EXPERIMENT 1

Determination of Rate Laws

Introduction

The speed of a reaction is an important component to consider when setting up an experiment. Will the reaction be so fast that it is over in a few seconds, or so slow that it does not reach completion for many days? If the speed of a reaction can be measured, then the length of time needed for a reaction to take place can then be predicted.

Rate of reaction

The rate of a reaction is influenced by many factors. Two of these variables, concentration of the reactants and reaction temperature are often varied to modify the rate of a reaction. In this experiment, we will study how changes in both of these variables affect the reaction rate.

Effect of Concentration on Reaction Rate

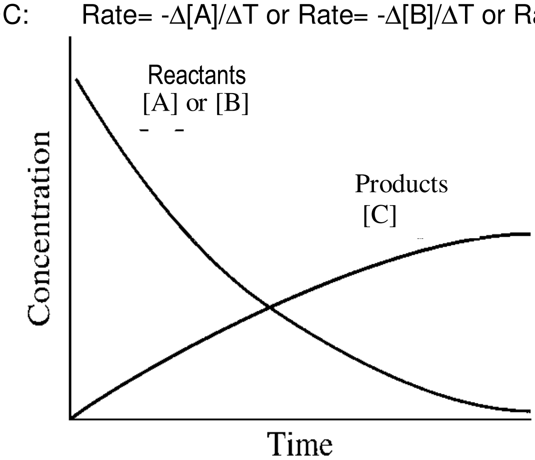
An increase in the concentration of the reactants often increases the speed of a reaction. If two molecules, A and B must collide in order to react, anything that increases the frequency of those collisions increases the rate of the reaction. Increasing the concentration of a reactant most often results in an increased reaction rate as the molecules are closer together so collisions can occur more frequently.

In the example below, your goal is to react all of reactant A with a second reactant, B, to form product C. If you set the amount of A used as 1 mole, you will need 1 mole of B to fully use up all of reactant A. By increasing the concentration of reactant B in the second box, you can see that you are increasing the chance that A will collide with reactant B. Thus, by increasing the chances of collision by increasing the concentration of a reactant, you are likely to increase the reaction rate as well.

$$A+B \rightarrow C$$

The rate of a reaction can be defined in terms of either the loss of a reactant over time or the increase in the product over time. Any chemicals involved in the reaction can be monitored to determine how fast the reaction is progressing, as their concentrations throughout the reaction are related to the ratio of products to reactants seen in the chemical equation.

Thus for a reaction $A+B \rightarrow C$: Rate= $-\Delta[A]/\Delta T$ or Rate= $-\Delta[B]/\Delta T$ or Rate= $\Delta[C]/\Delta T$



For this experiment, we will monitor the rate of disappearance of one reactant, potassium permanganate, $KMnO_4$, by monitoring the disappearance of the purple color according to the following reaction.

$$KMnO_4(aq) + H_2C_2O_4(aq) \rightarrow Mn^{2+}(aq) + CO_2(g) + H_2O(l)$$

(purple) (colorless)

$$\text{Rate of reaction} = -\Delta[KMnO_4]/\Delta T = -\Delta[H_2C_2O_4]/\Delta T = \Delta[Mn^{2+}]/\Delta T$$

When all of the purple color is gone, we can say that the reaction is finished and that the final concentration of the $KMnO_4$ is now zero. Since the initial time for ΔT is zero, the equation for the rate of disappearance of the potassium permanganate becomes:

$$\text{Rate} = \text{Initial concentration of } KMnO_4/\text{elapsed time} = \Delta KMnO_4]/\Delta T = (0-[\text{initial } KMnO_4])/(\text{elapsed time} -0)$$

Rate Laws

While knowing the rate of a reaction after the reaction is completed provides us with some information, in order to cause predicted changes in the reaction rate, we need to find the **rate law** for the reaction.

A Rate Law is an equation that directly relates the concentration of the reactants to the speed of the reaction when all other conditions, such as temperature, pressure, etc are held constant.

For a reaction $A+B\rightarrow C$

The general rate law would be: $\text{Rate} = k[A]^m[B]^n$

Once the variables, k, m and n have been determined experimentally, the specific rate law allows you to predict the rate of a reaction for any combination of concentrations of A and B.

The rate constant, k is a constant that incorporates the variables associated with the state of the system at the time of the experiment. These variables include the temperature of the reactants, any catalysts present increase the speed of the reaction and any other experimental conditions, such as the phase of a reactant or the pressure of any gases in the system. Thus, k will only be constant when all conditions are held constant except for the concentration of the reactants.

