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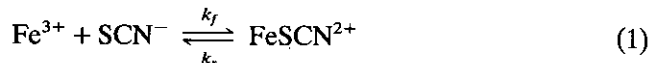
EXPERIMENT 25 KINETICS OF A FAST REACTION

Although conventional kinetic methods have proved very useful in studying a wide range of chemical reactions, special techniques are needed for investigating fast reactions (i.e., reactions with half-lives less than a few seconds). Such techniques may also provide a way to elucidate the rapid steps of reaction mechanisms for which only the slow rate-controlling step can be investigated by classical methods. In recent years, a wide variety of new methods have been developed for fast reactions in solution.^{1,2} The earliest of these are the various flow methods (both continuous and stop-flow), which are suitable for reactions with $\sim 1 \text{ s} > t_{1/2} > 10^{-3} \text{ s}$.³ For half-lives below 10^{-3} s , it is necessary to use methods that avoid the mixing of reactants, and several sophisticated techniques (such as relaxation methods) are now available for studying very fast reactions with $t_{1/2}$ values as short as 10^{-9} s .^{1,2}

In this experiment, the simplest fast-reaction technique—the continuous-flow method—will be used to study the kinetics of the formation of the ferric thiocyanate complex FeSCN^{2+} .

THEORY

For the fast reaction between ferric and thiocyanate ions in an acid solution of constant pH, the observed behavior is consistent with the simple mechanism⁴



where k_f is the bimolecular forward rate constant and k_r is the unimolecular reverse rate constant.† The rate law resulting from mechanism (1) is

$$\frac{d(\text{FeSCN}^{2+})}{dt} = k_f(\text{Fe}^{3+})(\text{SCN}^-) - k_r(\text{FeSCN}^{2+}) \quad (2)$$

Let us recall that the equilibrium constant K is related to the rate constants by

$$K = \frac{k_f}{k_r} = \frac{(\text{FeSCN}^{2+})_\infty}{(\text{Fe}^{3+})_\infty(\text{SCN}^-)_\infty} \quad (3)$$

where the subscript ∞ denotes the equilibrium ($t = \infty$) value. Let us also note that

$$(\text{FeSCN}^{2+}) + (\text{SCN}^-) = (\text{FeSCN}^{2+})_\infty + (\text{SCN}^-)_\infty \quad (4)$$

at any time t . Using these relations, we can rewrite Eq. (2) in the form

$$\frac{d(\text{FeSCN}^{2+})}{dt} = k_f(\text{Fe}^{3+})[(\text{FeSCN}^{2+})_\infty + (\text{SCN}^-)_\infty] - k_r[(\text{Fe}^{3+}) + K^{-1}](\text{FeSCN}^{2+}) \quad (5)$$

In order to simplify the integration of Eq. (5), let us choose the experimental conditions such that $(\text{Fe}^{3+}) \gg (\text{SCN}^-)$. This will allow us to assume that (Fe^{3+}) is essentially constant during the course of the reaction. If, in addition, the initial conditions are chosen so that $(\text{FeSCN}^{2+}) = 0$ at $t = 0$, we find

$$\ln \frac{(\text{FeSCN}^{2+})_\infty - (\text{FeSCN}^{2+})}{(\text{FeSCN}^{2+})_\infty} = -[(\text{Fe}^{3+}) + K^{-1}]k_f t \quad (6)$$

This is an approximate solution which becomes exact only when (Fe^{3+}) is constant (you can check Eq. (6) by direct differentiation). In actual practice, $(\text{Fe}^{3+})_0$ will be chosen to be ten times larger than $(\text{SCN}^-)_0$, so that (Fe^{3+}) will vary by about 10 percent during the reaction.‡

† In fact, the detailed mechanism is more complex, since both a direct and a base-catalyzed path exist.⁴ The value of k_f as used in mechanism (1) is found to be dependent on the H^+ concentration: $k_f = k_1 + k_2/(\text{H}^+)$. Since this experiment is restricted to a single value of (H^+) , the more general mechanism is omitted.

