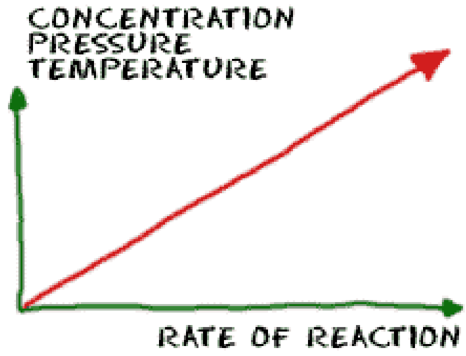
CEAC 104
GENERAL CHEMISTRY

Experiment 2

Rates of Chemical Reactions I: Kinetic Study of the Reaction Between Ferric and Iodine Ions



Purpose: To study kinetics of the reaction between ferric (Fe^{3+}) and iodide (I^{-}) ions, i.e. to determine order of the reaction with respect to both ions.

APPARATUS AND CHEMICALS:

1-mL pipets	25-mL pipet
clock or watch with second hand	50-mL pipet
100-mL beaker	distilled water
250-mL beaker	KI
thermometer	$Na_2S_2O_3$ (freshly prepared)
water bath	$Fe(NO_3)_3$
pipet bulb	starch solution
ring stand	HNO_3

THEORY:

Parts A and B of this experiment are concerned with the evaluation of exponents a and b respectively in the rate expression.

The initial rate is determined by measuring the time in seeonds required for 4x 10^{-5} mole of $Fe^{3+}$to be reduced to Fe^{2+}. This is indicated by adding stareh salution and a small, constant amount of $S_20_3^{2-}$ to each mixture. The following reactions then occur:

$$2Fe^{3+} + 3I^{-} \rightarrow 2Fe^{2+} + I^{3-} \qquad \text{(SLOW)}$$

$$I_3^{-} + 2S_2O_3^{2-} \rightarrow 3I^{-} + S_4O_6^{2-} \qquad \text{(FAST)}$$

Rate expression fort his reaction is

$$Rate = -1/2\ dFe^{3+}]/dt = d[I_3^{-}]/dt = k[Fe^{3+}]^a[I^{-}]^b$$

As soon as the $S_2O_3^{2-}$ has been consumed, any additional I^{3-} formed by the reaction between ferric and iodide ions will react with the starch to form a characteristic blue color. Note that when the blue color first appears, the decrease in the 2 concentration of Fe^{3+} from its initial value is just equal to the initial concentration of S_2O^{2-} in the mixture. Thus the initial rate, $-1/2d[Fe^{3+}]/dt$, is equal to $1/2[S_2O_3^{2-}]_i/\Delta t$, where $[S_2O_3^{2-}]_i$ is the initial concentration of $S_2O_3^{2-}$ and Δt is the time in seconds between mixing and the appearance of the blue color. In order to obtain reasonable reaction times, it is necessary to use initial rate intervals that allow the Fe^{3+} concentration to decrease slightly (about 4 to 10 percent) from its initial value. To compensate for this change, it is suggested that the average Fe^{3+} concentration during this time interval be used in place of the initial concentration.

REVIEW QUESTIONS:

Before beginning this experiment in the laboratory, you should be able to answer the following questions:

1. What four factors influence the rate of a reaction?
2. If the rate law for a reaction is rate = $k[A]^2[B]$,

   (a) What is the overall order of the reaction?

   (b) If the concentration of both A and B are doubled, how will this affect the rate ofthe reaction?

   (c) What name is given to k?

   (d) How will doubling the concentration of A while the concentration of B is kept constant affect the value of k (assume temperature does not change)? How is the rate affected?
3. Write the chemical equation for the iodide-catalyzed decomposition of H_2O_2.
4. It is found for the reaction $2A + B \rightarrow C$ that doubling the concentration of either A or B quadruples the reaction rate. Write a rate law for the reaction.
5. When the concentration of a substance is doubled, what effect does it have on the rate if the order with respect to that reactant is (a)0; (b) 1; (c) 2; (d) 3; (e) ½?
6. The following data were collected for the volume of O_2 produced in the decomposition of H_2O_2.

Time (s)	mL O_2
0.0	0.0
45.0	2.0
88.0	3.9
131.0	5.8

Calculate the average rate of reaction for the time intervals between measurements.

PROCEDURE:

Cautious:

1. Be careful about performing in all the experiments at the same temperature since temperature changes affect the rate constant; use water bath to keep temperature constant.
2. HNO_3 does not participate the reaction between ferric and iodide ions but it is used to prevent hydrolysis of the Fe^{3+} in the water environment.

3. Use 50 mL burettes to dispense H_2O, $Fe(NO_3)_3$, and HNO_3 solutions; 10 mL pipettes to dispense the KI and $Na_2S_2O_3$ solutions, and 10 mL graduated cylinder to dispense the starch solution.

