EXPERIMENT VI

KINETICS OF A FAST REACTION

In this experiment, the forward, k_f, and backward, k_b, rate constants for the equilibrium

$$Fe^{3+} + SCN^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} FeSCN^{2+} \quad \text{(equilibrium constant } K = k_f / k_b) \qquad (1)$$

will be measured using the stop-flow technique rather than the continuous flow method described in Shoemaker and Garland (4th ed, Expt. 29). Although a full description of the experiment is presented here, students are urged to read the corresponding chapter in S&G to better appreciate the differences between these two techniques.

In principle, the continuous flow method can follow reactions with half-lives of the order of 10^{-3} s but, although very cheap to set up, its application is practically limited by the large volumes of solution needed (typically, several litres). The stop-flow technique can reach a similar time range using only a few ml's of solution. This feature is particularly valuable when a very small amount of material is available, as is the case, for instance, in enzymatic kinetics.

The theory for the reaction studied is to be found in S&G. In the following, the principle of stop-flow measurement, the apparatus used and the experimental procedure will be described.

1. Safety

The preparation of the reacting solutions requires moderately concentrated nitric acid and sodium nitrate which can be corrosive; please wear your safety goggles at all times.

2. Principle of the method

To understand the concept of the stop-flow technique, let us first look at the continuous flow method. In this technique, two reagents, A and B, are allowed to mix at some point, T, while the mixture flows into a long capillary. If the flow is steady (and the capillary has a fixed bore), the distance, x, from the mixing point is directly proportional to the time t elapsed after mixing (the age of the mixture). Thus, by monitoring the concentration of one of the reactants (or products) for different distances x, information is obtained on the time profile of the reaction.

Let us now assume that the point of observation is fixed (x fixed) and that the mixture is flowing steadily. At this stage, one observes a constant signal (constant concentration) since one is looking at a mixture of fixed age. If the flow is abruptly stopped, one will observe at point x the aging of the mixture (decrease or increase of the concentration of the reactants or product(s), respectively), as depicted in Fig. 1.

The main limitations of the technique are:

- The duration of mixing (typically, a couple of milliseconds) has to be much shorter than the lifetime of the reaction.
- The point of observation has to be as close as possible from the mixing point in order to observe the early part of the reaction. The so-called *dead-time* of the apparatus is the time it takes for the mixture to reach the observation point, also a few milliseconds in conventional stop-flow.

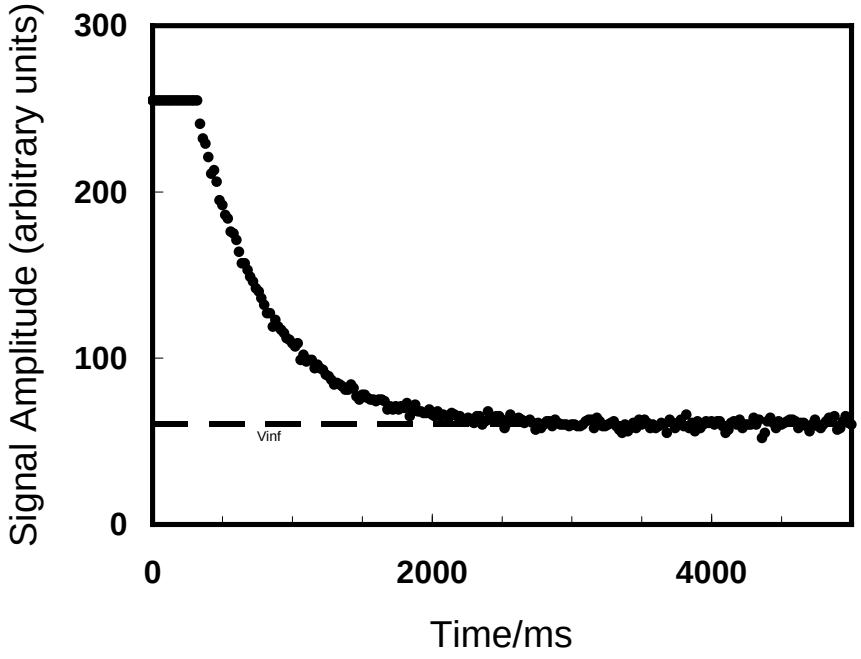

Figure 1. Typical Stop-Flow trace.