‡ With this choice of an initial ferric concentration, which is much larger than the thiocyanate concentration, any formation of $\text{Fe}(\text{SCN})_2^+$ species can be neglected. Also we shall work at a low pH value so that the hydrolysis of ferric ions can be neglected.

If a plot of first-order dependence on tested in this ex

METHOD

The continuous reactant solution and then the re that the solution much shorter th various position times. A quanti x from the mixing measuring the ti flow through th capillary, the av on the average,

It is import "mass flow" as p located at some length of time at since it is fast nea Exp. 4). Since tu rates that are gr see Eq. (4-11)]. I to a given distan more than 2 to 3 for streamline flo

In this exper meter with a rath absorbance readi than 1 s), it is no Exp: 23. Howev study fast reaction

† The principal disad required. Although th limitation in studying to use a stop-flow met

If a plot of $\ln[(\text{FeSCN}^{2+})_{\infty} - (\text{FeSCN}^{2+})]$ versus t is linear, then the first-order dependence on (SCN^-) and (FeSCN^{2+}) is confirmed. The rate dependence on (Fe^{3+}) has been established as first order⁴ and will not be tested in this experiment.

METHOD

The continuous-flow method^{3,5} is a simple and straightforward technique. Two reactant solutions are forced under pressure into a T-shaped mixing chamber, and then the reacting mixture flows down a long capillary tube. It is important that the solutions mix well and rapidly ($\sim 10^{-3}$ s). When the mixing time is much shorter than the half-life of the reaction, a steady state is set up such that various positions along the capillary tube correspond to different reaction times. A quantitative correlation between the reaction time t and the distance x from the mixing chamber to a given point along the tube can be achieved by measuring the time interval $\Delta\tau$ needed for a known volume ΔV of solution to flow through the tube. Assuming a constant cross-sectional area \mathcal{A} for the capillary, the average linear flow velocity \bar{v} is given by $\bar{v} = \Delta V / (\mathcal{A} \Delta\tau)$. Thus, on the average, the reaction time is related to x by

$$t = x \frac{\mathcal{A} \Delta\tau}{\Delta V} \quad (7)$$

It is important that the flow of the reacting solution should be as close to "mass flow" as possible, so that all the fluid arriving at a small volume element located at some fixed point along the tube will have travelled for the same length of time after leaving the mixing chamber. Laminar flow is undesirable since it is fast near the center of the capillary and quite slow near the walls (see Exp. 4). Since turbulent flow is much closer to mass flow, we wish to use flow rates that are greater than $1000 \eta/\rho r$ [the minimum value for turbulent flow; see Eq. (4-11)]. Deviations from mass flow will blur the time value appropriate to a given distance x . Fortunately, the resulting error in the rate constant is no more than 2 to 3 percent for turbulent flow; but it may be as high as 10 percent for streamline flow.^{3,5}

In this experiment, the reaction is to be followed using a spectrophotometer with a rather slow response, several seconds being required to make an absorbance reading. Since the reaction to be studied is rapid (half-life of less than 1 s), it is not possible to follow the progress of the reaction directly as in Exp. 23. However, the continuous-flow method is an appropriate way† to study fast reactions with a slowly responding instrument. The design described

†The principal disadvantage of this method is the fact that large quantities of solution are required. Although the present chemicals are cheap and easily obtained, this would be a serious limitation in studying reactions involving rare or costly reactants. In those cases, one would need to use a stop-flow method with a rapidly responding spectrophotometer.³

in the experimental section is based directly on that first used by Dalziel; excellent detailed descriptions of his equipment are available in the literature.^{3,5}