A. Reaction order with respect to Fe^{3+}

1. Prepare the mixtures for experiment 1 by adding the solutions specified in Table 2.1 to 250 and 100 mL beakers, respectively.
2. Swirl the contents of each beaker briefly, and place the beakers in a constant temperature water bath set at room temperature to reach temperature equilibrium. (Al1ow 10 to 15 minutes for this).
3. Meanwhile, prepare the solutions for experiment 2 in a second set of beakers, and place these a1so in the water bath. By this time the solutions for experiment 1 should be at bath temperature.
4. Measure and record the initial temperature of the solutions then simultaneously start the timer and add (rapidly) the contents of the 100 mL beaker to the 250 mL beaker. You may remove the solutions temporarily from the water bath for this.
5. Swirl the solutions until mixed, then return the 250 mL beaker to the bath.
6. Stop the timer at the first appearance of the blue color. Again measure the temperature, and calculate the average temperature of the solution during the reaction. Record the time interval, Δt, and the average temperature in the table in the data part.
7. Clean and dry the beakers, add the solutions for experiment 3, and place the beakers in the water bath.
8. Then measure the temperature of the solutions for experiment 2, mix the solutions and follow the reaction as you did for experiment 1.
9. Continue in this manner through experiment 5.

B. Reaction order with respect to I^-

1. This part is performed exactly as in Part A, except that the concentration of ferric ion is kept constant while the concentration of iodide ion is varied. The composition of the various reaction mixtures to be used is given in the Table 2.1, experiments 6, 7 and 8.

TABLE 2.1

	250 mL beaker			100 mL beaker			
EXP	**0.04 M Fe^{3+}, mL**	**0.15 M HNO_3, mL**	**H_2O, mL**	**0.04 M KI, mL**	**0.004 M $S_2O_3^{2-}$, mL**	**Starch, mL**	**H_2O, mL**
1	10	20	20	10	10	5	25
2	15	15	20	10	10	5	25
3	20	10	20	10	10	5	25
4	25	5	20	10	10	5	25
5	30	0	20	10	10	5	25
6	10	20	20	5	10	5	30
7	10	20	20	15	10	5	20
8	10	20	20	20	10	5	15

CALCULATIONS:

1. By performing the calculations, fill up the Table 2.1.
2. Calculate $[S_2O_3^{2-}]$, which is constant in all experiments.
3. Calculate initial reaction rate by using time data above.
4. Take logarithm of the rate.
5. Calculate initial Fe^{3+} concentration.
6. Calculate aveage Fe^{3+} concentration by using the equation below:

   $[Fe^{3+}]_{av} = [Fe^{3+}]_i - 4x10^{-4}/2 = [Fe^{3+}]_i - 2x10^{-4}$
7. Take Iogarithm of average Fe^{3+} concentrations.
8. Calculate initial I^- concentration. This will be equal to average I^- concentration.
9. Take logarithm of average I^- concentrations.
10. Plot log rate vs. log $[Fe^{3+}]_{av}$ for experiments 1 to 5.
11. Find the slope of the line, this will be equal to a, reaction order with respect to ferric ion.
12. Plot log rate vs. log$[I^-]$ for experiments 1, 6, 7, 8.
13. Find the slope of the line; this will be equal to a, reaction order with respect to iodide ion.

QUESTIONS:

1. What is the overall rate of this reaction?

2. How would you evaluate reaction rate constant, k, of this reaction?

3. If you use 0.20 M KI instead of 0.10 M KI, how would this affect (a) the slopes of your curves, (b) the rate of the reactions, and (c) the numerical value of k for the reaction?

DATA SHEET

Rates of Chemical Reaction II: Kinetic Study of the Reaction Between Ferric and lodine Ions

Student's Name : Date:

Laboratory Section/Group No :

Assistan's Name and Signiture :

TABLE 2.1

Temperature ^{o}C	**EXP**	**ΔT (s)**
	1	
	2	
	3	
	4	
	5	
	6	
	7	
	8	

TABLE 2.2

EXP	$[S_2O_3^{2-}]_i/\Delta t$	**Rate=1/2** $[S_2O_3^{2-}]_i/\Delta t$	**log rate**	$[Fe^{3+}]_i$
1				
2				
3				
4				
5				
6				
7				
8				

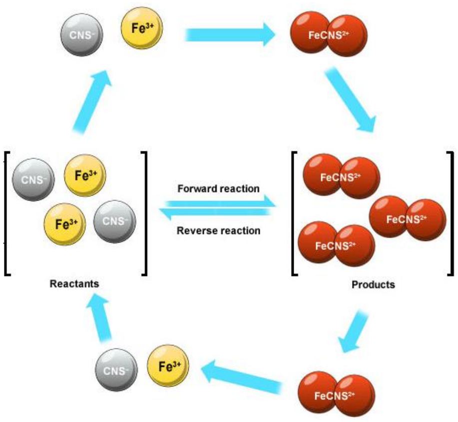
EXP	$[Fe^{3+}]_{av}$	$\log[Fe^{3+}]_{av}$	$[I^-]_{av}$	$\log[I^-]_{av}$
1				
2				
3				
4				
5				
6				
7				
8				