In the present apparatus, these two conditions are met for the speed of the reaction studied. The mixing of the two reactants is accomplished by an offset T junction, and the observation point is located approximately 2 mm away from the mixing point with an optical path length of ≈ 0.5 cm.

The reaction is followed by monitoring the change in optical density of the product $FeSCN^{2+}$ which absorbs strongly at 450 nm (Fe^{3+} and SCN^- have negligible absorption at this wavelength). More precisely, as described in the experimental section, the voltage output of a photodetector is the monitoring signal. This voltage is directly proportional to the light intensity transmitted through the observation point. If I_o and I_t are the incident and transmitted light intensities and V_o and V_t the corresponding voltage outputs from the photodetector, the optical density (or absorbance) may be written as

$$OD_t = \log_{10}\frac{I_0}{I_t} = \log_{10}\frac{V_0}{V_t} \tag{2}$$

Using pseudo-first order conditions ($[Fe^{3+}] >> [SCN^-]$)[1], the concentration of the product $FeSCN^{2+}$ as a function of time is expressed as (see S&G)

$$\ln\frac{[FeSCN^{2+}]_\infty - [FeSCN^{2+}]_t}{[FeSCN^{2+}]_\infty} = -\left([Fe^{3+}] + K^{-1}\right)k_f t = -(k_f[Fe^{3+}] + k_b)t \tag{3}$$

Since according to Beer's law, the optical density is proportional to concentration, one has:

$$\frac{[FeSCN^{2+}]_\infty - [FeSCN^{2+}]_t}{[FeSCN^{2+}]_\infty} = \frac{OD_\infty - OD_t}{OD_\infty} \tag{4}$$

From Eq. (2)

$$OD\infty \text{ - } ODt = \log_{10}\frac{V_o}{V_\infty} - \log_{10}\frac{V_0}{V_t} = \log_{10}\frac{V_o}{V_\infty}\frac{V_t}{V_o} = \log_{10}\frac{V_t}{V_\infty} \tag{5}$$

This last equation can be rewritten as

$$OD_\infty - OD_t = \frac{1}{2.303}\ln\left(1 + \frac{V_t - V_\infty}{V_\infty}\right) \tag{6}$$

For small *OD* changes (*i.e.* when $V_t - V_\infty << V_\infty$), the following approximation is valid:

$$\ln\left(1 + \frac{V_t - V_\infty}{V_\infty}\right) \approx \frac{V_t - V_\infty}{V_\infty} \tag{7}$$

Therefore:

$$OD_\infty \text{ - } OD_t \approx \frac{1}{2.303}\left(\frac{V_t \text{ - } V_\infty}{V_\infty}\right)1 \tag{8}$$

Finally, combining this last result with Eq. (3) and (4), one gets:

$$\ln(V_t - V_\infty) \approx c - (k_f[Fe^{3+}] + k_b)t = c - k_{obs}\,t \tag{9}$$

where *c* is some constant.

Eq. (9) shows that a plot of $\ln(V_t - V_\infty)$ *versus* time should be linear with a slope $-k_{obs} = -(k_f[Fe^{3+}] + k_b)$. By repeating the experiment at various $[Fe^{3+}]$, k_f, k_b and K may be determined from a plot of k_{obs} *versus* $[Fe^{3+}]$. In addition, both rate constants are

[1] Although, in principle, pseudo-first order conditions could be obtained with $SCN^- >> Fe^{3+}$, complication would arise due to the formation of multi-substituted thiocyanato species since excess SCN^- ions present in would be available for further reaction.

dependent to some extent on the ionic strength of the medium. To minimize ionic strength effects, the reaction will be performed at a constant ionic strength of ≈1 M[1].

3. Experimental Set-up

A schematic diagram of the setup is shown in Fig. 2. The two driving syringes A and B can be connected to either the reservoir syringes or to the flow tubes through the three-way valves V_A and V_B. Once A and B are filled and V_A and V_B are in "RUN" position, the reagents can be mixed to react by pushing the syringes simultaneously with a pneumatic piston. The solutions mix at point T, flow through the observing chamber, O, then to waste. When the pushing block hits the stopping block, a micro switch triggers the start of data collection, namely, the monitoring of the voltage output of the photodetector.

