

Experiment 6A

KINETICS OF THE PERMANGANATE-ISOPROPYL ALCOHOL REACTION

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PURPOSE

Determine the reaction order, rate constant, and half-life of a reaction. The reaction studied will be the oxidation of isopropyl alcohol by the permanganate ion, which can be followed spectrophotometrically due to permanganate's color.

BACKGROUND

Chemical reactions are not as simple as you might guess by looking at their balanced equations. Rather, they proceed by a sequence of so-called **elementary steps**. Those steps comprise the **mechanism** of the reaction.

Chemists want to know reaction mechanisms for two reasons. The first is simple curiosity: inquiring minds like ours want to know what the atoms and molecules are really doing. The second reason is that knowing the mechanism gives us the power to control the reaction.

A **rate law** is a mathematical equation that describes the rate of a reaction. It is the most crucial piece of information needed to deduce the mechanism of a reaction. However, even if the mechanism eludes us, knowing the rate law still permits us to predict, and possibly control, the rate of the reaction.

The most general type of rate law is an equation showing how the rate depends on the concentrations of the chemicals in the reaction. For example,

$$\text{rate} = k[A]^x[B]^y[C]^z \dots \quad (1)$$

where k is the **rate constant**; $[A]$, $[B]$, and $[C]$ are the concentrations of reactants that affect the rate; and, x , y and z are the **reaction orders**. The rate constant k is the rate when all of the concentrations equal 1; it has whatever units are necessary to balance the units in the remainder of the rate law. The order of a reaction tells how sensitive the rate is to concentration. For example, if the concentration of A is doubled, the rate will double if the reaction is first order in A ($x=1$), but will go up by a factor of four if the reaction is second order in A ($x=2$). Non-integer as well as negative reaction orders are also possible.

The other type of rate law describes how the concentration of one of the chemicals depends on time, t . This type is often called an **integrated rate law** because it is derived from the first type by using *integral* calculus. Integrated rate laws do not have a standard mathematical form and the simple, useful ones apply only to the case where a single reactant influences the rate.

$$\text{rate} = k[A]^x \quad (2)$$

For example, when $x=1$, the reaction is first-order in $[A]$. Using calculus, it is possible to derive the integrated rate law

$$\ln \frac{[A]}{[A]_0} = -kt \quad (3a)$$

which is typically re-written as

$$\ln[A] = -kt + \ln[A]_0 \quad (3b)$$

while a reaction second order in $[A]$, $x=2$, obeys the integrated rate law

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad (4)$$

where $[A]_0$ is the initial concentration of A (at $t=0$). Both equations (3b) and (4) have a linear form, $y=mx+b$. Thus, by making the appropriate plots and determining which is linear, the reaction order, rate constant, and $[A]_0$ may be found.

Thus, a plot of $\ln[A]$ vs. t is linear if the reaction is first order and a plot of $1/[A]$ vs. t is linear if the reaction is second order. In either case, the slope of the line yields the rate constant, k . Although for a first order reaction, the sign of the slope must be changed as the slope equals $-k$ (and we know that k always has a positive value).

The rate constant k has the same meaning as before, but, in addition, now can be related to the reaction's half-life. The half-life $t_{1/2}$, defined as the time at which $[A] = [A]_0/2$, can be found simply by substituting $[A] = [A]_0/2$ when $t = t_{1/2}$ into the integrated rate law, and solving for t . For a first order reaction, this yields

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad (5)$$

and for a second order reaction,

$$t_{1/2} = \frac{1}{k[A]_0} \quad (6)$$

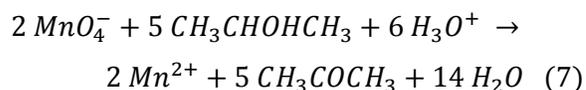
We see that the half-life depends upon $[A]_0$ for a second order reaction. This, too can be easily

obtained from the y-intercept of the relevant graph.

Integrated rate laws are usually handier to use because concentrations and times are what we actually measure and care about, and the work of calculating rates can be avoided. However, they are limited to a few, very simple forms.

