

Experiment 12D

FV 3/18/03

THERMODYNAMICS OF THE FORMATION OF THE THIOCYANATOIRON(III) COMPLEX ION

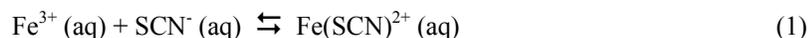
MATERIALS: Eight 25 x 150 mm test tubes, grease pencils, three 250 mL beakers, three 600 mL beakers, two 10 mL graduated cylinders, one 25 mL graduated cylinder, three Pasteur pipets, three glass stirring rods, thermometer, Spectronic 20 spectrometer, four sample cuvettes, 0.00200 M KSCN, 0.00300 M Fe(NO₃)₃ (in 2.0 M in HNO₃).

PURPOSE: To determine the values of the thermodynamic properties for the formation of the thiocyanatoiron (III) ion.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Use the Spectronic 20 spectrometer.
2. Use Beer's Law to determine concentrations.
3. Experimentally determine equilibrium constants.
4. Use equilibrium constants to calculate ΔH , ΔS , and ΔG .

DISCUSSION: In this experiment you will determine the thermodynamic quantities ΔH , ΔS , and ΔG for the reaction



by measurement of the equilibrium constant for the reaction at several temperatures. Because the complex ion Fe(SCN)²⁺ is the only component of this system that absorbs light in the visible region, the reaction is especially suitable for measurement by spectrophotometric means.

The equilibrium constant expression for this reaction is given by

$$K_c = \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]} \quad (2)$$

The value for K_c can be calculated from the equilibrium concentrations of all three components. The equilibrium concentration of Fe(SCN)²⁺ is readily determined for the product complex ion by application of Beer's Law

$$A = \epsilon \ell c \quad (3)$$

where ϵ is the molar absorptivity of the ion at the wavelength of interest, c is the molar concentration of the ion, and ℓ is the length (in cm) of the light path through the solution. The value of ϵ for Fe(SCN)²⁺ at 447 nm is $4.70 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. The nominal path length, ℓ , which is the internal diameter of the sample cell, is 1.17 cm. Thus, a measurement of the absorbance of the solution will enable the determination of the concentration of the absorber, [Fe(SCN)²⁺]_{eq}, at equilibrium. Since the reaction was begun with solutions of known initial concentrations of Fe³⁺ and SCN⁻, the equilibrium concentrations of those species can be determined from the measured [Fe(SCN)²⁺]_{eq} and the known stoichiometry of the reaction by use of an ICE table.

At any given temperature, the equilibrium concentrations of the components of a reaction can vary over a wide range, but the equilibrium constant K_c is a constant value. The numerical value of the equilibrium constant is, however, dependent on temperature, and the nature of its dependence can be used to extract the thermodynamic properties ΔG , ΔH and ΔS of the system. At equilibrium,

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

where R is the gas constant ($R = 8.314 \text{ J/mol-K}$), T is the temperature (in Kelvin) and ΔG° is the standard free energy change for the reaction. When this is combined with the defining equation for free energy,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

and the equations are rearranged, the following relation is obtained,

$$\ln K_c = \left(\frac{-\Delta H^\circ}{R} \right) \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (6)$$

(assuming that ΔH° and ΔS° are not highly temperature dependent). Since this relation has the form of a linear equation, $y = mx + b$, a plot of $\ln K_c$ vs. $1/T$ will give a straight line; the slope and intercept provide the thermodynamic parameters.

PROCEDURE:

1. Thoroughly clean, rinse and dry eight 25x150 mm test tubes and three 250 mL beakers. Number the test tubes one through eight with a marker pencil; mark the 250 mL beakers with the identities of the reagents they will contain. Use one of the 250 mL beakers to obtain about 100 mL of 0.00200 M KSCN solution. Record, in the Data Section, the exact concentration labeled on the bottle. In another 250 mL beaker, place about 100 mL of the 0.00300 M $\text{Fe}(\text{NO}_3)_3$ solution. Record the exact concentration of this solution also. (Note that this solution is also 2.0 M in HNO_3 to prevent precipitation of $\text{Fe}(\text{OH})_3$. This additional component has no impact on any of your volumes, concentrations, calculations, or conclusions.) Place about 200 mL of distilled water in the third 250 mL beaker, for use in the preparation of samples.
2. Using one 10 mL graduated cylinder for the $\text{Fe}(\text{NO}_3)_3$ solution, the other 10 mL graduated cylinder for the KSCN solution, and the 25 mL graduated cylinder for the water, fill your cleaned and marked test tubes with the reagents and distilled water as indicated in the table below. (Note that the care with which you prepare samples can markedly affect your results.) Use different plastic pipets for each reagent solution to "top off" to accurate volumes in the graduated cylinders. Do additions of one reagent to all test tubes first, and then move on to the next. Allow adequate time to drain the contents of the graduated cylinders into the test tubes. Be sure to pre-rinse the graduated cylinders with the solution to be used next, to prevent contamination and/or dilution of the reagents. When all components have been added, mix each solution in order with a clean stirrer; rinse and dry after each use. Note the slight gradation in color in the test tubes.