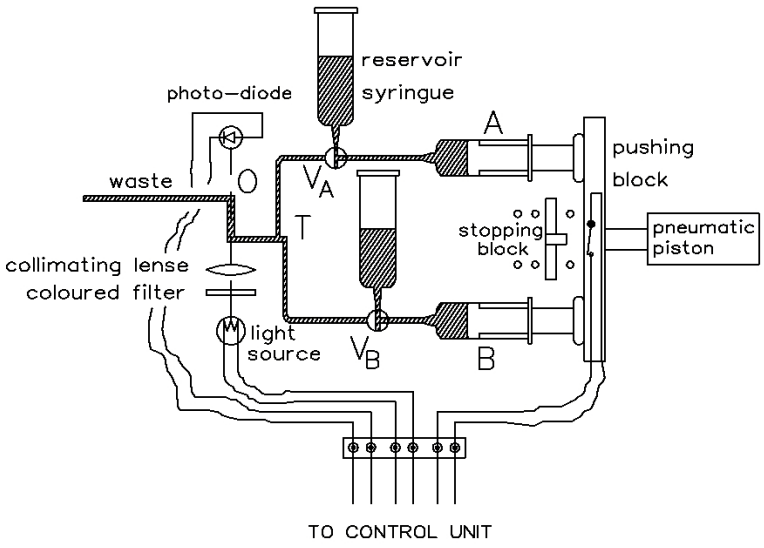

Figure 2. Schematic diagram of the stop-flow apparatus. The pneumatic piston pushes the "driving" syringes A and B containing the reagents which mix at point T. The change in absorbance of the mixture is observed at point O.

The electrical connections from the stop-flow apparatus to the control unit are the following: power for the light source, triggering signal, photodetector signal. The control unit integrates the following elements:

1) Stabilized power supply to energize the light source;

The noise should have much lower amplitude than the signal of interest. Also, any ripple present should have a period much longer than the reaction time. Ideally, the light source should have a broad spectrum output. The wavelength of interest may be selected by means of a monochromator located before the sample. In the present setup,

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[1] The ionic strength is defined by $I = \frac{1}{2} \Sigma C_i z_i$ where C_i is the concentration (mole l^{-1}) of ionic species i and z_i is the corresponding charge.

a tungsten lamp is used in conjunction with a coloured filter which has a maximum transmission at ≈ 450 nm.

2) Photometer and offset potentiometer

The photometer must provide a linear response to light intensity change. For the present purpose, a photodiode is adequate. More sophisticated setups use photomultiplier tubes or a photodiode array in combination with a light dispersing device located after the sample; this last arrangement allows for the spectrum of transient species to be recorded in one shot.

For most systems studied, the change in light intensity during the reaction is small compared to the initial intensity. It is therefore necessary to amplify the output signal. Since the digitizing range of the transient recorder is 0 - 5 V, it may be necessary to offset the amplified signal in order to bring it back within this range. Accordingly, if needed the absolute value V_t of the output voltage may be found by the expression

$$V_t = (V_{read} / G) + V_{offset} \qquad (10)$$

where V_{read} and V_{offset} are the recorded and offset voltages, respectively and G is the gain of the amplification.

3) Digital transient recorder (Control Unit)

The digital recorder consists of an array of 256 memories which, upon triggering (provided by the pushing block hitting the micro-switch), can be addressed sequentially at a rate specified by the time base (from 0.2 ms/point to 100 ms/point). The output voltage from the photodetector is stored in digital form in each of the memories. The address (time axis) and content of the memories (signal amplitude) can be read using an appropriate output device (scope, computer, printer, or other).

4. Procedure

1) Equipment

Switch the power on all the equipment: computer, scope, stop-flow control unit.

2) Solution preparation

The solutions will be kept acidic (0.5 M HNO_3) to avoid complication due to hydrolysis of Fe^{3+} to $Fe(OH)^{2+}$ which itself may form absorbing thiocyanato species (see discussion), and the ionic strength will be kept at 1 M. The stock solutions provided are: 2.5 M $NaNO_3$ and 2.5 M HNO_3 for acidity and ionic strength adjustment, and ≈ 0.2 M Fe^{3+} (0.5 M HNO_3); record the exact concentration of this last solution.