The concentrations of the reactants are represented by [A] and [B]. In this experiment, the units used are molarity. Note that the product, C, has no effect on the rate. Once a reactant has been removed from the reaction, any products formed do not affect how fast the remaining reactants will react. The rate being monitored is only that of a reactant disappearing, not the amount of product that has formed.

The exponents, m and n determine the degree to which the concentration affects the reaction rate. For example, if m is 1, doubling the [A] doubles the rate, but if m is 2, the rate would increase by a factor of 4. If m is zero increasing the concentration has no effect on the rate of the reaction. These exponential variables are called **reaction orders** and are found experimentally through a series of experiments called **the method of initial rates.**

Method of Initial Rates

The method of initial rates is a method used to solve for the variables, m, n and k in the rate law equation. The exponents, m and n are found by running a reaction with a standard set of concentrations, and then varying the concentration of 1 of the reactants. A comparison of the rates at the different concentrations results in the ability to calculate the order of reaction for the reactant for which you changed the concentration.

You start by conducting a control experiment wit a set of standard conditions. To determine the orders of reaction for the different reactants, you must perform the same experiment two more times, altering the concentration of one reactant at a time in each experiment. The example below illustrates how to set up an initial rates experiment to determine the rate law equation.

Example of an Initial Rates Problem

Setting up the Experiment for the reaction, A+B→C: *2 reactants, so 3 experiments required.*

Experiment	[A]	[B]	Rate	Analysis
Control	1M	1M	2M/minute	Use this as your comparison experiment
1st exp.	2M	1M	2M/minute	Changing [A] has no effect on rate
2nd exp.	1M	2M	8M/min	Changing [B] significantly affects rate

Determining order of reactants from the general rate law: Rate = k[A]^m[B]^n

From control experiment	$2 = k[1]^m[1]^n$
From 1st experiment	$2 = k[2]^m[1]^n$
From 2nd experiment	$8 = k[1]^m[2]^n$

To solve for m and n, you need to divide one experiment by another to force all but one of the variables to cancel out. You can then solve for the variable that does not cancel.

From control experiment	$\cancel{2} = \cancel{k}[1]^m\cancel{[1]^n}$	Leaves the following equation: $1=[1/2]^m$
From 1st experiment	$\cancel{2} = \cancel{k}[2]^m\cancel{[1]^n}$	m must equal 0 for this equation to be true.

To solve for the other variable, n:

From control experiment	$\cancel{2} = \cancel{k}\cancel{[1]^m}\ [1]^n$	Leaves the following equation: $1/4=[1/2]^n$
From 2nd experiment	$\cancel{8} = \cancel{k}\cancel{[1]^m}\ [2]^n$	n must equal 2 for this equation to be true.

Determining k, the rate constant: k = Rate / [A]^m[B]^n

You have now solved for all variables except for k, so you can choose any of the experiments, plug in the values for the variables and solve for k. k should be the same value regardless of which experiment you choose. The units on k will correspond to the units used for concentration and time.

Experiment	[A]	[B]	Rate	m	n	k
Control	1M	1M	2M/minute	0	2	2/mol-min
1st exp.	2M	1M	2M/minute	0	2	2/mol-min
2nd exp.	1M	2M	8M/min	0	2	2/mol-min

Writing the final Rate Law Equation

Once you have solved for all of the variables, insert them into the rate law equation to give you a specific equation that relates the rate to the concentrations of all of the reactants.

For the example given the rate law equation is Rate = 2/mol-min$[A]^0[B]^2 = 2[B]^2$

Your units for concentration must be in molarity and the units for time in minutes. If you change units, you must change the value of k to match. You must also redo the initial rates if you change any parameters of the experiment, especially the temperature.

Effect of Temperature on Reaction Rate

The value calculated for the rate constant is dependent on the temperature at which the reaction is performed. If the temperature varies, the rate of the reaction and thus the rate constant will also change. In the second part of this experiment, you will run the same permanganate/oxalic acid reaction that was done to determine the initial rates experiment. You will then recalculate k for the experiment run at different temperatures. Since m and n are independent of temperature, they will have the same values as calculated from the initial rates performed in the first part of the experiment. You will then write new rate law equations for the reaction at different temperatures.

Chemical Hazards

Oxalic Acid

NFPA RATING: HEALTH: 0 FLAMMABILITY: 0 REACTIVITY: 0

DERMAL EXPOSURE: Immediately wash skin with soap and water.
EYE EXPOSURE: Flush with copious amounts of water for at least 15 minutes. Assure adequate flushing by separating the eyelids with fingers. Contact your TA immediately.

