Experiment 6B

KINETICS: INITIAL RATES

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PURPOSE

Learn how to measure initial rates. Determine the order of the permanganate-isopropyl alcohol reaction with respect to isopropyl alcohol and hydronium ion, and combine with the results of the previous experiment to determine the complete rate law.

WHEN LAST WE MET

In the previous experiment, the following reaction was studied:

$$2\,MnO_4^- + 5\,CH_3CHOHCH_3 + 6\,H_3O^+ \rightarrow$$
$$2\,Mn^{2+} + 5\,CH_3COCH_3 + 14\,H_2O \quad (1)$$
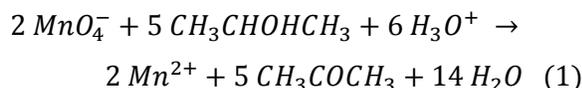
Under the conditions used in that experiment, the reaction rate was alleged to depend *only* on the concentration of MnO_4^-, meaning it obeys the relatively simple rate law,

$$rate = k[A]^x \qquad (2)$$

We saw that such a single-concentration rate law can be expressed as a so-called **integrated rate law:** either, assuming x=1,

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

or, assuming x=2,

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

By determining which of equation (3) or (4) best "fit" experimental [MnO₄⁻] versus t data, we determined k and x, and declared ourselves to have determined the rate law for the reaction. Now, the rest of the story must be told.

In chemistry, as in life, the truth is often more complicated than first supposed. For this reaction, the rate actually depends on the concentrations of all three reactants: isopropyl alcohol, permanganate, and hydronium ion. Therefore, a complete rate law would be

$$rate = k'[MnO_4^-]^x[IP]^y[H_3O^+]^z \quad (5a)$$

where [IP] is the isopropyl alcohol molarity. ("IP" is only a convenient shorthand notation; it is not a proper chemical formula.)

How can both equations 2 and 5a be correct, and why didn't we do it right the first time? Equation 2 is a special case of the more general equation 5a. It is a simplification that applies only under carefully selected conditions, such as those in the previous experiment. We did this partly to keep your introduction to kinetics from being ridiculously confusing, but primarily because we had no choice. The only way complicated rate laws can ever be determined is by evaluating a series of simplified forms.

There are two tricks used to simplify rate laws: the **method of reagents in excess** (or **isolation method)**, which was used silently in the previous experiment, and the **initial rates method**, which will be used openly here.

THE METHOD OF REAGENTS IN EXCESS

Looking back at the concentrations in the previous experiment, we see that both [IP] and [H_3O^+] were about 1000 times greater than the [MnO_4^-]. Therefore, there was not enough MnO_4^- to react with even one percent of the IP or H_3O^+, and the $[IP]^y$ and $[H_3O^+]^z$ factors in equation 5a were very nearly constant. The rate constant k of equation 2 was, in effect, a combination of these "constant" $[IP]^y$ and $[H_3O^+]^z$ factors and k',

$$k = k'[IP]^y[H_3O^+]^z \qquad (6)$$

By this strategy, equation 5a, with the four unknowns k', x, y, and z (hopelessly too many to solve), was simplified to equation 2 with only the two unknowns k and x, which we could evaluate. The simplified equation 2 is often called a **pseudo-xth-order rate law** since it *appears* the reaction is xth order.

In principle, the same ploy could be used to find y, the reaction order with respect to IP. This would require making [MnO_4^-] and [H_3O^+] both large and constant, relative to [IP], and monitoring [IP] as a function of time.

However, IP does not absorb in the visible region of the spectrum (it is colorless), only MnO_4^- is colored. Thus, making the [MnO_4^-] large and constant would mean the absorbance wouldn't change and no useful data would be obtained. Rather than use a different experimental technique, in this case it is simpler to employ another trick from the kineticist's bag.

THE INITIAL RATES METHOD

The initial rates method is another clever way to make the concentration of a reactant effectively constant. The **initial rate** of a reaction is the rate of the reaction at the instant the reactants are first mixed.   The important thing about initial rates is that they correspond to the *initial* concentrations, which, unlike concentrations later on in the reaction, are under our control and *can be kept constant.* So what?