IN THIS EXPERIMENT

The oxidation of isopropyl alcohol ($\text{CH}_3\text{CHOHCH}_3$) by permanganate ion (MnO_4^-) will be studied. The reaction is



Notice that the Mn is reduced (oxidation number decreased), and the middle carbon in isopropyl alcohol is oxidized (oxidation number increased) to produce acetone. This oxidizing ability of permanganate has many practical applications, including bleaching, dyeing, water purification, and veterinary antiseptic. Permanganate is commercially available as the potassium salt, KMnO_4 (where K^+ is a spectator ion).

Because of the ion's intense purple color, permanganate reactions are conveniently studied spectrophotometrically. First, we will scan the A vs. λ spectrum to determine the wavelength of maximum absorbance, λ_{max} . From the absorbance at λ_{max} , the molar absorptivity of MnO_4^- will be determined. Next, a kinetic run will be performed by mixing isopropyl alcohol and permanganate solutions, and using a spectrophotometer to monitor permanganate disappearance. Beer's law will be used to convert absorbances to MnO_4^- concentrations. Finally, the data will be analyzed, using integrated rate laws, to determine the reaction order with respect to MnO_4^- and the rate constant. This can be done since, under the reaction conditions used, the reaction's rate depends only on the concentration of MnO_4^- .

PRE-LABORATORY PREPARATION

1. Read the procedure and data analysis sections of the experiment.
 2. Complete the PRELAB assignment in Canvas. Refer to the procedure and data analysis sections of the experiment as needed. The prelab questions for this experiment replicate the questions in the data analysis section.
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EXPERIMENTAL SECTION

REAGENTS PROVIDED

KMnO_4 , $2.00 \times 10^{-3} \text{ M}$.

Sulfuric acid, 1.00 M and 9.0 M.

Isopropyl alcohol, 100%, 60.096 g/mol, 0.782 g/mL at 25°C.

NaF, solid, 41.988 g/mol

Hazardous Chemicals

Concentrated H_2SO_4 is very reactive, as both acid and oxidant. Be very careful not to get it on your person or possessions. Neutralize spills with sodium bicarbonate.

H_2SO_4 . An explosive amount of heat can be generated when concentrated H_2SO_4 is diluted with water. To minimize the violence of the dilution reaction, **always add the acid to the water**, slowly and with stirring. **Never add water to concentrated H_2SO_4** . We have considerably reduced the danger of the H_2SO_4 dilutions in this experiment by having you start with 9 M H_2SO_4 , which is already a 50% dilution of commercial sulfuric acid.

Because concentrated H_2SO_4 is a strong oxidant, it should never be mixed full-strength with a pure organic compound (such as isopropyl alcohol). Always have one or both of the compounds previously diluted with water.

KMnO_4 . The MnO_4^- ion stains everything it touches. Don't spill it.

WASTE DISPOSAL

Waste KMnO_4 , in the small amounts generated in this procedure, and all other wastes from this experiment, may be safely disposed of by washing down the sink.

PROCEDURE

You will do this experiment with a partner.

STANDARD SOLUTION PREPARATION

1. Pour about 20 mL of $2.00 \times 10^{-3} \text{ M}$ KMnO_4 into a small (50- or 100-mL) beaker and pour about 20 mL of 1.00 M H_2SO_4 into a separate small beaker.

There are two different H_2SO_4 concentrations available — be careful to use the proper one.

2. Pipet 5.00 mL of 1.00 M H_2SO_4 and 1.00 mL of the stock $2.00 \times 10^{-3} \text{ M}$ KMnO_4 provided into a clean test tube. Mix thoroughly!

When measuring exactly 5.00 mL, it is better to use the volumetric pipet than the graduated pipet. Also, it is better to have a separate pipet for each solution. If you need to use a pipet with multiple solutions, be sure to rinse it thoroughly.

This solution must be thoroughly mixed! This can easily be accomplished by pouring the solution back and forth between two test tubes (previously cleaned and dried) several times. Visually, the solution should appear uniform after mixing.

3. Calculate the concentration of the permanganate solution you just prepared.

This is Data Analysis question 1(a).

4. Rinse a cuvet with distilled water and then once with the solution prepared in step 2. Finally, fill the cuvet with the remaining solution from the test tube.

