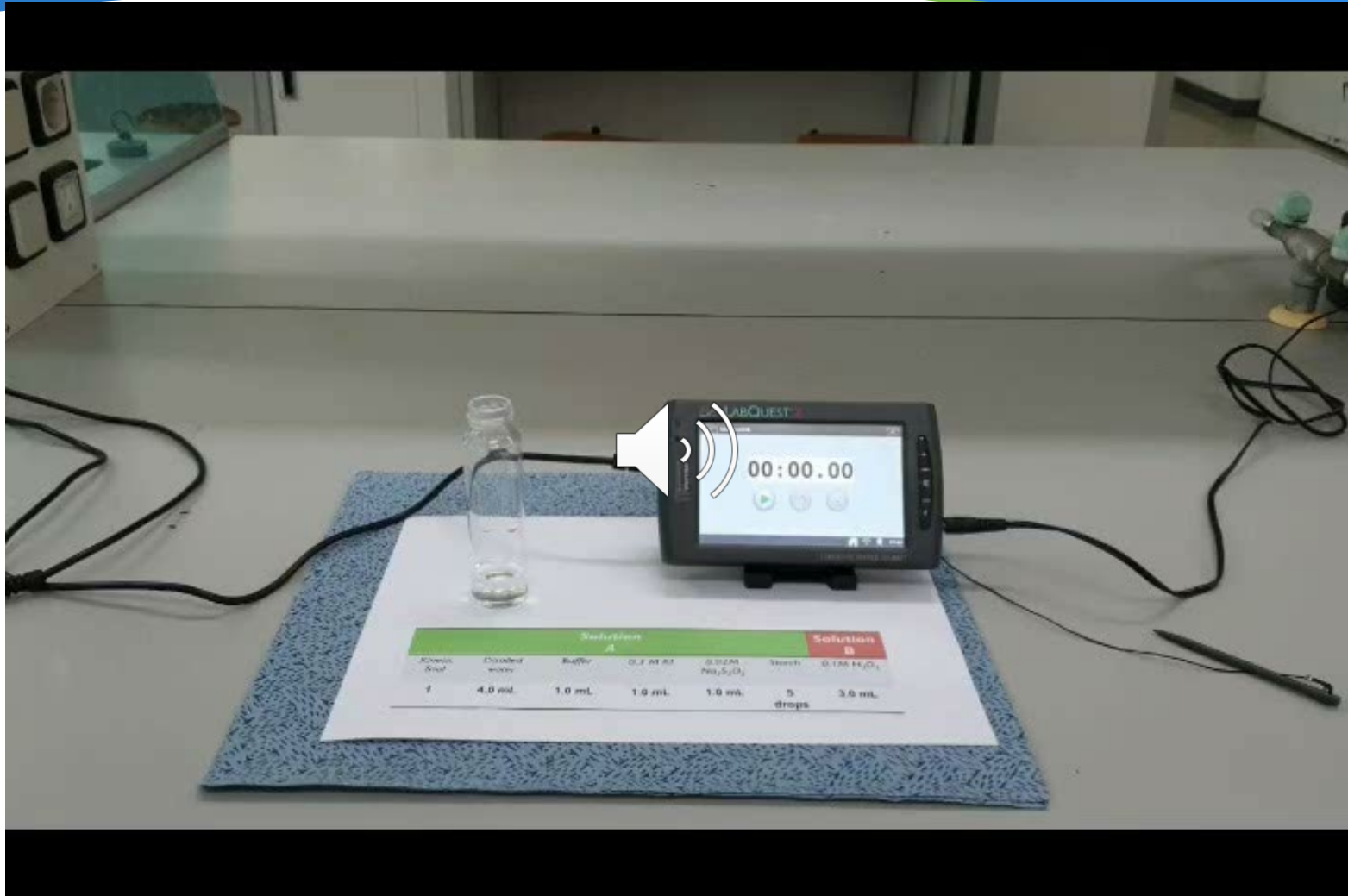
3. Prepare for the reaction

- 1) The reaction begins when the H_2O_2 (**solution B**) is added to solution A; be prepared to start timing the reaction in seconds.
- 2) Place the beaker on a white sheet of paper so the deep-blue color change is more easily detected. As one student mixes the solutions, the other notes the time. All of the solutions should be at ambient temperature before mixing. Record the temperature.

