

## Stopped Flow Kinetics

When measuring the kinetics of a reaction it would be ideal to be able to mix the reactants and periodically sample the mixture in order to analyze the reactant or product. Unfortunately, for some reactions the time required to mix the reactants together may be comparable to the reaction time. That is, the half-life of the reaction occurs on approximately the same timescale as the mixing. This results in an uncertainty in both initial concentration and initial time.

A stopped-flow method can be used when reactions occur under these conditions. Figure 1 is a diagram of the stopped-flow apparatus. In this method, the reactants are injected simultaneously into a mixing chamber, where they begin to react, then moved quickly through a spectrophotometer cell and finally to a stopping syringe. This stopping syringe fills and drives its plunger back against a stopping block. This stops the flow and triggers the activation of data acquisition on a computer. The progress of the reaction is followed by monitoring a change in absorbance of either a reactant or product in the spectrophotometer cell. The time that is required for the reactant and products to travel to the spectrophotometer cell is known as the “dead time.” In this method the mixing time plus the dead time is on the order of milliseconds, which allows for reactions with half-lives of milliseconds or tens of seconds to be measured.

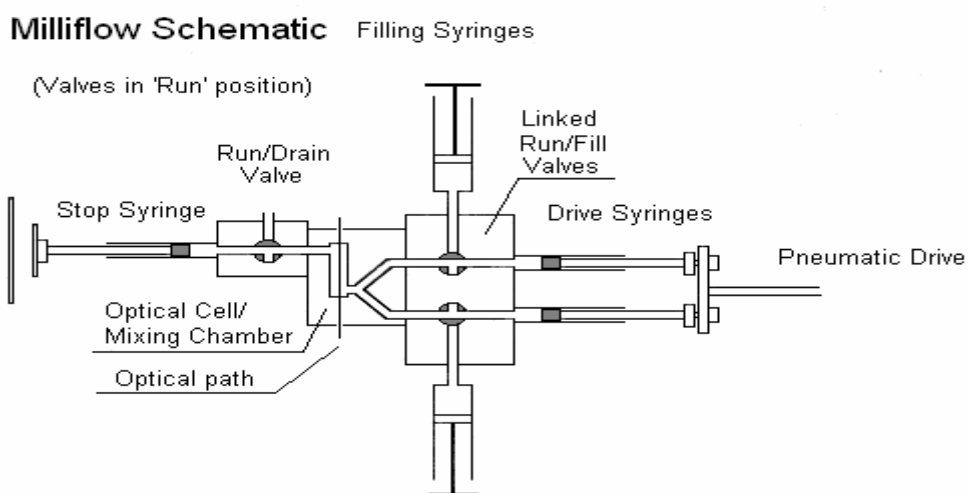
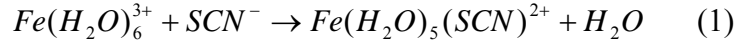
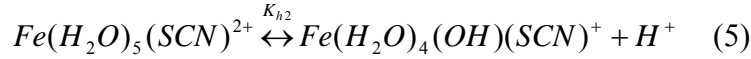
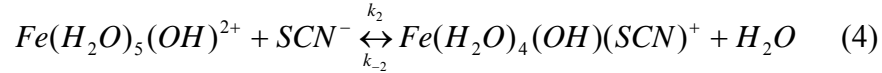
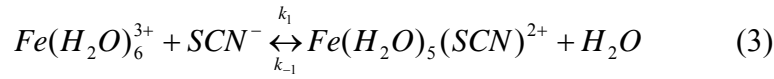
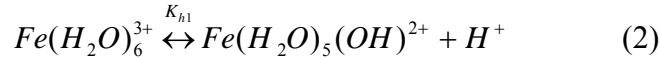


Figure 1 – Diagram of stopped flow apparatus.

In this experiment, the reaction between hydrated iron (III) and the thiocyanate ion ( $SCN^-$ ) will be studied in order to determine rate constants described by the mechanism. The reaction forms a red complex from clear solutions, therefore allowing it to be followed in a spectroscopic manner. The overall reaction is



and the reactions mechanism is as follows.



Here  $K_{h1}$  and  $K_{h2}$  are equilibrium constants for the hydrolysis reactions, and  $k_1$ ,  $k_{-1}$ ,  $k_2$ , and  $k_{-2}$  are the rate constants that we are interested in measuring.

