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:

\[
2 \text{MnO}_4^- + 5 \text{CH}_3\text{CHOHCH}_3 + 6 \text{H}_3\text{O}^+ \rightarrow 2 \text{Mn}^{2+} + 5 \text{CH}_3\text{COCH}_3 + 14 \text{H}_2\text{O} \tag{1}
\]

Under the conditions used in that experiment, the reaction rate was alleged to depend only on the concentration of \(\text{MnO}_4^-\), meaning it obeys the relatively simple rate law,

\[
\text{rate} = k[A]^x \tag{2}
\]

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

\[
\ln[A] = -kt + \ln[A]_0 \tag{3}
\]

or, assuming \(x=2\),

\[
\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{4}
\]

By determining which of equation (3) or (4) best "fit" experimental \([\text{MnO}_4^-]\) 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

\[
\text{rate} = k'[\text{MnO}_4^-]^x[\text{IP}]^y[\text{H}_3\text{O}^+]^z \tag{5a}
\]

where \([\text{IP}]\) 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 [H₃O⁺] were about 1000 times greater than the [MnO₄²⁻]. Therefore, there was not enough MnO₄²⁻ to react with even one percent of the IP or H₃O⁺, and the [IP]ᵢ and [H₃O⁺]ᵢ² factors in equation 5a were very nearly constant. The rate constant k of equation 2 was, in effect, a combination of these "constant" [IP]ᵢ and [H₃O⁺]ᵢ² factors and k',

$$k = k' [IP]^{y} [H_3O^+]^z$$  \hspace{1cm} (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 [MnO₄²⁻] and [H₃O⁺] 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 MnO₄²⁻ is colored. Thus, making the [MnO₄²⁻] 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 use 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:

$$\text{initial rate} = k' [MnO_4^{-}]^x_0 [IP]^{y}_0 [H_3O^+]^z_0$$  \hspace{1cm} (5b)

Then, if initial rates are measured for different starting concentrations of isopropyl alcohol but the same starting concentrations of permanganate and hydronium, the [MnO₄²⁻]₀⁰ and [H₃O⁺]₀² 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:

$$\frac{\text{initial rate } 1}{\text{initial rate } 2} = \frac{k' [MnO_4^{-}]^x_0 [IP]^{y}_0 [H_3O^+]^z_0}{k' [MnO_4^{-}]^x_0 [IP]^{y}_0 [H_3O^+]^z_0}$$

$$\frac{\text{initial rate } 1}{\text{initial rate } 2} = \frac{[IP]^{y}_0}{[IP]^{y}_0}$$

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

$$\frac{\text{initial rate } 1}{\text{initial rate } 2} = \frac{[IP]^{y}_0}{[IP]^{y}_0}$$  \hspace{1cm} (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).

$$y = \log \left( \frac{\text{initial rate } 1}{\text{initial rate } 2} \right)$$  \hspace{1cm} (8)

We can derive an equation identical to equation (8) for z in terms of the concentration of H₃O⁺.
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:

\[
\text{initial rate} = \frac{M_2 - M_1}{t_2 - t_1} \quad (9a)
\]

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

\[
\text{initial rate} = -\frac{M_2 - M_1}{t_2 - t_1} \quad (9b)
\]

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:

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

Since rate is defined as change in concentration per unit time, the 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} \text{ M in MnO}_4^- \text{ ion stains everything it touches. Do not spill it.}
Sulfuric acid, 1.00 \text{ 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.
WASTE DISPOSAL

The small amounts of KMnO₄ waste generated and all of the 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. Attach the SpectroVis spectrophotometer, start LoggerPro, and calibrate as follows:
   (a) Click on Experiment, then Calibrate…, then Spectrometer: 1.
   (b) Allow the spectrometer to warm up.
   (c) Insert the blank cuvet, containing distilled water.
   (d) Click on Finish Calibration, then click OK.
2. Pour about 25 mL of 1.00 M H₂SO₄ into a small beaker from which you may pipet.
3. Pour about 10 mL of 6.0 M H₂SO₄ into a small beaker from which you may pipet.
   Label your beakers (or use different sizes) so you know which solution is which.
4. Pour about 20 mL of 2.00x10⁻³ M KMnO₄ into a small beaker.
5. You may use the values for λ_max and ε found in the last experiment (if so, copy them onto your data sheet) OR you can remeasure them (the preferred method) as follows:
   (a) Pipet 5.00 mL of 1.00 M H₂SO₄ and 1.00 mL of 2.00x10⁻³ M KMnO₄ into a clean test tube. Mix thoroughly!
   (b) Pour this solution into a cuvet, insert it into the spectrometer, and click on Collect. Wait a few seconds for the spectrum to stabilize, then click on Stop.
   (c) Record λ_max on your data sheet. Use the absorbance at λ_max to calculate the molar absorptivity of MnO₄⁻ (as done in the previous experiment) and record it, as well.
6. Click on the Configure Spectrometer icon and then on Abs vs. Time and select λ_max.
   This changes the data collection mode so that a single wavelength can be selected. If you just remeasured λ_max then the proper wavelength should already be selected. Otherwise, click on the value of λ_max found in the last experiment.
7. Choose Experiment then Data Collection… and change the length from 200 to 60 seconds. Then click on Done.