4. Time the reaction.

- 1) Rapidly add **Solution B** to solution **A**. **START TIME** and swirl (once) the contents of the mixture. Continued swirling is unnecessary.
- 2) The appearance of the deep-blue color is sudden. Be ready to **STOP TIME**.
- 3) Record the time lapse to the nearest second on the Report Sheet.
- 4) Repeat if necessary.





Notice! If the time for the color change of trial 4 is less than 10 seconds, STOP. Add an additional 10 mL of boiled, deionized water to each solution A for each kinetic trial (total volume of the reaction mixtures will now be 20 mL instead of 10 mL). A consequence of this dilution will result in a much longer time lapse for a color change in Trial 1—be patient!

5. Repeat for the remaining kinetic Trial.

1) Mix and time the test solutions for the remaining seven kinetic trials. If the instructor approves, conduct additional kinetics trials, either by repeating those in Table 24.1 or by preparing other combinations of KI and H_2O_2 . Make sure that the total diluted volume remains constant at 10 mL.

Part B. Calculations for Determining the Rate Law

Perform the calculations, carefully one step at a time. Appropriate and correctly programmed software would be invaluable for completing this analysis. As you read through this section, complete the appropriate calculation and record it for each test solution on the Report Sheet.



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1. Moles of I_3^- produced. Calculate the moles of $S_2O_3^{2-}$ consumed in each kinetic trial. From 24.11, the moles of I_3^- that form in the reaction equals one-half the moles of $S_2O_3^{2-}$ that react. This also equals the change in the moles of I_3^- , starting with none at time zero up until a final amount that was produced at the time of the color change. This is designated as “ $\Delta(\text{mol } I_3^-)$ ” produced.



2. Reaction Rate. The reaction rate for each kinetic trial is calculated as the ratio of the moles of I_3^- produced, $\Delta(\text{mol } I_3^-)$, to the time lapse, Δt , for the appearance of the deep-blue color. Compute these reaction rates, $\Delta(\text{mol } I_3^-)/\Delta t$, and the logarithms of the reaction rates (see equations 24.7 and 24.8) for each kinetic trial and enter them on the Report Sheet. Because the total volume is a constant for all kinetic trials, we do not need to calculate the molar concentrations of the I_3^- produced.

3. **Initial iodide concentrations.** Calculate the initial molar concentration, $[I^-]_0$, and the logarithm of the initial molar concentration, $\log[I^-]_0$, of iodide ion for each kinetic trial. See **Prelaboratory Assignment**, question 4d.



4. **Initial hydrogen peroxide concentrations.** Calculate the initial molar concentration, $[H_2O_2]_0$, and the logarithm of the initial molar concentration, $\log [H_2O_2]_0$, of hydrogen peroxide for each kinetic trial. See **Prelaboratory Assignment**, question 4e.

***Part C. Determination of the
Reaction Order, p and q , for
each Reactant.***



1. Determination of p from plot of data. Plot on the top half of a sheet of linear graph paper or preferably by using appropriate software $\log (\Delta \text{mol I}_3^- / \Delta t)$, which is $\log (\text{rate})$ (y-axis), versus $\log [\text{I}^-]_0$ (x-axis) at constant hydrogen peroxide concentration. Kinetic trials 1, 2, 3, and 4 have the same H_2O_2 concentration. Draw the best straight line through the four points. Calculate the slope of the straight line. The slope is the order of the reaction, p, with respect to the iodide ion.