Prepare the following solutions:

- Five Fe^{3+} solutions according to Table 1:

- One 2×10^{-4} M SCN^- solution obtained by diluting 4.00 mL of 5×10^{-3} M NaSCN[1] + 20.0 mL of 2.5 M $NaNO_3$ + 20.0 ml of 2.5 M HNO_3 into a 100 ml volumetric flask with distilled water.

Make sure that all the solutions are equilibrated at room temperature. Record this temperature. The first run should be done with the lowest Fe^{3+} concentration. Rinse and flush each reservoir and the corresponding driving syringe at least four times with small portions of the relevant solution[2], then fill the driving syringe, taking care to flush out all bubbles from the system. Since the SCN^- solution stays the same for all runs, only the side containing the Fe^{3+} solution will have to be rinsed and refilled with each new solution.

Table 1. Recommended volumes of various components to prepare a series of Fe^{3+} solutions*.

Solution #	0.2 M Fe^{3+}	2.5 M $NaNO_3$	2.5 M HNO_3	Diluted to
1	1.0 mL	*Exact volumes will depend on the particular* $[Fe^{3+}]$ *in the solution provided; check the EXCEL file IONICSTR.XLS to determine the required volumes.*		100 mL
2	1.0 mL			50 mL
3	2.0 mL			50 mL
4	5.0 mL			50 mL
5	10.0 mL			50 mL

* Acidity is kept at 0.5 M, and ionic strength at 1.0 M

3) Running the experiment.

Once the driving syringes are filled, manually push both syringes at the same time to fill the observing chamber with the mixture and return the valves to the "FILL" position.

Adjusting the gain and time base. On the control unit, move the toggle and rotary switches to the following positions:

STORE, DISABLE, CONT., SCOPE, RESPONSE D, GAIN 1 (or 5,or 10)[3] (Adjust mode)

Check that the trace on the scope can be moved up and down by turning the offset potentiometer. Adjust the offset such that the trace is ≈ 3/4 down its vertical range. If not already filled, refill the driving syringes. Position the stopping block into a set of locating holes such that it is ~ 1.5 to 3 cm away from the pushing block. Adjust the TIME BASE to 20 ms (or 10 ms).

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[1] Prepare first 100 mL of 5×10^{-3} M NaSCN in distilled water (this requires ≈ 40 mg of NaSCN).

[2] Pour ~2ml of solution into the reservoir. With the valve V_A (or V_B) in the "FILL" position, gently pull out the *pushing block* to transfer the solution to the *driving syringe* (careful not to take in air bubbles), then turn the valve to "RUN" position and push in the *pushing block* to flush the solution through the system. Always leave a little bit of solution in the reservoir to prevent air from being taken in.

[3] The choice of the value of the gain depends on the signal amplitude; small signal will require large gain and vice-versa.

Set to "Ready" mode. Move the control unit switches to the following position

STORE, ENABLE, SINGLE, RUN. (All toggle switches "UP") (Ready mode)

Check that you still have control of the spot on the scope with the offset knob. Turn all the valves to the "RUN" position.

Collecting data. To initiate the mixing and the data collection, release the pneumatic piston. Hold your finger down on the trigger button until the scope sweep is over, release your finger, return the valves to the "FILL" position, then move the switches to the following position (*in this order*):

READ, DISABLE, CONT., SCOPE. (All toggle switches "DOWN") (Read mode)

The kinetic trace is displayed on the scope. If it is not satisfactory, reposition the stopping block and repeat the run (*i.e.* go back to the Ready mode). The GAIN and the TIME BASE may have to be re-adjusted to get a better trace.

Perform at least two determinations for each Fe^{3+} concentration. When finished, rinse the apparatus thoroughly with distilled water and leave it filled with distilled water. Switch off all the electrical components.

Note: *As long as the MODE switch is left in the READ position, the memory content of the control unit is not affected. The RESET push-button moves the memory pointer to the address of the first element of the memory array.*

5. Data output

1) Oscilloscope display

With the switches in the position

READ, DISABLE, CONT., SCOPE

the location (horizontal axis) and the memory content (vertical axis) are displayed in analog form on the oscilloscope screen.

2) Digital output

The data can be written as an ASCII file through a PC.

- Make sure that the blue ribbon cable at the back of the control unit is connected to the PC.
- Move the switches to the positions

READ, DISABLE, SINGLE, EXT.