The rate law (eq. 5a), which describes the reaction both initially and at later times, can be re-written to focus on what it predicts initially by using the subscript "$_0$" to indicate initial-value:

$$initial\ rate = k'[MnO_4^-]_0^x[IP]_0^y[H_3O^+]\,_0^z \ \ (5b)$$

Then, if initial rates are measured for different starting concentrations of isopropyl alcohol but *the same* starting concentrations of permanganate and hydronium, the $[MnO_4^-]_0^x$ and $[H_3O^+]_0^z$ factors would be constant. If we set up a ratio of two initial rates expressions, we can see the good thing that happens when these factors are constant:

$$\frac{initial\ rate\ 1}{initial\ rate\ 2} = \frac{k'[MnO_4^-]_{0,1}^x[IP]_{0,1}^y[H_3O^+]\,_{0,1}^z}{k'[MnO_4^-]_{0,2}^x[IP]_{0,2}^y[H_3O^+]\,_{0,2}^z}$$

Everything that is constant can be cancelled and the expression simplifies to

$$\frac{initial\ rate\ 1}{initial\ rate\ 2} = \frac{[IP]_{0,1}^y}{[IP]_{0,2}^y} \qquad (7)$$

Using some basic algebra we realize the right side can be simplified to the ratio of concentrations quantity raised to the yth-power. Then taking the log (or ln – it does not matter) of both sides, it is possible to solve for the exponent (see your lecture textbook or instructor for the details, if necessary).

$$y = \frac{\log\left(\frac{initial\ rate\ 1}{initial\ rate\ 2}\right)}{\log\left(\frac{[IP]_{0,1}}{[IP]_{0,2}}\right)} \qquad (8)$$

We can derive an equation identical to equation (8) for z in terms of the concentration of H_3O^+.

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MEASURING INITIAL RATES

Initial rates are always *estimations*; it is obviously impossible to make measurements from the exact instant a reaction starts. There is always a finite "mixing time" while the chemicals are mixed, the cuvet is inserted, and the absorbance reading settles down. The best we can do is to start taking measurements as soon as it is possible to get reliable readings.

Initial rates, like all reaction rates, are defined as change in concentration (usually molarity, M) per unit time (t, usually in seconds). *If only two data points are available, the initial rate can be calculated using the formulas below:*

$$initial\ rate = \frac{M_2 - M_1}{t_2 - t_1} \qquad (9a)$$

If M is a *reactant* concentration, a negative sign is inserted, giving

$$initial\ rate = -\frac{M_2 - M_1}{t_2 - t_1} \qquad (9b)$$

This ensures a *positive* rate, since M decreases as t increases.

When more data points are available, the initial rate can be determined more accurately from a graph of concentration vs. time:

$$slope = \frac{rise}{run} = \frac{\Delta y}{\Delta x} = \frac{\Delta(concentration)}{\Delta(time)} \quad (10)$$

Since rate is defined as change in concentration per unit time, t**he initial rate approximately equals the slope** (or –slope if the slope is negative) **of the earliest, reasonably-linear section of a concentration-vs.-time plot.**

IN THIS EXPERIMENT

Kinetic runs will be made using different initial concentrations of isopropyl alcohol but the same initial concentrations of permanganate and hydronium ion. As in the last experiment, the reaction will be followed spectrophotometrically. Because initial rates are desired, readings only need to be taken for a relatively short time.

Absorbance readings will be converted to concentrations using Beer's law in order to determine the initial rate for each run. Equation (8) will then be used to determine the order with respect to [IP].

The above procedure will be repeated to determine the order with respect to hydronium ion. Finally, the rate constant for the complete rate law will be calculated.

PRE-LABORATORY PREPARATION

1. Read the procedure and data analysis sections of the experiment.
2. There is no prelab assignment for this experiment.

EXPERIMENTAL SECTION

REAGENTS PROVIDED

Potassium permanganate, 2.00 x 10⁻³ *M* in The MnO_4^- ion stains everything it touches. Do not spill it.
Sulfuric acid, 1.00 *M* and 6.0 *M*.

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.

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WASTE DISPOSAL

The small amounts of $KMnO_4$ waste and all other chemicals used in this experiment may be safely disposed of by washing down the sink.

PROCEDURE

Unless told otherwise, continue with the same partner(s) as for the previous experiment.

SETUP

1.   Turn on the LabQuest2.   Connect and calibrate a SpectroVis spectrometer using a distilled water blank.

Tap on **Sensors**, then **Calibrate,** and then **USB: Spectrometer** and follow the prompts.

2. Pour about 25 mL of 1.00 M H_2SO_4 into a small beaker from which you may pipet.

3.   Pour about 10 mL of 6.0 M H_2SO_4 into a small beaker from which you may pipet.

Label your H_2SO_4 beakers (or use different sizes) so you know which solution is which.