DETERMINATION OF λ_{max} AND THE MOLAR ABSORPTIVITY AT λ_{max}

5. Turn on the LabQuest2 by pressing the red power button on the top and connect the cable from the SpectroVis spectrometer to the USB port on the LabQuest2.

The USB port is on the left side of the Lab Quest2 near the top.

6. Calibrate the spectrometer.

- Tap on **Sensors**. Next choose **Calibrate** and then **USB: Spectrometer**.
- Allow the spectrometer to go through the 90 second warm up.
- Insert a blank cuvet, filled with distilled water. The clear sides of the cuvet should be facing in the direction of the ► on the spectrometer.
- Tap **Finish Calibration**. The calibration will finish in a couple of seconds. Then tap **OK**.

7. Insert the sample cuvet, prepared in step 4, into the spectrometer, and tap the Start button. Wait a few seconds for the spectrum to roughly stabilize, then tap the Stop button.

The spectrum should have a peak somewhere close to 530 nm.

8. Record λ_{max} and the absorbance at λ_{max} .

The absorbance at the selected wavelength is displayed in a box on the right side of the graph. **If the selected wavelength is NOT equal to λ_{max} , tap on your A vs. λ curve at its highest point to change the boxed reading to λ_{max} .**

This is very important since the subsequent readings you take will be at this wavelength.

Typically, absorbances are displayed to the nearest 0.001 and should be recorded as such.

9. Calculate the molar absorptivity of MnO₄⁻ at λ_{max} .

This is Data Analysis question 1(b).

10. Title your graph and then print it, as follows:

- Tap **File** from the top menu.
- Tap **Print** and then **Graph**.
- Tap on **Print Graph Title**.
- Enter an appropriate graph title (e.g., Absorbance vs Wavelength).
- Tap **Print**.

11. Tap on the Meter icon.

12. Tap on the Mode box. Choose *Time Based* from the scroll box at the top and change the duration to 300 seconds. Tap *Done*.

13. Tap *OK*. Choose to *Discard* the spectral data.

KINETIC RUN #1

14. Prepare 100.0 mL of a solution which is 0.60 M in isopropyl alcohol, 0.120 M in NaF, and 1.00 M in H₂SO₄. In a 100 mL volumetric flask, mix the g of NaF and the volumes of 9.0 M H₂SO₄ and pure isopropyl alcohol that you calculated in the prelab exercise, in the following order:

- Weigh the calculated amount of NaF onto glassine paper, and carefully transfer it into the volumetric flask.**

The purpose of the F⁻ ion is to form a complex with the Mn²⁺ product, and prevent it from undergoing further complicating reactions.

- Add about 50 mL distilled water to the flask, and swirl to dissolve the NaF.**
- Use a graduated cylinder to slowly add the calculated amount of 9.0 M H₂SO₄, while swirling to mix.**

Be sure you use the correct concentration of H₂SO₄ here. If you don't you will get poor results (and lose points) for both this lab and the next lab.

If the flask begins to get warm, cool it to room temperature by running tap water over the bulb while swirling the contents. Don't get any tap water into the flask!

- d. **Using a 5-mL graduated pipet, add the calculated amount of isopropyl alcohol and swirl to mix.**

Thoroughly rinse this pipet before using it again!

- e. **Fill to the mark with distilled water, cap the flask and invert it several times to mix.**

15. Perform the kinetic run.

Read the following directions carefully before beginning so that you can quickly perform them.

- a. **Clean a cuvet and have it ready to use.**
 b. **Pipet 4.00 mL of the 0.60 M isopropyl alcohol solution you prepared into a (clean, dry) test tube.**
 c. **Pipet 1.00 mL of 2.00×10^{-3} M KMnO_4 and 1.00 mL of 1.0 M H_2SO_4 into a second test tube.**

The solutions in the two test tubes will be mixed below. Notice that, after mixing, this will give the same $[\text{MnO}_4^-]$ used in the spectrum determination.

- d. **Pour the isopropyl alcohol from its test tube into the KMnO_4 test tube. To insure complete mixing, immediately pour the mixture back and forth between the test tubes two more times.**

Be sure to mix quickly and thoroughly!