CEAC 104

GENERAL CHEMISTRY

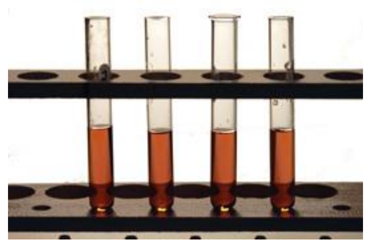
Experiment 3

Chemical Equilibrium



$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

(yellow) (clear) (red/brown)



Purpose: Given the equation for a chemical equilibrium, predict and explain, the direction of a shift in the position of an equilibrium caused by a change in the concentration of the species on the basis of LeChatelier's principle and finally to find the value of an equilibrium constant, K_{eq}, experimentally.

APPARATUS AND CHEMICALS:

distilled water	test tubes
sodium thiocyanate (NaSCN)	graduated cylinder
ferric nitrate ($Fe(NO_3)_3$)	white paper
ruler	250-mL beaker

THEORY:

Most of the chemical reactions occur so as they approach a state of chemical equilibrium. The equilibbrium state can be characterized by specifying its equilibrium constant, i.e., by indicating the numerical value of the mass-action expression. In this experiment you will determine the value of the equilibrium constant fort he reaction between ferric ion Fe^{3+} and isothiocyanate ion SCN^-,

$$Fe^{3+} + SCN^- \leftrightarrow FeSCN^{2+}$$

for which the equilibrium condition is

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

To find the value of K, it is necessary to determine the concentration of each of the species Fe^{3+} , SCN^-, and $FeSCN^{2+}$ in the system at equilibrium. This will be done calorimetrically, taking advantage of the fact that $FeSCN^{2+}$ is the only highly colored species in the solution. The color intensitty of a solution depends on the concentration of the colored species and on the depth of solution viewed. Thus, 2 cm of a solution of a 0.1 M colored species appears to have the same color intensity as a 1 cm of a 0.2 M solution. Consequently, if the depths of two solutions of unequal concentrations are chosen so that the solutions appear to be equally colored, then the ratio of concentrations is simply the inverse of the ratio of the two depths. it should be noted that this procedure permits only a comparison between concentrations. it does not give an absolute value of either one of the concentrations. To know the absolute values, it is necessary to compare unknown solutions with a standard of known concentration.

For color determination of $FeSCN^{2+}$ concentration, you must have astandard solution in which the concentration of $FeSCN^{2+}$ is known. Such a solution can beprepared by starting with a small known concentration of SCN^- and adding such a large excess of Fe^{3+} that essentially all the SCN^- is converted to $FeSCN^{2+}$ Under these conditions, you can assume that the final concentration of $FeSCN^{2+}$ is equal to the initial concentration of SCN^-.

REVIEW QUESTIONS:

Before beginning this experiment in the laboratory, you should be able to answer the fol1owing questions:

1. How could temperature changes affect the equilibrium?
2. What is the unit of the equilibrium constant?
3. Which factors affect the equilibrium constant?

PROCEDURE:

1. Clean six 15-cm test tubes with distilled water and let them drain.
2. To each of these test tubes add 5 mL of 0.0020 M NaSCN.
3. To the first test tubes add 5 mL of 0.20 M $Fe(NO_3)_3$. This tube will serve as the standard.
4. For the other test tubes proceed as follows:

Add 10 mL of 0.20 M $Fe(NO_3)_3$ to a graduated cylinder. Add 15 mL distilled water so that you have a 25 mL of diluted solution. Stir thoroughly to mix. Take 5 mL from this solution and pour it into the second test tube.

5. Discard 10 mL of the diluted solution in the graduated cylinder and add 15 mL of distilled water and again you complete it to 25 mL. Stir thoroughly. Take 5 mL from this solution and pour it into the third test tube.