4.   Pour about 20 mL of 2.00×10^{-3} *M* $KMnO_4$ into a small beaker.

5.   If you are using the exact same SpectroVis instrument, you may use the values for λ_{max} and ε, found in question 1(b), from the last experiment.   If so, copy them onto your data sheet and skip to step 6.   Otherwise re-measure them as follows:

a.   Pipet 5.00 mL of 1.00 *M* H_2SO_4 and 1.00 mL of 2.00×10^{-3} *M* $KMnO_4$ into a clean test tube. Mix thoroughly!

b.   Pour this solution into a rinsed cuvet, insert it into the spectrometer, and tap **Start**.   Once the spectrum stabilizes, tap **Stop**.

c.   Record λ_{max} and the absorbance at λ_{max}. (Tap on the A vs. λ curve at its highest point to select λ_{max} if your Labquest2 does not select it for you automatically). λ_{max} should be close to 530 nm.

d.   Use the absorbance to calculate the molar absorptivity of MnO_4^-, as in question 1 of the last experiment. Record it on your data sheet.

6.   Set up the spectrometer for kinetic runs.

a.   Tap on the **Meter** icon in the upper left (if you are not already on the Meter screen).

b.   Tap on the **Mode** box.

c.   Choose *Time Based* from the scroll box and change the Duration to *60* seconds.

d.   Tap *OK*. If necessary, choose to *Discard* the spectral data.

7.   If you did NOT remeasure the molar absorptivity (in step 5), you need to specify the wavelength for the LabQuest2 to monitor.

To do this, tap on the large red meter box (which shows the measured absorbance), select *Change Wavelength*, and enter the numerical value of λ_{max} found in the last experiment.

KINETIC RUNS

8.   Perform kinetic run #1, using the amounts found in Table I (see next page), as follows:

a.   Clean a cuvet and have it ready to use.

b.   Pipet the indicated volumes of 0.60 *M* isopropyl alcohol (saved from the previous experiment) and of 1 *M* H_2SO_4 into a clean, dry test tube. **Important:** *Each pipet should only be used with a single solution. If not, rinse them thoroughly!*

c.   Pipet 1.00 mL of 2.00×10^{-3} *M* $KMnO_4$ from the beaker into a <u>separate</u> small test tube.

d.   Pour the IP test tube into the $KMnO_4$ test tube and then pour the mixture back-and-forth two or three more times to completely mix.

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 with a Kimwipe and insert it into the SpectroVis.

f.   Tap the **Start** button. If asked, choose to *Discard* the data from the previous run.

9. Data collection will end after data has been collected for 60 seconds. Remove the cuvet, empty it, and rinse it with distilled water.

10. Determine the initial rate as follows:

a. After run #1 (only), create a column of concentrations in the data table:

  i. Select the **Data Table** icon. Then select **Table**, and then **New Calculated Column**.

  ii. Enter *conc* for the name and *M* for the units.

  iii. 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 <u>molar absorptivity</u>.

  iv. Tap **OK**. The graph should now re-appear with *conc* on the y-axis.

  This column will remain in the data table for all subsequent runs (#2-#6).

b. Inspect the plot of conc vs time for bad points. If there are some early-time data points that are not linear (typically, due to incomplete mixing), drag your finger/stylus over the *linear region of the graph* to select it.

c. Tap on **Analyze**, then **Curve Fit**, then on the data set name (**conc**) when it appears. Select **Linear** for the Fit Equation. The magnitude of the slope equals the initial rate. <u>Record this value</u> (recalling rates are always given as positive quantities). Finally, tap **OK**.

d. Print the graph <u>for run 1 (only)</u> by tapping **File**, then **Print**, then **Graph**. Add a title (*conc vs time for run 1*). Then tap **Print**. If you forget to print the graph for the first run, print it for a different run instead.

e. Have an instructor check your graph for run #1 to make sure everything is correct before continuing.

11. Repeat steps 8-10 for each of run mixtures 2-6, as described in Table I.

  Note that you need to add both 1.0 M and 6.0 *M* H_2SO_4 for runs 5 & 6. Add the 6.0 M H_2SO_4 to the same test tube with the IP and the 1.00 M H_2SO_4 in step 8b.

  Do NOT print the graphs for runs 2-6.

  You can *Discard* the data after each run, once you have recorded the initial rate.

12. Shutdown the LabQuest2.

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

13. You can discard the IP solution and your other waste solutions down the drain (followed by running some water). Wash your glassware and your hands.

RETURN EVERYTHING TO WHERE IT WAS AT THE START OF LAB. HAVE AN INSTRUCTOR CHECK YOUR STATION BEFORE LEAVING.

TABLE I. Composition of reaction mixtures.