2. Determination of q from plot of data. Plot on the bottom half of the same sheet of linear graph paper or preferably by using appropriate software $\log (\Delta \text{mol I}_3^- / \Delta t)$ (y-axis) versus $\log \log [\text{I}^-]_0$ (x-axis) at constant iodide ion concentration using kinetic trials 1, 5, 6, and 7. Draw the best straight line through the four points and calculate its slope. The slope of the plot is the order of the reaction, 1, with respect to the hydrogen peroxide.

Part D. Determination of k' , the Specific Rate Constant for the Reaction.



1. Substitution of P and q into rate law. Use the values of p and q (from PART C) and the rate law,

$$\text{rate} = (\Delta \text{mol I}_3^- / \Delta t), = k' [\text{I}^-]^p [\text{H}_2\text{O}_2]^q$$


To determine k' for the seven solutions. Calculate the average value of k' with proper units. Also determine the standard deviation and relative standard deviation (%RSD) of k' from your data.

2. Class Data. Obtain average k' values from other groups in the class. Calculate a standard deviation and relative standard deviation (%RSD) of k' for the class.



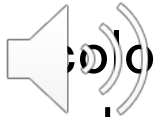
PART E.
Determination of
Activation Energy

1. Prepare test solutions.

- 1) Refer to Table 24.1, [kinetic trial 4](#). In separate, clean 50-ml vials prepare two additional sets of solution A and solution B.
- 2) Place one (solution A/  solution B) set in an ice bath. Place the other set in a warm water (~ 35 °C) bath.
- 3) Allow thermal equilibrium to be established for each set, about 5 minutes.
- 4) Test solutions prepared at other temperatures are encouraged for additional data points.



2. Mix solutions A and B.

- 1) When thermal equilibrium has been established, quickly pour solution B into solution A, START TIME, and agitate the mixture.
- 2) When the deep-blue  color appears, STOP TIME. Record the time lapse as before.
- 3) Record the temperature of the water bath and use this time lapse for your calculations.
- 4) Repeat to check reproducibility and for the other set(s) of solutions.

3. The reaction rates and “new” rate constants

- 1) The procedure for determining the reaction rates is described in PART B.2.
- 2) Calculate and record the reaction rates for the (at least) two trials (two temperatures) from PART E.2 and re-record the reaction rate for the (room temperature) kinetic trial 4 in PART A.5. Carefully complete the calculation on the **Report Sheet**.
- 3) Use the reaction rates at the three temperatures (ice, room, and $\sim 35^{\circ}\text{C}$ temperatures) and the established rate law from PART C to calculate the rate constants, k' , at these temperatures.
- 4) Calculate the natural logarithm of these rate constants.

In an ice bath

		Solution A				Solution B	
<i>Kinetic Trial</i>	<i>Distilled water</i>	<i>Buffer</i>	0.3 M KI	0.02M $\text{Na}_2\text{S}_2\text{O}_3$	Starch	0.1M H_2O_2	
4	1.0 mL	1.0 mL	4.0 mL	1.0 mL	5 drops	3.0 mL	

LABQUEST 2
File Sensors
CH 1: Temperature
1.6 °C
Mode: Time Based
Rate: 2 samples/s
Duration: 180.0 s

LABQUEST 2
Stopwatch
02:14.23
CONNECTED SCIENCE SYSTEM™



4. Plot the data

- 1) Plot in k' versus $1/T(K)$ for the (at least) three trials at which the experiment was performed. Remember to express temperature in kelvins and $R = 8.314 \text{ J/mol}\cdot\text{K}$.



5. Activation energy

- 1) From the data plot, determine the slope of the linear plot ($= -E_a/R$) and calculate the activation energy for the reaction.

CLEANUP

Rinse the beakers or vials twice with tap water and discard in the Waste Iodide Salts Container. Dispose of two final rinses with distilled water in the sink..

Disposal: Dispose of the solutions from the kinetics trials in the Waste Iodide Salts container.