The complex FeSCN^{2+} has an absorption maximum near 450 nm, whereas neither Fe^{3+} nor SCN^- absorbs in that region.⁶ Therefore,

$$(A_\infty - A) = \epsilon d[(\text{FeSCN}^{2+})_\infty - (\text{FeSCN}^{2+})] \quad (8)$$

where A is the absorbance, ϵ is the molar absorption coefficient, and d is the optical path length. From Eqs. (6) and (8) we see that a plot of $\log(A_\infty - A)$ versus t should give a straight line of slope $-k_f[(\text{Fe}^{3+}) + K^{-1}]/2.303$. Note that A_∞ values obtained at different points along the tube may not all agree with each other, since there may be variations in the capillary tube and its placement with respect to the light beam. Also note that errors in $(A_\infty - A)$ caused by a drift in the zero setting of the spectrophotometer could cause appreciable errors in the rate constant. Readings corresponding to a large percent reaction are most sensitive since the $(A_\infty - A)$ values are then small.

Finally, we must remember that there will be a salt effect⁷ on the rate of this reaction: both the rate constant k_f and the equilibrium constant K are functions of the ionic strength I . An (approximately constant) ionic strength of 0.40 M will be chosen here to facilitate comparison with previous work.⁴

EXPERIMENTAL

A sketch of the complete assembled apparatus is shown in Fig. 1, and more detailed drawings of the capillary support frame are given in Fig. 2. There are two important differences between this design and that of Dalziel:⁵ (1) the carboys of reactant solutions are mounted in a stationary thermostat bath and are connected to the movable capillary support frame by rubber pressure tubing, and (2) the mixing chamber is machined from a block of Lucite instead of being fabricated from glass. A detailed drawing of this mixing chamber is given in Fig. 3.

The spectrophotometer setup shown in Fig. 1 is based on the use of a Beckman Model DU instrument in which the cell holder unit (sample chamber) has been replaced by a special housing that allows the capillary support frame to slide back and forth. The Beckman Model DU is an old and simple design. Many other spectrophotometers are available that will provide excellent absorbance measurements, and any of these can be used as long as suitable adaptation of the sample chamber can be made. A modular spectrophotometer PTR model SP-100, available from PTR Optics Corp., is one example of a modern instrument with a flexible geometric design; similar components for modular instruments are available from Oriol Corp. and other manufacturers. No matter what instrument is being used, make sure that the alignment is correct (so that the capillary frame moves smoothly) before bolting the special adapter housing to the spectrophotometer. It is convenient to have the spectrophotometer sitting on a base with adjustable legs to

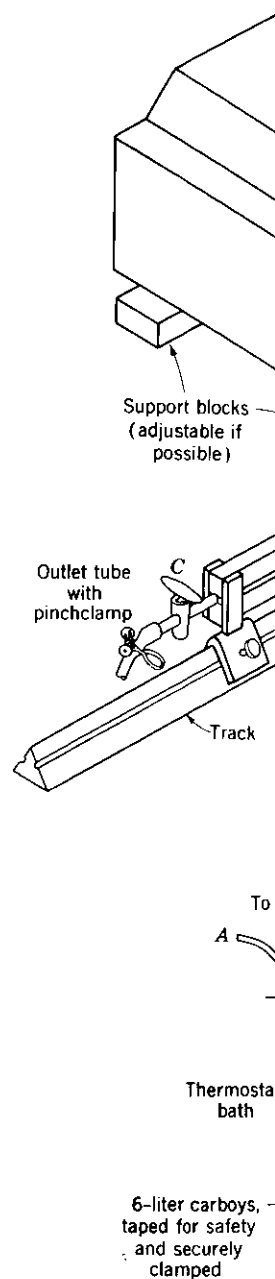


FIGURE 1
Flow-kinetics apparatus
reactant solutions.

