Chemistry 141 Laboratory
Lab Lecture Notes for Kinetics Lab
Dr Abrash

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 the way that the concentrations of reactants and products change with time, and how this 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 dissociation of ferroin. Ferroin is the orange compound we made in our first lab to determine the concentration of iron in our unknowns. In this case we're going to start with a ferroin solution, and add acid, which separates the iron (II) cation from the three phenanthrene molecules that bind it. The reaction can be symbolized by the equation

$$Fe(phen)_3^{2+} + 3H_3O^+(aq) \rightarrow Fe^{2+}(aq) + 3phenH^+(aq) + 3H_2O(l)$$

In this equation phen stands for the phenanthrene molecule which is drawn in your lab manual.

How do we determine the concentration of the ferroin?

We use the same approach that we did in the first experiment. Remember that an aqueous solution of Fe^{+2} is colorless, while the Ferroin is a deep orange. As the ferroin is dissociated by the acid, the color will gradually fade away.

Gradually fade away seems a bit qualitative. Is there any way to be more precise about this?

Yes. We can use the same type of spectrophotometer that you used in the first experiment. As the color fades, the absorbance of the sample decreases.

But how does that help us determine the concentration of the ferroin?

Beer's law, which we used in the first experiment, connects concentration with absorbance, with the equation,

$$A = \varepsilon bc,$$

where A is the absorbance, b is the path length (1.0 cm in this experiment) and c is the concentration of the substance. So when you're following absorbance as a function of time, you're also following concentration as a function of time.

How does this help us understand how the rate of reaction depends on concentration?

We need to determine a rate law, a function that tells us first, how the rate of reaction depends on the concentrations of the reactants and catalysts, and later, how the concentration of the reactants and products change with time.

Q: O.K., but what's a rate of reaction?

It's defined slightly differently for a reactant and a product. When following the concentration of a reactant, it is defined as the negative of the change in concentration divided by the time elapsed, i.e.

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

In this experiment we'll be following the concentration of the product.

Q: How does a reaction rate depend on concentration?

The dependence of a rate on concentration is given by a differential rate law. A differential 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:

$$rate = k[A]^x [B]^y [C]^z.$$

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.

What are our reactants today?

In today's experiment, you'll have two reactants, the ferroin and hydronium ion, H_3O^+, which we obtain from sulfuric acid. Our job is simplified because the rate of our reaction does not depend on the hydronium ion concentration. Therefore the form of our rate law is particularly simple:

$$rate = k[\,ferroin\,]^x.$$

Our job in the first part of the experiment is to determine the value of k, the rate constant, and of x, the order of the reaction.

Q: How do we determine the order?

In this experiment, we determine an integrated rate law for various orders, and compare the equation we obtain with our measurements of absorbance versus time.

How do we determine the integrated rate law?

We use calculus to integrate our differential rate law for various orders. Your book goes into the details of this, but for this lab I'm just going to show you the results.

What do we get if x is zero?

If our reaction is zero order, i.e, if x is zero in our differential rate law, then our differential rate law is

$$rate = -k[ferroin]^0 = -k$$

And our integrated rate law is

$$[ferroin]_t - [ferroin]_0 = -kt$$

What do we get if x is one?

If x is one in our differential rate law, the reaction is called first order. Our differential rate law is

$$rate = -k[ferroin]^1$$

and our integral rate law is

$$\ln[ferroin]_t - \ln[ferroin]_0 = -kt$$

What do we get if x is two?

If x is two in our differential rate law, the reaction is called second order. Our differential rate law is

$$rate = -k[ferroin]^2$$

and our integrated rate law is

$$\frac{1}{[ferroin]_t} - \frac{1}{[ferroin]_0} = kt$$

How do we tell which of the integrated rate equations describes our results?

You collect data for absorbance vs time, and then make three different graphs. One will be absorbance (y axis) vs. time for zeroth order, the second will be ln absorbance (y-axis) vs. time for first order, and the third will be 1/absorbance (axis) vs. time for second order. Then you see which plot gives you the straightest line. The plot with the straightest line tells you the order, and therefore the proper rate equation.

How will we tell which line is the straightest if they all look sort of the same?

You'll choose the one with the highest value of r^2 from your linear regression.

Q: How do we determine the rate constant k?

You determine it based on your slope. If the reaction is zeroth order, then your slope will be $-kb\varepsilon$. If the reaction is first order, then your slope will be $-k$. Finally if your reaction is second order, then your slope will be $\frac{k}{\varepsilon b}$.

Q: How do we determine ε?

All you have to do is to take the absorbance of a sample with known concentration. Since you know the concentration of ferroin in your ferroin stock solution, you can take it's absorbance and then use Beer's law to get

$$\varepsilon = \frac{A}{bc}$$

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 –E_a/R and an intercept equal to ln A. Therefore the best way to determine E_a and A is to do the following:

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

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

The lab report is described in detail on page 98-99 of the manual.

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

You can collaborate with your lab partner on the entire lab report. Only one lab report needs to be turned in for each pair of partners.