Although this mechanism appears complicated, it is well understood. It explains the first order rate dependence on acidity. To study this reaction mechanism, it is necessary to assume that the equilibria of the hydrolysis reactions occur quickly with respect to the other reactions that are occurring.

Using the mechanism, it is possible to formulate an equation to describe the disappearance of ferrocyanate anion.

$$\begin{aligned} \frac{-d[SCN^-]}{dt} &= k_1[Fe(H_2O)_6^{3+}][SCN^-] - k_{-1}[Fe(H_2O)_5(SCN)^{2+}] + \\ &\frac{k_2 K_{h2}[Fe(H_2O)_6^{3+}][SCN^-]}{[H^+]} - \frac{k_{-2} K_{h2}[Fe(H_2O)_5(SCN)^{2+}]}{[H^+]} \end{aligned} \quad (6)$$

Upon rearrangement, this equation becomes

$$\frac{d[SCN^-]}{dt} = \left( \frac{k_1 + k_2 K_{h1}}{[H^+]} \right) [Fe(H_2O)_6^{3+}][SCN^-] - \left( \frac{k_{-1} + k_{-2} K_{h2}}{[H^+]} \right) [Fe(H_2O)_5(SCN)^{2+}] \quad (7)$$

It is possible for one to define a forward and a reverse rate constant,  $k_f$  and  $k_r$ , as follows

$$k_f = \frac{k_1 + k_2 K_{h1}}{[H^+]} \quad \text{and} \quad k_r = \frac{k_{-1} + k_{-2} K_{h2}}{[H^+]} \quad (8) \text{ and } (9)$$

If these rate constants are substituted into equation 7 the disappearance of the ferrocyanate anion is found to be

$$\frac{-d[SCN^-]}{dt} = k_f [Fe(H_2O)_6^{3+}] [SCN^-] - k_r [Fe(H_2O)_5(SCN)^{2+}] \quad (10)$$

This experiment can be carried out under pseudo-first-order conditions. That is,  $[Fe(H_2O)_6^{3+}] \gg [SCN^-]$ , and equation 10 can be integrated.

$$\ln \left( \frac{[Fe(H_2O)_5(SCN)^{2+}]_\infty}{[Fe(H_2O)_5(SCN)^{2+}]_t - [Fe(H_2O)_5(SCN)^{2+}]_\infty} \right) = k_{obs} t \quad (11)$$

Here  $k_{obs} = k_f [Fe(H_2O)_6^{3+}] + k_r$ . It is possible to expanded  $k_{obs}$

$$k_{obs} = (k_1 [Fe(H_2O)_6^{3+}] + k_{-1}) + (k_2 K_{h1} [Fe(H_2O)_6^{3+}] + k_{-2} K_{h2}) / [H^+] \quad (12)$$

Since the reaction progression is being following by monitoring the reactant spectroscopically, a relation between the measured absorbance and the concentration must be known. Here, for a certain concentration of  $H^+$ , the absorbance is proportional to the concentration of  $Fe(H_2O)_5(SCN)^{2+}$ .

$$\ln(A_\infty - A_t) = -k_{obs} t + \ln(A_\infty - A_t) \quad (13)$$

where in the case of this fast reaction, we can consider  $t = \infty$  to be one minute, due to the short half-life of the reaction. This allows one to plot  $\ln(A_\infty - A_t)$  vs  $t$  where the slope of the linear trendline is equal to  $-k_{obs}$ .

Since these are ionic reactions they depend not only on concentrations but on ionic strength of the solutions. Ionic strength is defined as

$$I_m = \frac{1}{2} \sum_j z_j^2 m_j \quad (14)$$

where  $m_j$  is the molality of ion  $j$  with charge  $z_j$ . To account for this, the solutions used in this experiment will be at a constant ionic strength. Since the reactions depend on  $[H^+]$ , the rate constant will be measured as a function of acidity. Considering equation 12, a

plot of  $k_{\text{obs}}$  vs  $1/[\text{H}^+]$  can be fit with a linear trendline. One can express  $k_1$ ,  $k_2$ ,  $k_{-1}$ , and  $k_{-2}$  in terms of two equations described by the slope and the intercept of this graph. It is also possible to define an equilibrium constant based on equation 3

$$\frac{k_1}{k_{-1}} = \frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})^{2+}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]} = K_{\text{eq}} \quad (15)$$

Similarly this could be done for the reaction expressed by equation 4 and, it is possible to solve for a fourth equation:

$$\frac{k_2}{k_{-2}} = \frac{K_{h2}k_1}{K_{h1}K_{-1}} = \frac{[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})(\text{SCN})^+]}{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}][\text{SCN}^-]} \quad (16)$$

Given that  $K_{h1}=1.89 \cdot 10^{-3}$ ,  $K_{h2}=6.5 \cdot 10^{-5}$  and  $K_{\text{eq}}=139$  at  $25^\circ\text{C}$ , it is possible to find  $k_1$ ,  $k_2$ ,  $k_{-1}$ ,  $k_{-2}$  from four equations and four unknowns.