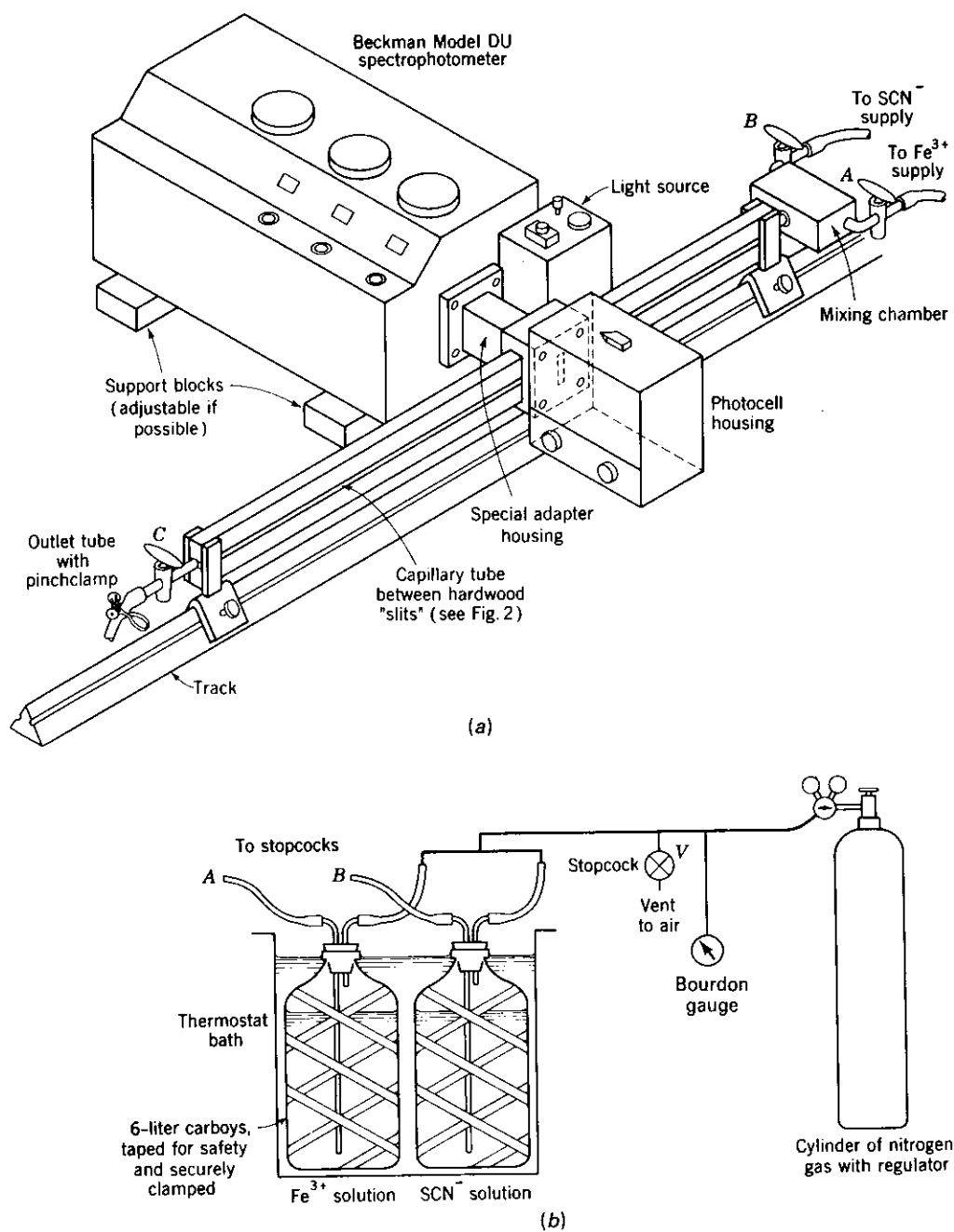


FIGURE 1
 Flow-kinetics apparatus: (a) spectrophotometer setup; (b) schematic diagram of system for driving reactant solutions.