- Type from the keyboard the command STOPFLOW (or activate the appropriate Windows icon) which will load the data transfer program, then follow the instructions appearing on the PC monitor.

- At this stage, if a printer is available, a screen dump of the kinetic trace may be obtained; use the "Print Screen" key. Do not forget to record the run#, the values of the Gain, Time Base and Offset reading.
- Do not forget to save your data corresponding to each new run with a different file name!

The data file consists of a column of numbers; the first line is an identification, the second line is the time base you entered (in ms), then the rest of the numbers represents the digitized voltage amplitude[1] recorded at consecutive times separated by "time base".

6. Calculations

For each run, the observed rate constant is obtained from the slope of the line $\ln(V_t - V_\infty)$ versus t (see below for suggestions on how to process these data).

Tabulate and plot all the observed rate constants as a function of $[Fe^{3+}]$ *in the reacting mixture* (which is half the prepared concentration due to the 1:1 mixing with the other reagent). From the slope and the intercept of this plot, k_f, k_b and K can be deduced. Give the proper units for these quantities. Compare your value of K with a literature value.

In your report, present only a couple of representative plots of the $\ln(V_t - V_\infty)$ versus t fits (for instance the best and the worst looking plots). Do not include a print out of the raw data stored in the computer, but provide information to retrieve this data (file name). Present your kinetic results tabulated in the format suggested in the MS-Excel sheet `stopflow_results.xls` (may be downloaded from the course web pages)

7. Discussion

Explain how your data support (or otherwise) the kinetic scheme presented above? What are the principal sources of error in this experiment? The fastest time-base of the present apparatus is 0.2 ms; with this information estimate the order of magnitude of the shortest reaction half-life which could be measured and what is (are) the limiting factor(s)? Justify your answers.

If the present experiment were to be carried out with SCN^- in excess to obtain the same kinetic information which series of solutions would have to be prepared?. Actually, this experiment is always performed with Fe^{3+} in excess; why?

Another pathway for this reaction is

[1] The range 0-5 V is digitized into an 8-bit word; *i.e.*, 0 V is represented by decimal 0 (binary 00000000), 5 V is represented by decimal 255 (binary 11111111).

$$Fe^{3+} \rightleftharpoons Fe(OH)^{2+} + H^{+} \quad \text{(fast hydrolysis of } Fe^{3+}\text{)} \tag{11}$$

$$FeSCN^{2+} \rightleftharpoons Fe(SCN)(OH)^{+} + H^{+} \quad \text{(fast hydrolysis of } FeSCN^{2+}\text{)} \tag{12}$$

followed by

$$Fe(OH)^{2+} + SCN^{-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Fe(SCN)(OH)^{+} \tag{13}$$

Why is the pathway (13) not important in the present experimental conditions?
In what pH range would the solutions have to be prepared to carry out a similar kinetic study in order to determine k_3 and k_4? (*Keep in mind that* Fe^{3+} *precipitates as* $Fe(OH)_3$ *if the pH is too high.*)

8. Notes on fitting the data

The software used to transfer the data can also be used to process the kinetics data; once in the program, choose the corresponding menu item. Alternatively, the analysis may be performed using the EXCEL template `STOPFLOW.XLS` available on some of the PCHEM lab computers or from the course web pages.

9. References

W.J. Moore, *Physical Chemistry*, 4th Ed., Prentice-Hall, 1972.

E.F. Caldin, *Fast Reactions in Solution*, Blackwell Scientific Publications, Oxford, 1964.

K. Kustin (Editor), *Methods in Enzymology*, Vol. XVI, 1969.

D.P. Shoemaker and C.W. Garland, *Experiments in Physical Chemistry*, McGraw-Hill Book Co., 2nd, 3rd or 4th Eds.

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Chem 366W report check list

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Student Name:_____

Report: Stop-Flow Kinetics

Title page.

Correct title of the experiment ☐
Student Name & student ID ☐
Partner name (*if applicable*) _____
Date of performance of experiment ☐
Abstract ☐
Introduction and theory ☐
Experimental
Changes from text description mentioned (*if applicable*) ☐
Sample ID, ser no, stock solution …etc recorded (*if applicable*) ☐
Results
Results as Tables ☐
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Axis labelled ☐
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Only significant figures ☐
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Discussion
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Comparison with literature value(s) ☐
Conclusion ☐

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