Run #	mL of 2.00 x 10^{-3} M KMnO$_4$	mL of 0.60 M IP in 1.00 M H$_2$SO$_4$	mL of 1.00 M H$_2$SO$_4$	mL of 6.0 M H$_2$SO$_4$
1 & 2	1.00	4.00	1.00	0
3 & 4	1.00	2.00	3.00	0
5 & 6	1.00	2.00	2.00	1.00

Two identical runs will be done for each set of initial concentrations. If reproducible results are obtained, this gives confidence that everything is being done properly. If two runs using the same concentrations yield very different results, you may want to do a third run. It is a good idea to do all 6 prescribed runs first, to help you see if the differences between paired runs are significant.

How the volumes were selected in Table I:

It should be obvious that the [IP]$_0$ in runs 1&2 is double what it is in runs 3-6. It is less obvious that the acid concentration in runs 5&6 is double that in runs 1-4. The relevant dilution calculations are shown below. Note that the total volume for each run is 6.00 mL and that the IP solution was made in 1.00 M H_2SO_4 (so the total volume of 1.00 M H_2SO_4 is the sum of the two middle columns).

Runs 1-4:
$$[H_2SO_4]_0 = \frac{(5.00\ mL)(1.00\ M)}{6.00\ mL} = 0.833\ M$$

Runs 5-6:
$$[H_2SO_4]_0 = \frac{(4.00\ mL)(1.00\ M) + (1.00\ mL)(6.0\ M)}{6.00\ mL}$$
$$= 1.67\ M$$

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Name _____   Station Used _____   Instructor/Day/Time _____

Partner _____   Station Checked & Approved _____

DATA SHEET

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

DATA FROM LAST EXPERIMENT   <u>OR</u>   MEASURED RESULTS

λ_{max} _____ λ_{max} _____

A at λ_{max} _____

Molar absorptivity _____   Molar absorptivity _____

DATA FROM KINETIC RUNS

TABLE II. Initial rate data.

run #	$rate_0$	Average $rate_0$
1		
2		
3		
4		
5		
6		

For each pair of good runs, calculate the average initial rate. If you only have one good run, fill in that value for the average initial rate. If any results don't seem to make sense, you might want to get an instructor's opinion or run an additional trial before discarding your solutions.

DATA ANALYSIS

1. Calculate $[KMnO_4]_0$ for kinetic run #1. This is a dilution calculation. See the volumes used in Table I in the procedure section. Show your calculation.

$[KMnO_4]_0$ for kinetic run #1 = _____

2. Calculate $[IP]_0$ for kinetic runs #1 and #3. Again, these are dilution calculations, see Table I for volume and concentration data. Show your sample calculation for run #1.

$[IP]_0$ for kinetic run #1 = _____

$[IP]_0$ for kinetic run #3 = _____

3. Complete the Initial Rates Table below using your calculated concentrations (above), the initial H_2SO_4 concentrations calculated for you below Table I, and your average initial rates from Table II.

Run #	$[KMnO_4]_0$ (M)	$[IP]_0$ (M)	$[H_2SO_4]_0$ (M)	Average Initial Rate (M/s)
1 & 2				
3 & 4				
5 & 6				

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4. Using the results tabulated in question 3, determine the order of the reaction with respect to IP.
Use equation (8) and the data from the two rows of the table where $[KMnO_4]_0$ and $[H_2SO_4]_0$ are constant, but $[IP]_0$ varies. Show your work below. *Round to the <u>nearest integer</u>.*

y (order with respect to IP, rounded to the nearest integer) = _____

5. Using the results tabulated in question 3, determine the order of the reaction with respect to H_3O^+. Note that the ratio of $[H_3O^+]$ is roughly equal to the ratio of $[H_2SO_4]$. Use equation (8) and the data from the two rows of the table where $[KMnO_4]_0$ and $[IP]_0$ are constant, but $[H_2SO_4]_0$ varies. Show your work below. *Round to the <u>nearest half-integer</u>.*

z (order with respect to H_3O^+, rounded to the nearest half-integer) = _____

6. Calculate k', the rate constant for the complete rate law, using your data for runs 3 & 4. These are the slowest runs and usually yield the best results. Show your calculations below, *including the units.*
    Solve equation 5(b) using the data from your Initial Rates Table (Data Analysis Question 3), except use $[H_3O^+]_0 = 0.85$ M (which can be obtained via a nontrivial polyprotic acid calculation), and the reaction orders, x (from last experiment), y and z (as rounded above). Note $[MnO_4^-] = [KMnO_4]$.

k' = _____

TURN IN your Data Sheet & Data Analysis pages and a printout of your concentration vs time graph for run #1.

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