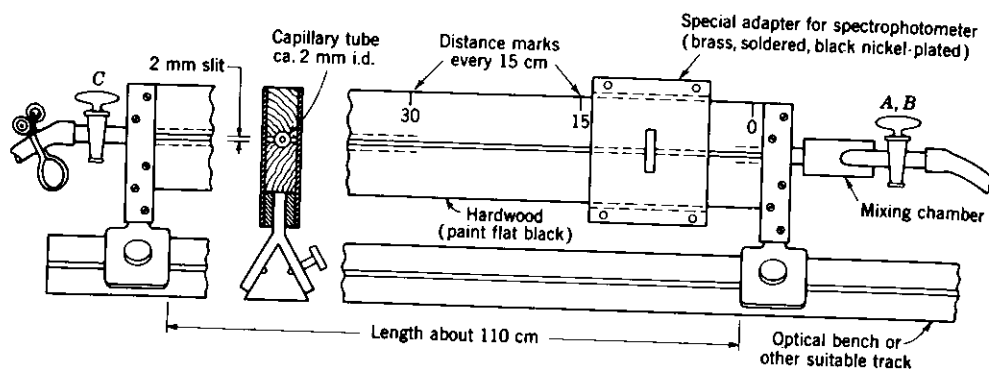


FIGURE 2
Detail of reaction capillary tube and support frame.

facilitate this alignment. Finally, attach the photodetector unit onto the rear of the adapter housing.

Next, fill the two carboys† with the appropriate solutions. Solution A should be 0.02 M in $\text{Fe}(\text{NO}_3)_3$, 0.2 M in HClO_4 , and 0.14 M in NaClO_4 ; solution B should be 0.002 M in NaSCN , 0.2 M in HClO_4 , and 0.14 M in NaClO_4 . Be careful in handling these solutions; perchloric acid will give you dishpan hands. Now mount the carboys in the thermostat bath and connect them by a long piece of flexible pressure tubing to the appropriate stopcocks,

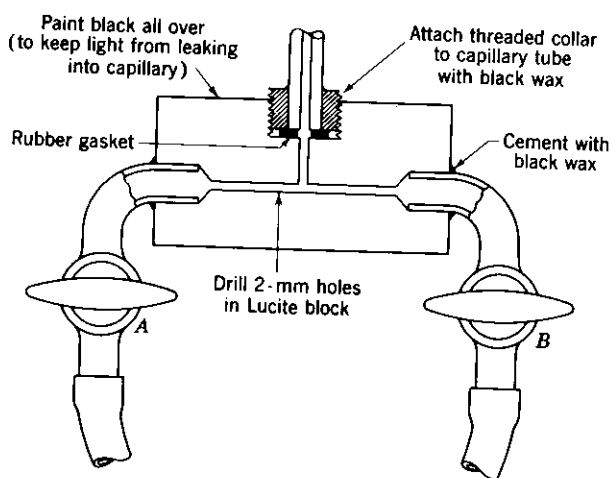


FIGURE 3
Detail of mixing chamber.

† Before being used in this experiment, each carboy should be pressure tested to verify that there are no flaws that would make it unsafe. It is recommended that the empty *but wet* carboy be placed behind a protective barrier and subjected to an internal gas pressure of 2 atm.

which are sealed will move smoothly if there is any misalignment is corrected by a series of reference marks on the spectrophotometer at regular intervals away from the

To compare the tube that leads to a suitable drive

It is important that the may be reflected by the spectrophotometer to reduce such stray light must still avoid the of the entire spectrophotometer housing on the

Success in this experiment should be followed by a look over the general operation and the instrument carefully the details of the instrument

Procedure. Turn the warm up prior to the entire experiment. With V closed, slowly Bourdon pressure gauge the outlet stopcock (one at a time) smoothly and then catch the outflow first fiducial mark following steps.

1. Open stopcock remove from (until the outlet C. In accordance

† As an optional step separate solution to within a few percent

which are sealed into the mixing chamber. Again, test that the capillary frame will move smoothly back and forth through its housing. Do not force it. If there is any difficulty, ask an instructor to check the alignment. Proper alignment is crucial. Along the top of the capillary support frame, there should be a series of fiducial marks (say six or seven) which can be lined up with a reference mark on the special housing. This enables one to set the spectrophotometer at reproducible points along the capillary that are at known distances x away from the mixing chamber.