Potassium Permanganate

NFPA RATING: HEALTH: 1 FLAMMABILITY: 0 REACTIVITY: 3

DERMAL EXPOSURE: Flush with water. Remove contaminated clothing and shoes to avoid further contact with skin. This chemical will permanently stain clothing and will also stain your skin.
EYE EXPOSURE: Flush with copious amounts of water for at least 15 minutes. Assure adequate flushing by separating the eyelids with fingers. Contact your TA immediately.
REACTIVITY: Oxidizing. Dangerous for the environment. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Do not use near sinks.

Chemical Disposal

Used Oxalic Acid and Potassium Permanganate solutions

Dispose of in waste container in the hood. Do not pour near sinks due to chemical toxicity of the potassium permanganate.

Laboratory Equipment Procedures

Using a Hot Plate

The hot plates used in lab have a ceramic top that will heat up very quickly. Unlike a stove burner, these hot plates will not get red as they heat up, thus a hot hot plate looks exactly like a cold hot plate. Please use the following precautions when using a hot plate in lab.

1. Make sure the power cord is not touching the hot plate at any time during use.
2. Keep the hot plate on the lowest setting possible for your experiment.
3. Do not leave your hotplate unattended.
4. Clear glassware should only be used on a hot plate if it contains a liquid or you are carefully monitoring a drying solid.
5. When drying a solid, the hot plate should be on a low setting.
6. Clean up any chemicals that may spill on the hot plate.
7. Many of the hot plates also have a stir setting. Make sure you are using the correct dial before notifying your TA that your hot plate does not work.
8. Turn off and unplug the hot plate before leaving the lab.

Using the MeasureNet System for Temperature Monitoring and Timing

Temperature Probe and Timer

The thermometer probe should already be connected to the MeasureNet system at the start of lab. Follow the instructions below to display the temperature and/or time on the workstation screen.

Starting system:

1. Press **ON**/**OFF** button to turn on the workstation.
2. Press **MAIN MENU** button on workstation to bring up the probe selection screen.
3. Press **F2** to select TEMPERATURE mode.
4. Press **F1** to select TIME VS TEMPERATURE.
5. Follow either or both of the instruction sets below depending on your experiment.
6. Press the **ON**/**OFF** button to turn off the workstation screen when finished.

If timing is needed:

1. Press **SETUP** to change the maximum time parameter.
   Note: Default is 500 seconds (8.3min).
2. Press **F1** to set limits for new acquisition.
3. Press → twice to bring up the xmax (time) parameter.
4. Enter **1800** to record 1800 seconds (30 min) of data.
5. Press **ENTER** to accept the value.
   Note: (This value will be saved and used in all experiments until **SETUP** is repeated.)
6. Press **START** to start the timer when ready.
7. Press **STOP** to stop the timer.
8. Press **DISPLAY** to return to your starting screen.

If temperature is needed:

1. Place the temperature probe in an ice water bath.
2. Press **CALIBRATE** to calibrate the temperature electrode.
3. Press **0** and then **ENTER** to set the temperature to 0°C.
4. When the value is relatively steady, press **ENTER**.
   Note: Temperature will not necessarily read 0°C, just make sure the display is steady. Temperature will record 0°C once **DISPLAY** is pressed.
5. Press **DISPLAY** to display current temperature on screen.

Experimental Procedures

Perform these steps very carefully; you will be graded on the accuracy of your results.
Directions to perform the calculations needed in the data table are given in the calculations section.
Use a separate(s) sheet in your laboratory notebook when writing out the calculations.
Do not show the calculations on the same sheet as the data/results table.
Be sure to have your TA sign all completed calculations and your data page(s) before leaving the lab or you will not receive credit for attending the lab.

Part 1: Preparation

1. Check that you have the following solutions present at your station in dropper bottles.
    a. Oxalic acid
    b. Potassium permanganate
    c. Distilled water
2. Record the concentrations of the oxalic acid and potassium permanganate solutions in your lab notebook.
3. These solutions are the stock solutions that will be used for the remainder of the experiments.
4. Set up a 250 mL beaker nearby to collect the waste solution after each trial.
5. Set up an ice water bath to calibrate the temperature probe. (Ice is near the soda machines)
6. Set up the MeasureNet system to record both time and temperature.
    a. See instructions under previous section: Equipment Procedures.

Part 2: Determining the Effect of Reaction Concentration on Reaction Rate

Decide which lab partner will do the timing and which one will do the mixing.
You will use the following instructions for each trial listed in Table 1.
All volumes are measured in drops, so be careful to make the drop size consistent by dispensing the drops in the same manner each time.