## EXPERIMENTAL

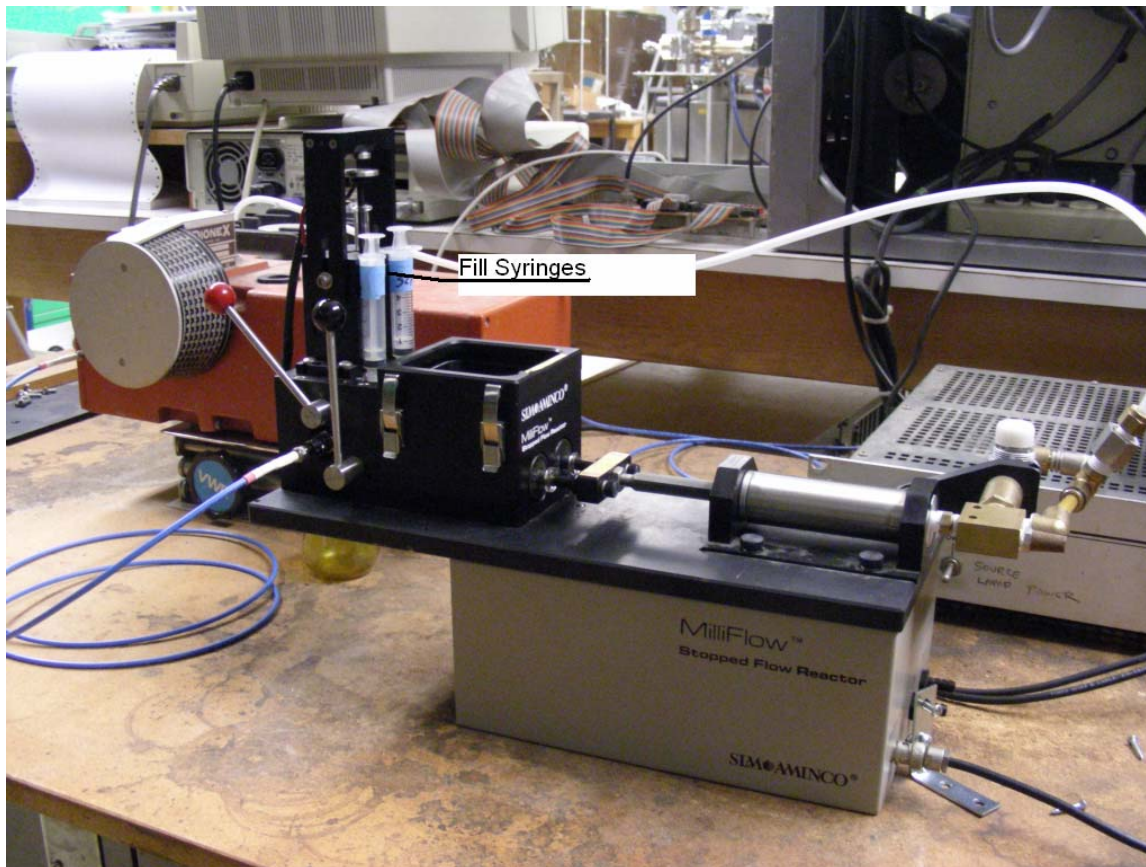
You will be determining the observed rate constant ( $k_{\text{obs}}$ ) for the reaction at five different values of  $[\text{H}^+]$ . First, five solutions of the iron reactant with five different values of  $[\text{H}^+]$  have been prepared along with a solution of thiocyanate, and are available in the lab.

Solution	A (mL)	B (mL)	C (mL)	D (mL)
Fe #1	0	95	25	0
Fe #2	5	90	25	0
Fe #3	10	85	25	0
Fe #4	25	70	25	0
Fe #5	50	45	25	0
SCN <sup>-</sup>	0	100	0	25

**Table 1.** Working Solutions, made from stock solutions A, B, C, and D. All volumes are in mL and are diluted to 250.0 mL total volume.