To complete the setup, connect the reagent carboys to each other via a T tube that leads to an open-tube mercury manometer and a regulated supply of a suitable driver gas (such as air or N_2).

It is important that stray light should not reach the capillary tube, since it may be reflected down the walls of the tube and be detected by the spectrophotometer. The support frame around the capillary is designed to reduce such stray light by providing a deep, narrow slit-like aperture; but one must still avoid horizontal light leaks. It may be worthwhile to cover both ends of the entire support frame with blackout cloths. Do not cover the source housing on the spectrophotometer, as it gets hot.

Success in this experiment depends on good technique; the procedure should be followed carefully. Before beginning the measurements, you should look over the general discussion of spectrophotometers given in Chapter XVIII and the instruction manual for the spectrophotometer to be used. Read carefully the detailed information given in the latter for the proper operation of the instrument.

Procedure. Turn on the spectrophotometer and allow at least 20 min for it to warm up prior to use. The wavelength setting should be 455 nm throughout the entire experiment. With both reagent stopcocks *A* and *B* and the vent stopcock *V* closed, slowly increase the gas pressure on the reagent solutions until Bourdon pressure gauge indicates about 500 Torr pressure above 1 atm. With the outlet stopcock *C* open, open and close the reagent stopcocks *A* and *B* (one at a time) several times to make sure that both solutions are flowing smoothly and to remove any air bubbles from the system. Use a beaker to catch the outflow from the capillary tube.† Then set the capillary frame at the first fiducial mark (one nearest to the mixing chamber) and carry out the three following steps.

1. Open stopcock *A* and allow the Fe^{3+} solution to flow for a sufficient time to remove from the capillary tube any solution containing $FeSCN^{2+}$ species (until the outflow is clear). Then close stopcock *A* and the outlet stopcock *C*. In accordance with the spectrophotometer operating instructions, zero

† As an optional step, you can record the time required for a given volume (say 250 mL) of each separate solution to flow through the capillary tube. The times for solutions *A* and *B* should agree within a few percent.

- the instrument with this Fe^{3+} solution (i.e., adjust the slit width and sensitivity controls so that the instrument reads 100 percent transmission or $A = 0$).
- To begin a run, open the outlet stopcock C and then turn both stopcocks A and B to their fully open positions. Catch the outflow of solution from the capillary in a beaker until the flow becomes stable (as indicated by a constant manometer reading, usually before 100 mL of solution is collected). Then *quickly* switch the outlet tube from the beaker to a 250-mL volumetric flask and simultaneously start a stopwatch. When this flask is full, stop the watch and record the elapsed time (~ 50 s). Return the outlet tube to the beaker. While one student is carrying out the above flow-rate measurement, his partner should determine the absorbance A of the reaction mixture and record that value together with the distance x from the mixing chamber. Work quickly to avoid any unnecessary waste of the reagent solutions.
 - When both the flow and absorbance measurements are complete, close the outlet stopcock C and then as soon as possible close both stopcocks A and B . This is a crucial step in the procedure; if A and B are left open, solution may siphon from one carboy to the other. After about 2 min, determine the absorbance again to obtain A_∞ (the infinite-time value). Verify that this value does not change after one more minute.

For the next run, move the capillary support frame so as to line up the second fiducial mark and repeat steps 1 to 3 at this new distance setting. Be careful in moving the capillary support frame.

Make two runs at each of the six or seven positions along the capillary tube. Use special care in making the absorbance readings at large values of x (corresponding to large percent reaction and a small $A_\infty - A$ value). If time permits, you should also take data at a different driving pressure. Either increase or decrease the gas pressure depending on whether you need more data at low percent reaction or at high, but it may not be safe to exceed about 700 Torr overpressure.