Table 1			
Reactants (in drops)			
	Trial 1	Trial 2	Trial 3
Oxalic acid	6	12	6
Potassium permanganate	1	1	2
Distilled water	7	1	6
Total volume	14	14	14

Instructions:

1. Record the room temperature.
2. Dispense oxalic acid solution into a clean dry 4” test tube.
3. Add water. Swirl to mix.
4. Add potassium permanganate solution to test tube and swirl to mix.
5. Immediately press **START** on the workstation to start timing.
6. Place test tubes in a test tube rack while waiting. The color will change from purple to yellow-brown.

    Note: Swirl test tube occasionally to make a thin layer of solution on the glass so that it is easier to see when the purple color has disappeared and only yellow solution remains. Putting a piece of white paper under the test tube may also help.

7. Stop timing when the last trace of purple disappears.
8. Record the elapsed time in your laboratory notebook.
9. Press **DISPLAY** to prepare workstation for next run.
10. Pour used solution into the waste beaker.
11. Rinse the test tube with distilled water and dry with a paper towel. You do not need to add the rinse water to the waste beaker; it can go into the sink.
12. Repeat these steps until you perform 3 tests in a row with times within 30s of each other.
13. Repeat the procedure for the remaining trials.

Part 3: Determining the Effect of Temperature on Reaction Rate

Preparing a warm water bath:

1. Fill a 250 mL beaker half full of tap water.
2. Heat the beaker on a hot plate until the water temperature is a constant ~10°C above room temperature. Stir the heating water to distribute the heat. Keep the water temperature constant to +/- 2°C by adding ice or increasing the heat while you perform the remaining steps. Your temperature must be constant to record an accurate rate.
3. Record the temperature of the water bath.

Performing Rate Determinations:

Use the following instructions for one trial at approximately 10°C above room temperature and a second trial at approximately 20°C above room temperature. You will then compare the data to the data collected at room temperature.

1. Dispense 6 drops of oxalic acid stock solution into a clean dry 4" test tube.
2. Add 7 drops of water into the same test tube. Swirl to mix.
3. Place this test tube into the warm water bath for approximately 2 minutes.
4. Add 1 drop of potassium permanganate to the diluted oxalic acid in the test tube, swirl and immediately start timing.
5. Press **START** on the workstation to start timing.
6. Immediately return the 4" test tube to the warm water bath.
7. Do not remove the solution from the water bath except to swirl occasionally.
8. Stop timing when the last trace of purple disappears.
9. Record the elapsed time in your laboratory notebook.
10. Press **DISPLAY** to prepare workstation for next run.
11. Pour used solution into the waste beaker.
12. Rinse the test tube with distilled water and dry with a paper towel.
13. Repeat these steps until you perform 3 tests in a row with times within 30s of each other.

Cleanup

1. Empty the contents of the waste beaker into the approved waste container. Remember to replace the cap on the waste bottle when you are finished.
2. Rinse out all test tubes and the waste beaker with soap and water until clean. Be especially careful to clean anything that contained permanganate as the residue can cause permanent stains.
3. Wipe down your lab bench area with a sponge to remove any traces of spilled chemicals.
4. Have your TA sign your data before leaving the lab.

Laboratory Data

Create a table for the following data in your lab notebook before coming to class.
Record the data in your laboratory notebook during lab in pen.
Include the **signed** white copy of this table and the separate pages with your written calculations when you turn in your lab report.
Include the correct number of significant figures for each measurement.

Part 1: Preparing Stock Solutions

Concentration of stock solution of oxalic acid	____________M
Concentration of stock solution of potassium permanganate	____________M
Recorded temperature	____________°C

Part 2: Determining the Effect of Reactant Concentration on Reaction Rate

Make a separate column for each test done (You should have at least 3 tests per trial)

Elapsed time for Trial 1	______s
Elapsed time for Trial 2	______s
Elapsed time for Trial 3	______s

Part 3: Determining the Effect of Temperature on Reaction Rate

Make a separate column for each test done (You should have at least 3 tests per trial)

Elapsed time for rate at room temperature	______s
Recorded temperature at RT	______°C
Elapsed time for rate at RT+10°C	______s
Recorded temperature at RT+10°C	______°C
Elapsed time for rate at RT+20°C	______s
Recorded temperature at RT+20°C	______°C

Results

Create a typed table containing the following information
Include the correct number of significant figures for each value
Include the correct units for each value

Part 2: Determining the Effect of Reaction Concentration on Reaction Rate

Trial Calculations (Create a data column for each of the 3 trials)