Stock solution A is approximately 1 M  $\text{HClO}_4$ ; stock solution B is approximately 1 M  $\text{NaClO}_4$ ; stock solution C is approximately 0.1 M  $\text{Fe}^{3+}$  and 0.2 M  $\text{HClO}_4$ ; stock solution D is 0.01 M  $\text{KCNS}$ . You will need to calculate the actual molarity knowing exactly how much of the compounds were used to make the solutions.

## Operation of the Milliflow Stopped-Flow Reactor



When not in use, the reactor should have two plastic syringes labeled 'dist. water' mounted in the fill syringe positions, with some water in them and in the drive and stop syringes. The drive syringe plungers should be attached to the drive bar. If this is not the case, have the lab coordinator or TA check the system before proceeding.

### Set up and test:

Turn on the lamp and PMT power supplies (if not already on.)

Start the computer. When the DOS prompt appears, change to the stop-flow directory with the command: `cd stpflo`

The programs are written in QuickBASIC and must be run from within the QuickBASIC environment.

To start QuickBASIC enter: `qb /l pro` (that's an "ell", not a "one")

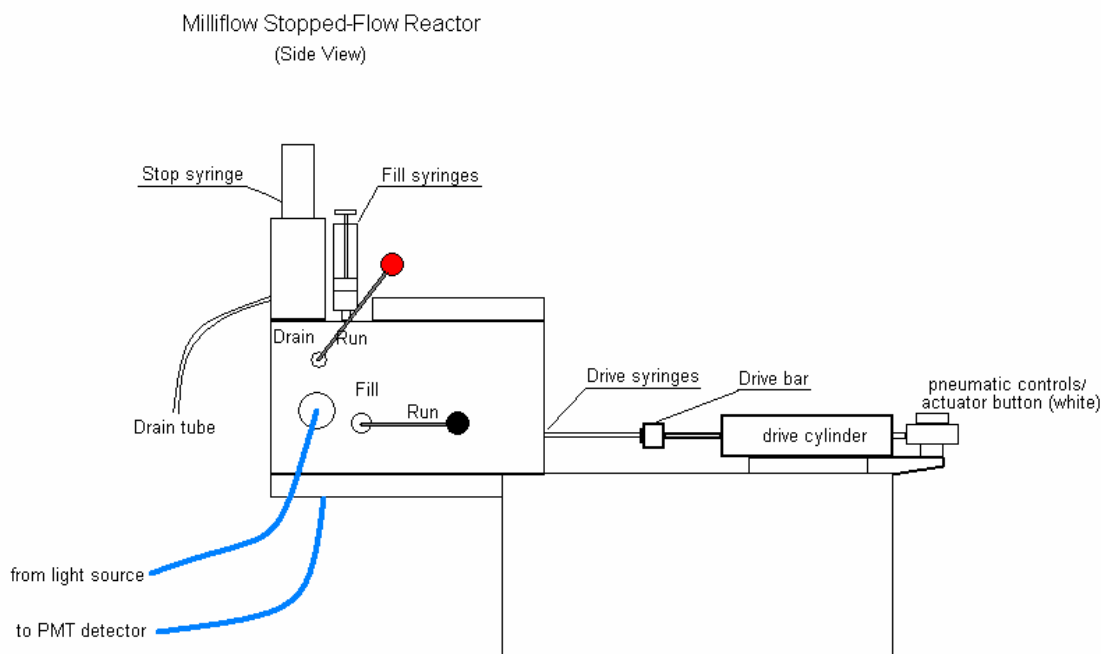
Use the mouse cursor and click "FILE" on the menu bar, then click on "OPEN PROGRAM."

On the list of program names that appears double click on "SFACHK.BAS."

After the program is loaded, click "RUN" on the menu bar, and then click "START."

This is a short program to check the signals from the reactor. We will be concerned with the upper left corner numeric field labeled 'Data' and the box in the center of the screen that displays the status of the stop syringe.

## Checking the reactor operation and data signals:



Make sure that the small plastic drain tube is in an appropriate waste collection vessel (an old 100ml volumetric works well.)

Move the black lever (Run/Fill valves) down (horizontal) (Run position).

Move the red lever (Run/Drain valve) to the left (Drain position).

Push down on the disk attached to the end of the stop syringe plunger to empty it.

[Box in center of computer screen should now be blue.]

Move the red lever (Run/Drain valve) to the right (Run position).