During the course of the experiment, more of solution A will be used up than solution B if the Fe^{3+} solution is always used in step 1 to make the zero adjustment of the spectrophotometer at each distance setting. The resulting change in the liquid level for solution A relative to that for solution B may change the relative flow rates of these solutions. This can be avoided by alternating the use of solutions A and B for making the zero adjustments (or, if necessary, corrected by merely running enough of solution B out through the capillary periodically to equalize the levels).

Before leaving the laboratory, record the concentrations of the reactant solutions, the temperature of the thermostat bath, the radius of the capillary tube, and the distances x corresponding to the various fiducial marks along the capillary support frame.

CALCULATION

Using Eq. (7), plot $\ln(A_\infty - A)$ versus t , and determine the slope of the line. From the literature value of k and you should be able to determine $t = 0$, but *after* the reaction has started, as calculated with the proper units for

DISCUSSION

What fraction of the hydrolysis constant is due to sources of error in the method measured with this method?

APPARATUS

Suitable spectrophotometer, SP-100; 6-V battery; adjustable support frame with retaining bolts for reaction vessel (~ 6 liters) for reaction pressure); cylinder of gas, regulated compressor; venting the carbon dioxide; volumetric flask;

Constant-temperature bath; carboys; solution of Fe^{3+} 0.14 M in NaClO_4 and 0.14 M in HClO_4 , and 0.14 M in HClO_4 , and 0.14 M in HClO_4 .

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CALCULATIONS

Using Eq. (7), calculate the reaction time t corresponding to each run; tabulate these times together with the appropriate $(A_\infty - A)$ values. Plot $\log(A_\infty - A)$ versus t , and determine the slope of the best straight line through the data points. From the value of this slope, calculate the rate constant k_f . The literature value⁴ of K is $146 \pm 5 \text{ L mol}^{-1}$ at 25°C and an ionic strength of 0.40, and you should take the (Fe^{3+}) value to be an average of the initial value ($t = 0$, but *after* mixing of the two solutions) and the equilibrium value ($t = \infty$, as calculated with K). Also report the back-reaction rate constant k_r . Give the proper units for each rate constant.

DISCUSSION

What fraction of the Fe^{3+} in solution A is hydrolyzed to $\text{Fe}(\text{OH})^{2+}$ if the hydrolysis constant K_h is known⁴ to be 2×10^{-3} ? What are the principal sources of error in this experiment? How fast a reaction do you think could be measured with this apparatus? What is the limiting design factor in this method?

APPARATUS

Suitable spectrophotometer, such as a Beckman model DU or PTR model SP-100; 6-V battery and battery charger (or regulated dc power supply); adjustable support for spectrophotometer (optional); movable capillary support frame with mixing chamber and special housing attached; set of four retaining bolts for mounting housing on the spectrophotometer; two carboys (~ 6 liters) for reactant solutions; Bourdon pressure gauge (0–700 Torr overpressure); cylinder of nitrogen gas with pressure regulator (or source of regulated compressed air); pressure tubing and hose clamps; stopcock for venting the carboys; gum-rubber tubing for outlet of capillary; a 250-mL volumetric flask; a beaker (~ 500 mL); stopwatch; blackout cloths (optional).

Constant-temperature bath (set at 25°C) with provision for mounting carboys; solution A which is 0.0200 M in $\text{Fe}(\text{NO}_3)_3$, 0.20 M in HClO_4 , and 0.14 M in NaClO_4 (5 liters); solution B which is 0.00200 M in NaSCN , 0.20 M in HClO_4 , and 0.14 M in NaClO_4 (5 liters).

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EXPERIMENTS

26. Surface tension
27. Physical adsorption

The capillary-rise function of concentration of sodium chloride. The data are plotted against the Gibbs isotherm

THEORY

If a body of material is directly proportional to

where Q is the experimental mass, and number of moles, respectively, the surface area per mole and have *int*

It is known,