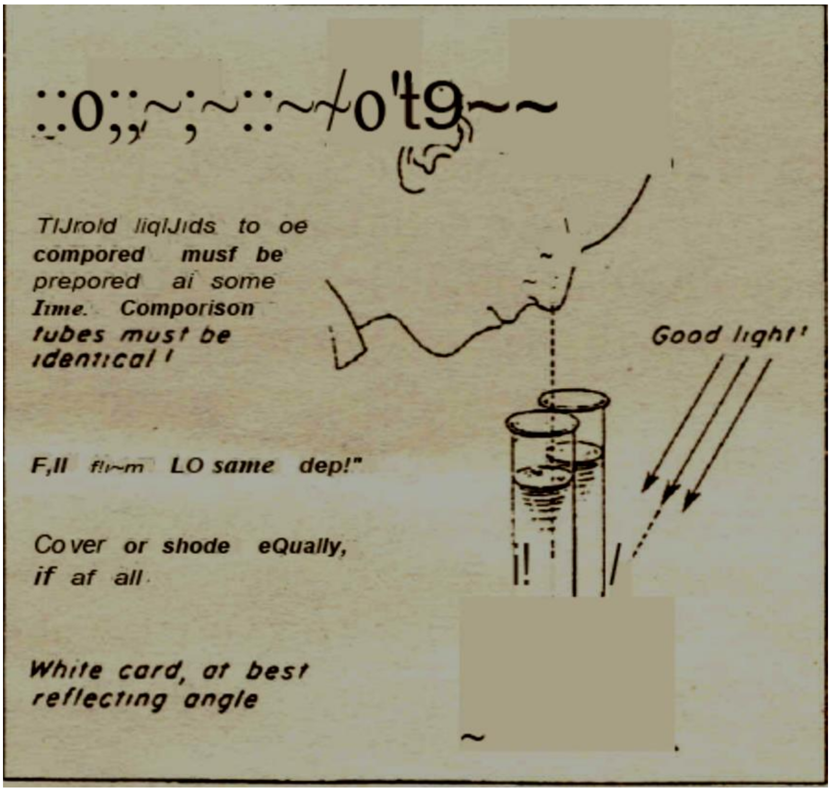


Figure 3.1 How to make a comparison of color.

6. Again discard 10 mL of the solution in the graduated cylinder and add 15 mL distilled water. Continue this procedure until you prepare six of the test tubes.
7. Now the problem is to determine the concentration of $FeSCN^{2+}$ in each test tube relative to the standard in test tube 1. Compare the color intensity in test tube 1 with that in each of the other test tubes (see Figure 3.1). To do it, take two tubes to be compared, hold them side-by-side and wrap a strip of white paper around both. Look down through the solutions as shown

in Figure. If color intensities appear identical, measure the heights of the solutions in the two tubes being compared. If not, take test tube 1 and pour out some of the standard into a clean beaker (you may need to pour some back) until the color intensities appear identical. Do this comparison for all five tubes.

CALCULATIONS:

In calculating initial concentrations, assume that each of $Fe(NO_3)_3$ and NaSCN are completely dissociated. Remember also that mixing two solutions dilutes both of them. In ca1culating equilibrium concentrations, assume that all the initial SCN^- has been converted to $FeSCN^{2+}$ in test tube 1, for the other test tubes; calculate $FeSCN^{2+}$ from the ratio of heights in the color comparison. Equilibrium concentrations of Fe^{3+} and SCN^- are obtained by subtracting $FeSCN^{2+}$ formed from initial Fe^{3+} and SCN^-. For each of test tube 2 to 6 calculate the value of K. Decide which of these values is most reliable.

QUESTIONS:

1. In this experiment you examine the equilibrium

$$Fe^{3+} + SCN^- \leftrightarrow FeSCN^{2+}$$

The following equilibria are somewhat competing with the above equilibrium

$$Fe^{3+} + SCN^- \leftrightarrow Fe(SCN)^{2+} \text{ and } Fe(SCN)^{2+} + 2SCN^- \leftrightarrow Fe(SCN)_3$$

a. To allow you to ignore these equilibria, how must their equi1ibrium constants be in comparison with that of the equilibrium being studied ?

b. Given that all ions are color1ess except for $FeSCN^{2+}$, what effect should competing equilibria have on the value of K determined in this experiment? Explain.

2. How reasonable was your assumption that all the SCN^- in test tube 1 was converted to $FeSCN^{2+}$? (Calculate the percent of SCN^- converted to $FeSCN^{2+}$ using your best K value.)

3. Why are the values of K determined for test tubes 3, 4 and 5 probably more reliable than those determined for tubes 2 or 6?

4. In your own words, give the rational behind the procedure and methodology in this experiment.

DATA SHEET

Chemical Equilibrium

Student's Name : Date:

Laboratory Section/Group No :

Assistan's Name and Signiture :

Test tube	**Height of liquid in cm**	**Comparison of height in cm of standard**
1	………………………	………………………………
2	………………………	………………………………
3	………………………	………………………………
4	………………………	………………………………
5	………………………	………………………………
6	………………………	………………………………

RESULTS:

Test tube	**Initial Concentrations**			**Equilibrium Concentrations**			
	[Fe^{3+}]	**[SCN^-]**	**[$FeSCN^{2+}$]**	**[Fe^{3+}]**	**[SCN^-]**	**[$FeSCN^{-2}$]**	**Keq**
1							
2							
3							
4							
5							
6							