Open the tank valve on the nitrogen tank. The outlet pressure should read 80 psi.

Open the outlet valve on the regulator.

'Fire' the reactor by pressing the white actuator button on the right end of the reactor; you should hear a hissing sound and the drive bar should move slightly to the left driving water from the drive syringes through the mixing chamber/optical cell and into the stop syringe forcing it up against the stop plate. [Box in center of computer screen should now be red.]

The data field at the top left of the screen should read  $-2.00 \pm .02$  volts. Record this reading.

Move the red lever to the left (drain) position and push down on the stop syringe plate to empty it then return the lever to the right (run) position. [Screen box now blue.] Fire it again and check the data field and box on the screen. Repeat a couple more times recording the data value each time. This number is the 100% transmittance (0 absorbance) signal.

Now check the 0% transmittance value by turning off the lamp power and reading the data value (should be 0.00 +/- .03 volts.) Turn lamp back on as soon as you have taken the reading.

This sequence - red lever left, empty stop syringe, red lever right, press actuator, record data - is the standard way to get multiple data runs on a single pair of reactants.

#### Preparing the reactor for the first run:

Move the red lever (Run/Drain valve) to the left (drain).

Move the black lever (Run/Fill valves) to vertical (fill).

Remove the two screws holding the drive syringe plungers to the drive bar (they should only be finger tight) and push the drive bar all the way to the right.

Push the drive syringe plungers to the left to empty any water in the drive syringes into the water syringes. Twist the water syringes counter-clockwise and remove them from the system. Empty them into the waste container and set them aside.

Rinse and fill the drive syringes with reactants:

Fill the 5cc plastic syringe (marked SCN-) with the thiocyanate solution and place it in the rear fill syringe position. Twist it clockwise to lock it in place. Gently pull the plunger of the back drive syringe to the right filling it with the thiocyanate solution. Move it back and forth from full to empty two or three times, ending with the drive syringe empty. Remove the plastic fill syringe and discard the solution into the waste container. Refill with thiocyanate solution, remount it on the reactor and carefully fill the drive syringe.

Repeat the above procedure, using the plastic syringe marked Fe+ and the first iron solution you plan to run to fill the front drive syringe.

Attach the syringe plungers to the drive bar and make sure that the drive is all the way to the right. (drive syringes full.)

You are now ready to start the runs.

On the computer, press the combination CTRL-BREAK to end the test program (you may get a line at the bottom of the screen that says 'press any key to continue', do so) Use the mouse cursor and click "FILE" on the menu bar, then click on "OPEN PROGRAM."

On the list of program names that appears double click on "SFSIMExx.BAS." (where xx is the highest letter number combination)

After the program is loaded, click "RUN" on the menu bar, and then click "START."

The program will ask for a name for the directory in which to store the data files. I suggested that you string together the initials of the people in your group (up to a maximum of 8 characters) to create a directory name. Type in the name and press the 'enter' key.

The computer will now ask which of the five iron solutions you will study. Enter the number (1-5) of the iron solution you loaded into the drive syringe.

You will now need to enter the signal values for the 0%T and 100%T that you took above or let the computer program read them. (You will be asked to do this each time you start a new iron solution. Before you run your first iron solution [whichever one it is], the optical cell contains a clear solution [water] on which you can record the 100%T value, once you start making runs what is left in the optical cell is reaction product on which you cannot take a 100%T reading.)

### **Taking data:**

The computer will prompt with "READY" and a reminder about setting the stop flow valves and will also check the stop syringe position. When the computer prompts, press the Actuator button on the Stop-flow apparatus.

When data acquisition is complete, the computer displays some diagnostic information (you do not need to record this) and a prompt to continue. On continuing, a graph of intensity (transmittance) vs. time is displayed (the vertical bar is the trigger point) followed by another prompt to continue. Upon continuing, the program asks if you want to save the data. If the graphed data are of good quality, answer "yes".

After saving the data the computer asks if you want to take more data on the same iron solution or go on to the next iron solution or quit. (Yes, you should take more data on the same iron solution. You can get about 15 runs from the fully loaded drive syringes.)

To prepare for the next run on the same solution, move the red lever to the left (drain) position and push down on the stop syringe plate to empty it then return the lever to the right (run) position. You're now ready to do the next run on the same solution.

After you have done as many runs as are possible on one solution, answer the computers question with "do a new iron solution" then proceed as follows to set up the next iron solution.

Move the red lever (Run/Drain valve) to the left (drain).