Test tube	Vol. $\text{Fe}(\text{NO}_3)_3$ (mL)	Vol KSCN (mL)	Vol H_2O (mL)
1	10.00	4.00	26.00
2	10.00	6.00	24.00
3	10.00	8.00	22.00
4	10.00	10.00	20.00
5	10.00	12.00	18.00
6	10.00	14.00	16.00
7	10.00	16.00	14.00
8	10.00	18.00	12.00

3. Set the wavelength on the Spectronic 20 spectrometer to **447 nm**, and set the zero and 100% transmittance, using a distilled water blank.

4. Rinse the cuvette twice with a small amount (< 1 mL) of the solution in test tube 1, discarding the rinse liquid in the drain. (None of the components are sufficiently toxic, corrosive or concentrated to cause problems). Fill the lower third of the cuvette with fresh solution from test tube 1, wipe off the outside, and place the cuvette in the instrument. Do not handle the lower part of the tube, or leave it in the instrument too long, as these could affect the temperature. Record the percent transmittance of the solution from test tube 1, as well as the temperature of the solution in the test tube.
5. Discard the solution in the cuvette, and rinse it twice with a small amount of the solution from test tube 2. Discard the rinse liquid, and fill the lower third with fresh solution from test tube 2. Wipe the cuvette clean, and measure and record the percent transmittance of the solution from test tube 2.
6. Repeat step 5, measuring and recording the percent transmittance values for all other test tubes in order. Be sure to always rinse with small amounts of the solution to be used next (and not water. Why?) Be careful about inadvertent heating of the solution. You can assume that the temperature measured for test tube 1 is the same as that of all other solutions for room temperature samples.
7. Use a mixture of ice in water to form a low temperature bath in a 600 mL beaker. Use hot tap water in a 600 mL beaker to form the medium temperature bath, and boiling water in a 600 mL beaker to form the hot water bath. Place test tubes 1 through 3 in the cold bath, test tubes 4 and 5 in the medium bath, and test tubes 6 through 8 in the hot bath, and let them come to temperature (thermally equilibrate) for about 10 minutes. Stir the mixtures occasionally during this period using a clean, dry stirring rod each time.
8. **(NOTE: Complete this step in a timely manner to minimize temperature changes.)** Remove test tube 4 from the medium bath. Rinse the cuvette twice with a small amount of the solution. Fill the lower third of the cuvette with the solution and return the test tube to the medium temperature bath. Measure the percent transmittance of the solution, and record that value in the table as well. Also measure the temperature of the solution in the test tube and record in the table.
9. Repeat step 8 with solution 5, which has remained in the medium bath. Since the bath and the solutions are constantly losing heat to the room, it will be necessary to measure and record the temperature of each one individually, unlike the room temperature solutions. It is not necessary that the two medium solutions be at the same temperature, but you should work quickly when dealing with individual solutions to be sure that the temperature measured in the test tube accurately reflects the temperature of the sample placed in the spectrometer.
10. Repeat steps 8 and 9 to measure and record the temperature and percent transmittance of the cold solutions in test tubes 1 through 3. Again, work quickly with individual solutions, and wipe off the outside of the cuvette each time, since water vapor from the air may condense on it and decrease the transmittance. Remember the cautions about rinsing the cuvette and about inadvertent heating of the sample.
11. Repeat steps 8 and 9 to measure and record the temperature and percent transmittance of the hot solutions in test tubes 6 through 8. Turn off the Bunsen burner and use test tube holders for both the sample test tube and cuvette while pouring. Again, work quickly with individual solutions and wipe off the outside of the cuvette each time, since water vapor from the air may condense on it and decrease the transmittance. Remember the cautions about rinsing the cuvette and about inadvertent heating of the sample.
12. When finished, discard all solutions down the drain and rinse the beakers with distilled water. Wipe off the identifying marks on the test tubes and turn them upside down in the test tube rack.