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 1 M H₂SO₄ 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 2.00x10⁻³ M KMnO₄ from the beaker into a separate small test tube.
   (d) Pour the IP test tube into the KMnO₄ test tube. Immediately pour the mixture back and forth between the test tubes, at least two more times to insure complete mixing.
   (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 into the spectrophotometer.
   (f) Click on the Collect button in the upper right of the screen to begin data collection.
9. After data has been collected for 60 seconds, data collection will end. Remove the cuvet, empty it, and rinse it with distilled water.
10. Determine the initial rate as follows:
   (a) Create a column of concentrations from the absorbances as follows:
      i. Select Data — New Calculated Column.
      ii. Long Name: Conc. Units: M. Equation: "Abs"/ε (where Abs is the heading of
          the column containing the absorbances and ε is the calculated value for the
          molar absorptivity from the last experiment, which should be recorded
          on your data sheet).
      iii. Under the Options tab change to display 3 significant figures
      iv. Change the graph’s y-axis to display the new Conc column you just created.
   (b) Inspect the plot of Conc versus time for wild points or other signs that the experiment
       obviously did not work. If there are some early-time data points that are not linear
       (typically, because the system was not completely mixed prior to data collection),
       click-and-drag to only select the linear region of the graph.
   (c) Click on the linear regression icon (R=) to obtain the initial rate (-slope). Record the
       value of the initial rate on your Data Sheet (recall rates are always given as positive
       quantities).
   (d) Print the graph for run #1 (only). Be sure everything is labeled appropriately (with
       units). Include the run number as part of the title. (If you forget to print the graph for
       the first run, it is okay to print it for a different run instead.)

11. Repeat steps 8-10 for each run mixture described in Table I until all 6 runs are complete.
    Note that you need to add both 1.0 M and 6.0 M H₂SO₄ for runs 5 & 6.
    Do NOT print the graphs for runs 2-6 (to save time and paper).
    In runs 5-6, add the 6.0 M H₂SO₄ to the test tube with the IP and the 1.00 M H₂SO₄ in step
     8(b).

12. Wash and store your glassware. Wash your hands and then complete the data analysis.

TABLE I. Composition of reaction mixtures.

<table>
<thead>
<tr>
<th>Run #</th>
<th>mL 2.00 x 10⁻³ M KMnO₄</th>
<th>mL 0.60 M IP in 1.00 M H₂SO₄</th>
<th>mL 1.00 M H₂SO₄</th>
<th>mL 6.0 M H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 &amp; 2</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>3 &amp; 4</td>
<td>1.00</td>
<td>2.00</td>
<td>3.00</td>
<td>0</td>
</tr>
<tr>
<td>5 &amp; 6</td>
<td>1.00</td>
<td>2.00</td>
<td>2.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Two identical runs will be done for each set of initial concentrations. If the results are
reproducible, 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
under those conditions. It is a good idea to do all 6 prescribed runs first, so that you can see if
the differences between paired runs are significant or not.

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. What is less
obvious is that the acid concentration in runs 5&6 is double that in runs 1-4. The dilution
calculations demonstrating this are shown below. Note that the total volume for each run is
6.00 mL and recall that the IP solution was also made in 1.00 M H₂SO₄ (so the total volume of
1.00 M H₂SO₄ is the sum of the volumes of the two middle columns).

Runs 1-4:

\[ [H₂SO₄]₀ = \frac{(5.00 \text{ mL})(1.00 \text{ M})}{6.00 \text{ mL}} = 0.833 \text{ M} \]

Runs 5-6:

\[ [H₂SO₄]₀ = \frac{(4.00 \text{ mL})(1.00 \text{ M}) + (1.00 \text{ mL})(6.0 \text{ M})}{6.00 \text{ mL}} = 1.67 \text{ M} \]
DATA SHEET

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

DATA FROM PREVIOUS EXPERIMENT

Molar absorptivity ____________________

Wavelength of maximum absorbance ____________________

DATA FROM KINETIC RUNS

TABLE II. Initial rate data.

<table>
<thead>
<tr>
<th>run #</th>
<th>rate_0</th>
<th>Average rate_0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
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<tr>
<td>3</td>
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<td>4</td>
<td></td>
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<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 [KMnO₄]₀ for kinetic run #1. This is a dilution calculation. See the volumes used in Table I in the procedure section. Show your calculation.

\[
\text{[KMnO}_4\text{]}_0 \text{ for kinetic run #1} = \underline{\quad} 
\]

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.

\[
\text{[IP]}_0 \text{ for kinetic run #1} = \underline{\quad} 
\]
\[
\text{[IP]}_0 \text{ for kinetic run #3} = \underline{\quad} 
\]

3. Complete the Initial Rates Table below using your calculated values above, the initial concentrations calculated for you below Table I, and your experimental initial rates.

<table>
<thead>
<tr>
<th>Run #</th>
<th>[KMnO₄]₀ (M)</th>
<th>[IP]₀ (M)</th>
<th>[H₂SO₄]₀ (M)</th>
<th>Average Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 &amp; 2</td>
<td></td>
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<tr>
<td>3 &amp; 4</td>
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</tr>
<tr>
<td>5 &amp; 6</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
4. Using the average initial rates results from your data table, determine the order of the reaction with respect to IP. Use equation (8) and show your work below. Round to the nearest integer.

\[ y (\text{order with respect to IP, rounded to the nearest integer}) = \_] 

5. Using the average initial rates results from your data table, determine the order of the reaction with respect to H$_3$O$^+$. Note that the ratio of [H$_3$O$^+$] is roughly equal to the ratio of [H$_2$SO$_4$]. Use equation (8) and show your work below. Round to the nearest half-integer.

\[ z (\text{order with respect to H}_3\text{O}^+, \text{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$_3$O$^+$]$_0 = 0.85$ 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.