Move the black lever (Run/Fill valves) to vertical (fill).

Empty the stop syringe.

Remove the two screws holding the drive syringe plungers to the drive bar (they should only be finger tight) and push the drive bar all the way to the right.

If there is enough thiocyanate solution in the fill syringe to refill the drive syringe, then carefully pull the back drive syringe to the right, refilling it with thiocyanate. Otherwise, remove the thiocyanate filling syringe, add more thiocyanate to it, remount it and fill the back drive syringe.

Push the front (iron) drive syringe to the left to empty any remaining iron solution in the drive syringe into the fill syringe.

Remove the iron filling syringe and empty it into the waste container. Rinse and fill the fill syringe with the next iron solution and mount it. Proceed to rinse and fill the drive syringe as you did before and proceed to take data on it.

Repeat until you have taken data on all five solutions.

Select quit on the data taking program and return to the QB program screen.

When finished, move the black lever to fill, push the drive syringes to the left, emptying the remaining reactants back into the fill syringes. Remove the fill syringes and empty into the waste container.

Rinse the system using the following procedure:

Retrieve the water syringes, fill them with distilled water and mount them on the fill fittings. Move the drive syringes back and forth 3-4 times ending with the drive syringes empty. Remove the water syringes and empty them into the waste. Refill the water syringes and repeat the process, again discarding the water into the waste container. Fill the water syringes a third time, mount them, and fill the drive syringes. Move the black lever to run. Empty the stop syringe. Now runs several shots of water through the system just as you did at the beginning of the experiment to test the system. Leave the system with water in the various syringes.

Getting the data from the computer:

Use the mouse cursor and click "FILE" on the menu bar, then click on "OPEN PROGRAM."

On the list of program names that appears double click on "CALCGRPx.BAS." (where x is the highest number)

After the program is loaded, click "RUN" on the menu bar, and then click "START."

The program will ask for a name for the directory in which you stored the data files. Type in the name and press the 'enter' key. Check the printer and continue. The computer will calculate & plot the  $\ln(A_{\infty} - A_t)$  vs. time plots and calculate and print a table of  $k_{obs}$ .

## **CALCULATIONS/ DISCUSSION**

- Calculate the actual concentrations of the stock and working solutions.
- Calculate the ionic strength of the working solutions.
- You find that the slope of a plot of  $\ln(A_{\infty} - A_t)$  vs. time gives you  $k_{obs}$ . You will have done several runs for each of the five values of  $[H^+]$ . This will give you several values for  $k_{obs}$  for each value of  $[H^+]$ .
- Plot  $k_{obs}$  vs.  $1/[H^+]$ . Using the slope and intercept and eqn 15 and 16 find  $k_1$ ,  $k_2$ ,  $k_{-1}$ , and  $k_{-2}$ , given that  $K_{h1}=1.89 \cdot 10^{-3}$ ,  $K_{h2}=6.5 \cdot 10^{-5}$  and  $k_{eq}=139$  at  $25^{\circ}C$ .
- Find the error in  $k_1$ ,  $k_2$ ,  $k_{-1}$ , and  $k_{-2}$ .
- Calculate a relative error between your experimental values  $k_1$ ,  $k_2$ ,  $k_{-1}$ , and  $k_{-2}$  and literature values. In your discussion compare the experimental values to literature values, which can be found from cited references at the end of these handouts. Keep in mind the ionic concentration of the literature values.
- In this lab the experiment is conducted under pseudo-first-order conditions. Is this a valid assumption?
- The accuracy of this experiment relies on the half-life of the reaction being longer than the dead time of the instrument. What are the implications on the results if the half-life is shorter than the dead time?

## REFERENCES

Below, J.F.; Connick, R.E.; Coppel, C.P. *J. Am. Chem. Soc.* **1958**, 80, 2961.

Funahashi, S.; Adachi, S.; and Tanaka, M., *Bull. Chem. Soc. Japan* **1973**, 46, 479.

Goodall, D.M.; Harrison, P.W.; Hardy, M.J.; Kirk, C.J.; H. *J. Chem. Educ.* **1972**, 49, 675.

Lister, M.W.; Rivington, D.E. *Can. J. Chem.* **1955**, 33, 1572.

Meiling, G.E.; Pardue, H.L. *Anal. Chem.* 1978, 50, 1333.

Sime, R.J. Physical Chemistry: Methods, Techniques, and Experiments. Saunders College Publications, Philadelphia. 1990, 577.