

Chemical Kinetics

Special mention goes to Ms. Rebecca Mack who single-handedly developed this experiment so that you could have a better understanding of kinetics.

Introduction

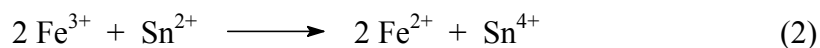
Chemical kinetics is the area of chemistry concerned with the speeds, or rates at which reactions occur. There are essentially three variables that affect the rate of a chemical reaction. These variables are the concentration of the reactants, the presence of a catalyst and temperature. Usually, the more concentrated the solutions of one or more of the reactants, the faster the reaction will proceed. A catalyst increases the rate of a reaction without being consumed in the reaction itself. As the temperature increases, the rate of the reaction usually increases.

The dependence of reaction rate on concentration is given by the rate law:

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

The symbol k is the rate constant for the reaction, $[]$ is the concentration of each reactant (in moles/liter), and x , y and z are the orders of reactant A, B and C, respectively. The rate law must be determined experimentally. It cannot be determined by looking at a balanced chemical equation. Temperature is usually held constant during a kinetic experiment because it does play a role in the rate.

In this experiment, you will be studying the concentration dependence on the rate of:



Because iron(III) precipitates out of solution unless in an acidic environment, all of the iron solutions are prepared in acidic solution. The tin(II) solutions are prepared the same way for the same reasons as iron. The concentration of acid also has an effect on the rate of this reaction, but will be held constant in this experiment. Iron(III) has a yellow color and iron(II) is colorless. In this experiment, you will add some thiocyanate (SCN^-) ion to form the intensely red colored FeSCN^{2+} ion from Fe^{3+} . Fe^{2+} does not combine with SCN^- , so the reaction mixture will go from red to colorless. The reaction, then is:



The intensity of the red allows you to follow the reaction over a longer period of time. You will monitor the reaction between iron(III) and tin(II) by observing the change in color of iron(III) to iron(II) using a spectrophotometer (Spectronic 20). As you know from last week's laboratory experiment, spectrophotometers do not measure concentration but instead measure absorbance. However, you also know from last weeks lab studying Beer's Law that concentration and absorbance are directly related. The reaction rate is a measure of how quickly a reactant is consumed or a product is formed. In this experiment you will be observing a decrease in the concentration of iron(III) over some specific time interval.

The rate law for our reaction is in the following form, where x , and y are to be determined experimentally:

$$\text{rate} = k[\text{Fe}^{3+}]^x[\text{Sn}^{2+}]^y \quad (4)$$

If the concentration of the tin(II) is in large excess compared to iron(III), then its concentration will not change appreciably over the course of the reaction and therefore, remain essentially constant throughout the reaction. The concentration of Sn^{2+} can be incorporated into a new constant, k' . The rate law under these conditions can be written

$$\text{rate} = k'[\text{Fe}^{3+}]^x \quad (5)$$

with

$$k' = k[\text{Sn}^{2+}]^y \quad (6)$$

Most, but not all, reactants are either zero, first or second order. Integrating the rate law will give a way to determine the order of a reactant. If the order is 1, then the integrated form of the rate law becomes

$$\begin{aligned} \ln[\text{Fe}^{3+}]_t &= -k't + \ln[\text{Fe}^{3+}]_0 \\ y &= mx + b \end{aligned} \quad (7)$$

This equation has the form of the general equation for a straight line. The slope is \mathbf{m} and \mathbf{b} is the y-intercept of the line. If a plot of $\ln[\text{Fe}^{3+}]_t$ versus time yields a straight line, this indicates that the reactant is first order ($x = 1$). The slope of the line is $-k'$.

If the order is 2, then the integrated form of the rate law is

$$\begin{aligned} \frac{1}{[\text{Fe}^{3+}]_t} &= k't + \frac{1}{[\text{Fe}^{3+}]_0} \\ y &= mx + b \end{aligned} \quad (8)$$

If a plot of $1/[\text{Fe}^{3+}]_t$ versus time yields a straight line, this indicates that the reactant is second order ($x = 2$). The slope of the line is k' .

If a direct plot of absorbance vs. time is the best straight line, then the order of the reactant is zero ($x = 0$), with a slope of $-k'$.

In this experiment, you will record the absorbance of the iron(III) thiocyanate solution as it reacts with tin(II) solution over a period of time. After you have treated your data properly, you will plot this data in three ways: 1. absorbance vs. time, 2. $\ln(\text{absorbance})$ vs. time and 3. $1/\text{absorbance}$ vs. time. The plot that gives the best straight line indicates the order of the reaction in iron(III). The slope of the best straight line gives the rate constant k' .

Changing the concentrations of Sn^{2+} by known amounts while keeping the concentration of the Fe^{3+} constant will allow you to determine the order of Sn^{2+} in the reaction (equation 6). You can also then calculate k and write the rate law of the reaction.