- e. **Quickly pour half this solution into the cuvet (to rinse it). Empty the cuvet. Pour the remainder of the solution from the test tube into the cuvet, wipe the outside of the cuvet with a Kimwipe and insert it in the spectrometer.**
 f. **Tap on the Start button.**
 g. **While data is being collected, you may wish to tap on the *Graph* menu and choose *Autoscale Once* to better see the graph as data is collected.**

16. After data has been collected for 300 seconds, data collection will end. Remove the cuvet from the spectrometer, empty it, and rinse it out with distilled water.

The absorbance should change by at least 0.100 during the kinetic run. If not, there is a problem. Common issues:

- You did not use the isopropyl alcohol solution that you made.
- You did not make (or mix) the isopropyl alcohol properly.
- You did not set λ_{max} to a wavelength near 535 nm.

KINETIC ANALYSIS

The steps below will allow you to convert the absorbances into concentrations and then plot the data from the kinetic run to determine the reaction order. Comparison of equations 3 and 4 with the equation of a straight line, $y = mx + b$, and substituting $[\text{MnO}_4^-]$ for $[A]$, indicates a plot of $\ln[\text{MnO}_4^-]$ vs. t should be linear if the reaction is first-order, and a plot of $1/[\text{MnO}_4^-]$ vs. t should be linear if the reaction is second-order.

17. Create a column of concentrations from the absorbances.

- a. Begin by tapping on the **Data Table** icon. Then select the **Table** menu, and then **New Calculated Column**.
 b. Enter *conc* for the name and *M* for the units.
 c. For the Equation Type, choose **X/A** from the scroll box. The Column for X should default to the Abs, which is what is desired. In the box for A, enter the calculated value for the molar absorptivity from Data Analysis question 1(b)).
 d. Tap **OK**. The graph should now re-appear with conc on the y-axis.

18. Create a column of *ln conc*.

- a. Tap on the **Data Table** icon, then **Table**, and then **New Calculated Column**.
 b. Enter *ln conc* for the name. Leave the units blank (since logarithms are unitless).
 c. For the Equation Type, scroll down and choose ***A ln(X)*** from the scroll box. The Column for X should be changed to *conc*. The value in the box for A can be left as 1.
 d. Tap **OK**. The graph should re-appear with *ln conc* on the y-axis.

19. Perform linear regression on your data.

By default, all of the points will be used. A smaller range of points can be selected by dragging your finger/stylus across the graph.

Choose **Analyze** then **Curve Fit**. Tap on the name of your data set that appears. Then select **Linear** for the Fit Equation. Record the slope and y-intercept (with units) on your data sheet. Tap **OK** to return to the Graph screen.

20. Print out your graph of *In conc* vs. *time* by tapping on *File*, then *Print*, then *Graph*. Add a title (*In conc* vs *time* for run 1). Then tap *Print*.**21. Create a column of *1/conc*.**

- Tap on the **Data Table** icon, then **Table**, and then **New Calculated Column**.
- Enter *1/conc* for the name. The units should be *1/M*.
- For the equation type, choose **A/X** from the scroll box. The Column for X should be changed to **conc**. The value in the box for A can be left as 1.
- Tap **OK**. The graph should re-appear with *1/conc* on the y-axis.

22. Repeat steps 19-20, to analyze, add a title, and print the graph of $1/[\text{MnO}_4^-]$ vs. *t*.

Save paper. Do NOT print out the data table.

It is a good idea to have an instructor check your graphs to make sure that everything is working before you delete your data during the next kinetic run.

KINETIC RUN #2**23. Repeat steps 15-16 to perform a second kinetic run.**

*When you tap the Start button to collect data, you will need to **Discard** the data from your earlier run – be sure both graphs have been printed and checked before discarding the data.*

The graph displayed will be *1/conc* vs *time*, since that was your most recent choice. At any time, you can tap on the y-axis and change what is plotted on it. If you do so, you will want to choose **Graph**, then **Autoscale Once**, to better see the plot.

Comment: It is good practice to do multiple trials using the same conditions to demonstrate that results are reproducible. Also, it is expected that experimental technique improves with practice. So, sometimes a second run will yield better results.