Name _____

Section _____

Partner _____

Date _____

DATA SECTION
Experiment 12D

Actual Concentrations: $\text{Fe}(\text{NO}_3)_3$ _____ KSCN _____

Beaker	ROOM TEMPERATURE		MEDIUM TEMPERATURE	
	Temp.	%T	Temp.	%T
1	_____	_____		
2	_____	_____		
3	_____	_____		
4	_____	_____	_____	_____
5	_____	_____	_____	_____
6	_____	_____		
7	_____	_____		
8	_____	_____		

Beaker	COLD TEMPERATURE		HOT TEMPERATURE	
	Temp.	%T	Temp.	%T
1	_____	_____		
2	_____	_____		
3	_____	_____		
4				
5				
6			_____	_____
7			_____	_____
8			_____	_____

DATA TREATMENT

Since many calculations will be repeated with each solution, the analysis of this experiment is especially amenable to the use of an electronic spreadsheet. A useful format might include table headings shown below:

<u>Test Tube</u>	<u>Temp.</u>	<u>%T</u>	<u>Abs.</u>	<u>[Fe(SCN)²⁺]_{eq}</u>	<u>Vol SCN⁻ (mL)</u>	<u>Vol Fe³⁺ (mL)</u>	<u>[SCN⁻]_i</u>	<u>[Fe³⁺]_i</u>
<u>[FeSCN²⁺]_{eq}</u>	<u>[SCN⁻]_{eq}</u>	<u>[Fe³⁺]_{eq}</u>	<u>K_c</u>	<u>1/T (K)</u>	<u>ln K_C</u>			

The formulas to determine the various quantities required should be entered into the spreadsheet for beaker 1. These can then be copied to the other cells for the remainder of the solutions.

1. Calculate the absorbance (Abs.) of each solution from the measured percent transmittance.
2. Using Beer's law, calculate the equilibrium concentration of the thiocyanatoiron(III) ion, [Fe(SCN)²⁺]_{eq}, for each solution.
3. From the known volumes and concentrations of the Fe(NO₃)₃ and KSCN reagents, calculate the initial concentrations [Fe³⁺]_i and [SCN⁻]_i for each solution (dilution calculation). Then use these initial values, and the known [Fe(SCN)²⁺]_{eq} to determine the equilibrium concentrations of the reactants, [Fe³⁺]_{eq} and [SCN⁻]_{eq}, by a standard equilibrium calculation (ICE table). Finally, knowing all of the equilibrium concentrations, calculate K_c for each mixture.

For test tube #1 at room temperature, show all calculations and the completed ICE table.

4. Plot your data in the form of $\ln K_c$ vs. $1/T$. Note that temperature must be in units of Kelvin. Do a linear regression fit to the data. Include the equation of the line and the R^2 value on your plot. Fill in the lines below and include the appropriate units.

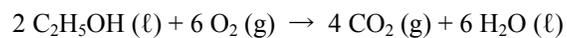
slope of line _____

y-intercept of line _____

5. Calculate the value of ΔH°_{298} . (Show your work.)
6. Using the values of the slope and intercept, calculate the value of K_c at 298 K. (Show your work.)
7. Calculate the value of ΔG°_{298} , using your value of the equilibrium constant K_c at 298 K. (Show your work.)
8. Using your experimentally determined values of ΔH°_{298} and ΔG°_{298} , calculate ΔS°_{298} . (Show your work.)

QUESTIONS
Experiment 12D

1. Using the standard molar heats of formation and standard absolute entropies listed in your text, calculate an estimate for the free energy change ΔG° associated with the following reaction at 400°C :



DATA:

	$\text{C}_2\text{H}_5\text{OH}(\ell)$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\ell)$	$\text{O}_2(\text{g})$
ΔH_f°				
S°				

Reference for data _____

2. In the calculation above, why is it possible to use tabulated values of ΔH_f° and S° , which refer to reactions at 298 K, but it is not appropriate to use values of ΔG_f° , which are also tabulated at 298 K?