One additional point to keep in mind as you treat the data. The data points collected at the end of the reaction are not reliable for obtaining usable rate data and will actually adversely affect your calculations. There are a couple of reasons for this. First, the reaction stops (reaches equilibrium) before it has gone to completion and so you are no longer measuring a reaction rate. Second, at low concentrations of FeSCN^{2+} , the detector of the Spec 20 does not respond as accurately to slight fluctuations in the amount of transmitted light. The overall effect will be data points that give a flat noisy line. The last of your data points should therefore be discarded **and noted in your notebook**.

Procedure

Part I Determining the Order of Iron(III)

Set the Spectronic 20 to 460 nm. Blank with a 1:1 mixture of 1.4×10^{-2} M Sn^{2+} and 0.32 M HCl solution.

Pipet 10.0 mL of 2.5×10^{-3} M Fe^{3+} into a small beaker. Add one drop of 4 M KSCN solution. Pipet 10.0 mL of 1.4×10^{-2} M Sn^{2+} into a different beaker. Mix **quickly** by pouring the contents of one beaker into the other and then quickly fill the cuvette. Record the first absorbance, then every 5 seconds for about 3 minutes (or until there is little to no change in the absorbance).

Part II Determining the Order of Tin(II)

Follow the procedure in Part I, using:

10.0 mL of 2.5×10^{-3} M Fe^{3+} and 10.0 mL of 2.1×10^{-2} M Sn^{2+} .

10.0 mL of 2.5×10^{-3} M Fe^{3+} and 10.0 mL of 2.8×10^{-2} M Sn^{2+} .

10.0 mL of 2.5×10^{-3} M Fe^{3+} and 10.0 mL of 3.5×10^{-2} M Sn^{2+} .

Blank with a 1:1 mixture of the appropriate Sn^{2+} solution and 0.32 M HCl solution.

Questions

1. What is the function of SCN^- in the experiment?
2. Why do you discard the last data points of the kinetic runs?
3. Why do the solutions have to be mixed **quickly** before measuring the absorbance data?
4. The following data were obtained in an **unrelated** kinetics experiment:

| <u>Time(s)</u> | <u>A</u> | <u>Time(s)</u> | <u>A</u> | <u>Time(s)</u> | <u>A</u> |
|----------------|----------|----------------|----------|----------------|----------|
| 0 | 1.174 | 35 | 0.324 | 70 | 0.100 |
| 5 | 0.979 | 40 | 0.271 | 75 | 0.086 |
| 10 | 0.813 | 45 | 0.227 | 80 | 0.075 |
| 15 | 0.676 | 50 | 0.190 | 85 | 0.065 |
| 20 | 0.561 | 55 | 0.162 | 90 | 0.058 |
| 25 | 0.467 | 60 | 0.138 | 95 | 0.052 |
| 30 | 0.388 | 65 | 0.117 | 100 | 0.051 |

Plot the **three** functions of **A** and determine the order of the reaction. You **may** discard data points for the reasons discussed in the introduction. Determine **k**.

Data Treatment and Discussion

Include the following, **with the appropriate discussion**. Show samples of **all** calculations.

- For Part I, using just your **good** data (noting which points you are not using (see above)) construct a table with columns for time, absorbance, $\ln(\text{absorbance})$ and $1/\text{absorbance}$. Make plots of absorbance vs. time, $\ln(\text{absorbance})$ vs. time and $1/\text{absorbance}$ vs. time. The graph, which gives the best straight-line (according to R^2), will indicate the order of the reaction in iron(III). The order of iron(III) is **fixed** for the rest of this experiment. Find the slope of the trendline to determine k'_1 .
- Plot the three sets of data from Part II **using only the function that gave the best straight line in Part I**. You are still following the change in the concentration of Fe^{3+} .
- Determine the rate constants k'_2 , k'_3 and k'_4** from the slope of each graph of Part II. Be sure to include proper units and significant figures.
- Taking the log of both sides of equation 6 gives a linear equation with a slope of y :

$$\log(k') = \log(k) + y\log[\text{Sn}^{2+}] \quad (9)$$

Plot $\log(k')$ versus $\log[\text{Sn}^{2+}]$. The slope of the plot, to the closest integer, is the order of the reaction in $[\text{Sn}^{2+}]$. The y-intercept is $\log(k)$.

- Give the rate law.
- Calculate the **average** value of k calculated from k'_1 , k'_2 , k'_3 and k'_4 (equation 6 with the exponent (y) of your rate law (determined above) and $[\text{Sn}^{2+}]_{1-4}$ used in Parts I and II and compare with the value obtained from the y-intercept.

Conclusion

Give the rate law, the average rate constant, **k** (from 6.) and **k** from the graph (4.).