Volume oxalic acid	____________	drops
Volume potassium permanganate	____________	drops
Volume of water	____________	drops
Total volume of final solution	____________	drops
Molarity of diluted oxalic acid	____________	M
Molarity of diluted potassium permanganate	____________	M
Average elapsed time	____________	s
Rate of disappearance of potassium permanganate	____________	M/s

Determination of Orders of Reactants

Order of reaction for oxalic acid (m)	____________
Order of reaction for potassium permanganate (n)	____________

Part 3: Determining the Effect of Temperature on Reaction Rate

Molarity of diluted oxalic acid from Part 2, Trial 1	____________	M
Molarity of diluted potassium permanganate from Part 2, Trial 1	____________	M

Room Temperature

Rate of disappearance of potassium permanganate	____________	M/s
Rate constant (k)	____________	M/s
Rate law	__________________________	

Room Temperature +10°C

Rate of disappearance of potassium permanganate	____________	M/s
Rate constant (k)	____________	M/s
Rate law	__________________________	

Room Temperature +20°C

Rate of disappearance of potassium permanganate	____________	M/s
Rate constant (k)	____________	M/s
Rate law	__________________________	

Calculations

Do not include all the calculations for each separate trial, just give one example of each of the calculations shown below. They may be handwritten.
Label each calculation with the section; part 1, part 2, etc. and the title below
Record the value of each calculation in your data table with the correct number of significant digits

Part 2: Determining the Effect of Reaction Concentration on Reaction Rate

Volumes of final solutions

Add the number of drops of water, potassium permanganate and oxalic acid together to get the total volume for the final solution for each trial.

Molarity of diluted solutions

Multiply the concentration of the stock solution by the volume of the stock solution and divide by the total volume of the final solution.

$M_iV_i=M_fV_f$ $\quad\quad$ $M_f = M_iV_i/V_f$

M_i = molarity of stock solution $\quad$ M_f = molarity of diluted solution
V_i = volume of stock solution (drops) $\quad$ V_f = volume of diluted solution (drops)

Average elapsed time

Add the values of the times in second and divide by the total number of tests performed at the same concentrations and temperature.

Rate of disappearance of potassium permanganate

Divide the molarity of the diluted potassium permanganate by the elapsed time in seconds.

Determination of order of reaction for oxalic acid

Use trials 1 and 2 and the method of initial rates given in the introduction to solve for m, the order of reaction for the oxalic acid.

Determination of order of reaction for potassium permanganate

Use trials 1 and 3 and the method of initial rates given in the introduction to solve for n, the order of reaction for the potassium permanganate.

Part 3: Determining the Effect of Temperature on Reaction Rate

Rate of disappearance of potassium permanganate

Divide the molarity of the diluted potassium permanganate by the elapsed time in seconds.

Rate constant, k

Rate = $\mathbf{k}[H_2C_2O_4]^m[MNO_4^-]^n$

m and n: Orders of reaction for oxalic acid and potassium permanganate
$[H_2C_2O_4]$: Concentration of diluted oxalic acid from trial 1
$[MNO_4^-]$: Concentration of diluted potassium permanganate from trial 1
Rate: Rate of disappearance of potassium permanganate from trial 1

Discussion Questions

You must use your data to answer these questions. If the answer you give does not reflect YOUR data and results, you will receive no credit for the question.

1) Compare the reaction rate at the three different temperatures. Divide the rate at room temperature by the rate at 10˚C above room temperature. How much does increasing the temperature affect the rate of the reaction?

2) Use the following equation to calculate the percent error in each elapsed time measurement for each of the tests in part 2 and part 3. You should have an error listed for each elapsed time measured.

$$\%Error = \frac{\left| Elapsed\ Time - Average\ Elapsed\ Time \right|}{Average\ Elapsed\ Time} x100$$

   The bars around the values in the numerator designate that you take the absolute value of the resulting number so that the percent error calculated will always be a positive number. Make a table of your results.

3) Average the percent errors for each elapsed time measurement for a set of trials. You should have 1 average percent error for each trial for a total of 6 calculations. Make a table showing these errors. To be confident of your results, your error should not be greater than 5%. Are any of your errors greater than 5%? If so, describe 2 modifications that you could have made to your lab technique that would have minimized these errors. Be sure to note these errors in your conclusion.

4) Calculate the rate of reaction using the rate law equation you derived for your data at room temperature if you start with an oxalic acid concentration of 0.25M and a potassium permanganate concentration of 0.30M. Include units in your answer.

5) What variable in the rate law equation changes as a result of the changing temperature? If you were to perform your experiment at 100°C above room temperature, would this variable be expected to increase or decrease? Briefly explain your answer.