Q: What is Kinetics?

Kinetics is the study of rates of reaction, i.e., the study of the factors that control how quickly a reaction occurs. Therefore the primary data that are collected in kinetics experiments are these rates of reaction, and how they depend on concentrations of reactants, concentrations of catalysts, and the temperature.

Q: What reaction are we going to study?

We’re going to study the iodine clock reaction, which is described in detail in your manual. The key reaction is

\[ S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2 \]

In the presence of starch, the iodine reacts to form a blue-black complex. Why doesn’t the solution immediately turn black when the \( S_2O_8^{2-} \) reacts? Because we also include some \( S_2O_3^{2-} \), which reacts to reconvert the \( I_2 \) back to \( I^- \).

\[ 2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-} \]

When we use up our \( S_2O_3^{2-} \), the solution turns black. At that point, we will have used up an amount of \( S_2O_8^{2-} \) equal to \( \frac{1}{2} \) of the \( S_2O_3^{2-} \). We will measure the time it takes to consume a fixed amount of the \( S_2O_8^{2-} \), which will be \( 7.70 \times 10^{-4} \) M for all runs.

Q: How are rates of reaction defined?

When following the concentration of a reactant, these are defined as the negative of the change in concentration divided by the time elapsed, i.e.

\[ \text{rate} = -\frac{\Delta}{\Delta t} . \]

To simplify your calculations in this experiment, the change in concentration of \( S_2O_8^{2-} \) for all runs is the same, \( -7.70 \times 10^{-4} \) M. The elapsed time in this experiment will be the amount of time that elapses between the mixing of your reagents, and the first sign of a color change from clear to black in your reaction mixture.

Q: How does a reaction rate depend on concentration?

The dependence of a rate on concentration is given by a so called rate law. A rate law simply says that the rate can be expressed as a function of the concentrations of
reactants. These equations can sometimes be complicated, but many reactions have a rate equation with a simple form:

\[ \text{rate} = k[A]^x \cdot B^y \cdot C^z. \]

In this equation, A, B, and C are either reactants or catalysts; x, y, and z are exponents, which are typically not related to the stoichiometric coefficients. The exponents are called either partial orders. k is called the rate constant. The rate constant is independent of concentration but depends on temperature.

For parts A, B and C of the experiment, the rate equation you’ll be trying to determine will be

\[ \text{rate} = k[I^-]^x [S_2O_8^{2-}]^y. \]

Your job will be to determine the exponents x and y and the constant k from your data.

In part D, the rate equation will be slightly different:

\[ \text{rate} = k[I^-]^x [S_2O_8^{2-}]^y [Cu^{2+}]^z. \]

Note that in this equation, the exponents x and y are not necessarily the same as the ones for runs A, B, and C, because a catalyst speeds up a reaction by creating a new reaction mechanism. However, in this section we only wish you to determine the new exponent z for the concentration of Cu^{2+}.

Q: How do we determine the exponents?

In order to do this you need to compare runs in which all variables but one are held constant. So in this experiment, to determine the order with respect to I\(^-\), you would need to do experiments in which both temperature and the concentration of S\(_2\)O\(_8\)\(^{2-}\) were held constant. The best way to determine the order once these data are collected is to use Excel. Note that if we take the ln of our rate equation for parts a, b, and c, we get

\[ \ln \text{rate} = \ln k + x \ln [I^-] + y \ln [S_2O_8^{2-}]. \]

For experiments in which the concentration of S\(_2\)O\(_8\)\(^{2-}\) is constant, this becomes

\[ \ln \text{rate} = \text{constant} + x \ln [I^-] \]
Thus if you make a graph with the ln of the rate on the y axis, and the ln of the concentration of the iodide on the x-axis, the slope of the trendline will be your order, x.

A similar graph for experiments in which everything but the concentration of S$\textsubscript{2}$O$\textsubscript{8}$$^{2-}$ is held constant will yield the order y.

For this experiment you should probably round your slopes to either the nearest integer or the nearest half integer, i.e. for this experiment orders will most typically be 0.5, 1, 1.5, 2, 2.5, and so on.

Determination of the order with respect to the catalyst Cu$^{2+}$ is carried out in a similar manner.

This is VERY important. NOTE that in these graphs, the intercept of the trendline is NOT the ln of k. That can only be determined once all of the orders are known.

Q: How do we determine the rate constant k?

Once we determine the value of the exponents x, y (and for the runs in Part D, z), we rearrange our rate law to solve for k:

\[
k = \frac{\text{rate}}{[I^-]^x [S_2O_8^{2-}]^y}
\]

for parts A, B, and C or

\[
k = \frac{\text{rate}}{[I^-]^x [S_2O_8^{2-}]^y [Cu^{2+}]^z}
\]

for part D.

Q: How does a reaction rate depend on temperature?

All of the temperature dependence of the reaction rate is contained in the rate constant k. The dependence of k on temperature is given by the Arrhenius Law,

\[
k = Ae^{\frac{-E_a}{RT}}
\]

Note that in this equation, the temperature must be in Kelvin units. If we take the natural log of both sides, we get:

\[
\ln k = \ln A - \frac{E_a}{RT}
\]
Thus a plot with ln k on the y axis and 1/T on the x axis will have a slope equal to –Eₐ/R and an intercept equal to ln A. Therefore the best way to determine Eₐ and A is to do the following:

- Determine your values of k for all of the runs in Part C.
- Make a plot using excel of ln k (y-axis) vs 1/T (x-axis)
- Create a trendline for your plot of ln k vs 1/T. The slope will be equal to -Eₐ/R and the intercept will equal ln A.
- Determine your Eₐ by multiplying your slope by –R. Note that your R value should be 8.314 J K⁻¹mol⁻¹, and that your units for R will be Joules.
- Determine your preexponential factor A, by taking the antilog of your intercept, e^intercept.

Q: Do you have any tips for us?

Sure!

- You’ll be working in groups of 4 (or 5) today. Each group will be doing half of the runs in the experiment. One half of the group will be doing runs 1, 2, 3, and 7 and the other half runs 4, 5, 6, 8, 9. Both halves of the group will come together to do runs 10 and 11. You’ll pool the data so that everyone has all 14 runs to use in your data analysis and lab report.
- We want to make sure that everyone has good data to work with. To ensure this, we’ll set up a big table on the whiteboard with all the runs listed. As you complete a run, write down the time it took for the black color to appear on the whiteboard. If your result doesn’t agree with the others, then you should redo that run.
- Whenever you reuse one of your flasks or beakers, make sure that you rinse it carefully with deionized (RA) water. Contamination between runs seems to be the primary source of poor data in this experiment.
- The temperatures in part B are approximate. It is more important that you exactly record the temperature than that you have increments of exactly 10 degrees. Make sure that you heat or cool the contents of the two flasks before you combine them.
- In Part C, make sure that you don’t use any EDTA
- Remember that you should dispense your solutions directly from the burets into the beakers you’ll be using for each run.

Q: What do we need to do for the lab report?

The lab report is described in detail on page 126-128 of the manual.

Q: What are we allowed to collaborate on and what must we do independently?

You can collaborate only on the experimental procedure and the table of data. All other work must be done individually.