24. After the second run has ended, tap on the y-axis and change the variable to *In conc*. Then repeat steps 19 and 20.

Be sure to record the slope and y-intercept, include a title indicating that it is for run 2, and print the graph.

25. Change the y-axis to *1/conc* and repeat steps 19 and 20 one final time.

Again, record the slope and intercept and print the appropriately-titled graph.

26. Carefully examine your results for the two kinetic runs.

If they are in good agreement, clean up and move on to the calculations. If they disagree on the order of the reaction, do a third run to break the tie (unless you have a very good reason for believing that one run is superior to the other).

CLEANUP**27. Shutdown the LabQuest2.**

Tap **File**, then **Quit**. Choose to **Discard** the data. Next, tap on the **System** folder and then **Shut Down** and, finally, **OK**.

28. Transfer your 0.60 M isopropyl alcohol solution to a 250 mL plastic bottle, to be saved for the next experiment, Kinetics: Initial Rates. Store this bottle in your drawer.

The F^- in this solution will attack the glass if it is stored in the volumetric flask.

29. Wash and store your glassware. Return everything to where it was at the start of lab. Wash your hands and then complete the data analysis.

HAVE AN INSTRUCTOR CHECK YOUR STATION BEFORE LEAVING.

Name _____

Station Used _____

Instructor/Day/Time _____

Partner _____

Station Checked & Approved _____

DATA SHEET

Record all values to the proper number of significant figures and with appropriate units (when applicable).

MOLAR ABSORPTIVITY DETERMINATION λ_{max} _____Absorbance of KMnO_4 solution at λ_{max} _____**PREPARATION OF ISOPROPYL ALCOHOL SOLUTION**

Record the quantities of NaF , $9.0\text{ M H}_2\text{SO}_4$ and pure isopropyl alcohol actually used to prepare the 100 mL isopropyl alcohol solution. These should be close to the values calculated in the prelab, but they should be recorded to the proper number of significant digits (according to how they were measured out).

Volume of $9.0\text{ M H}_2\text{SO}_4$ used _____

Volume of pure isopropyl alcohol used _____

Mass of NaF used _____**KINETIC RUNS**

Kinetic Run	Graph	Slope	y-intercept
1	$\ln [\text{MnO}_4^-]$ vs. t		
1	$1/[\text{MnO}_4^-]$ vs. t		
2	$\ln [\text{MnO}_4^-]$ vs. t		
2	$1/[\text{MnO}_4^-]$ vs. t		

For each kinetic run, in the table above, circle the label of the graph that is more linear.

Note that extra lines are provided in case you want/need to do a third run.

DATA ANALYSIS

1. (a) Calculate the concentration of the permanganate solution prepared for the molar absorptivity determination. This is a dilution calculation.

$[\text{MnO}_4^-]$ _____

1. (b) Calculate the permanganate's molar absorptivity, ϵ , at the wavelength of maximum absorbance. Use Beer's law ($A = \epsilon bc$) and the MnO_4^- concentration *in your cuvet solution*, as calculated in part (a). Show your calculation below, including the proper units.

molar absorptivity _____

2. Determine the order of the reaction with respect to permanganate. Examine the graphs for all of your kinetic runs. If your runs are in agreement or you have a valid reason to believe that one run is better than the other(s), use that information to determine your answers. Circle your choices below:

(a) The graph of $\ln [\text{MnO}_4^-]$ vs. t or $1/[\text{MnO}_4^-]$ vs. t is more linear.

(b) Therefore, the reaction is **first** or **second** order with respect to permanganate.

3. Based upon your more linear graph, determine the value of the rate constant, k (with proper units). Briefly explain how you obtained this value. If you have no basis for favoring the results of one run over the other, average the results from the linear graph for both runs to determine the rate constant.

$k =$ _____

4. Calculate the half-life, $t_{1/2}$ (with proper units). Show your calculation below:

$t_{1/2} =$ _____

5. State the rate law [which should look like equation (2), not the integrated rate law which looks like equations (3) or (4)] **incorporating the numerical values you determined for the reaction order, x, and k (with proper units)**. Do NOT substitute a numerical value for $[\text{MnO}_4^-]$ (since the rate law should hold for any concentration).

You should turn in five graphs, your data sheet, and your data analysis pages.